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Preparation and Properties of Bis(8-quinolinolato)silicon(IV) Dichloride and Bis(salicylaldehydato)dichlorosilicon(IV)[1]

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Bis(8-quinolinolato)silicon(IV) dichloride, prepared in the reaction of silicon tetrachloride with 8-hydroxyquinoline, is the chloride salt of a dipositive complex cation of silicon, probably tetracoordinate. This complex is remarkably stable in air but undergoes solvolysis in water and alcohol. Treatment of $Si(C_9H_6ON)_2Cl_2$ in aqueous solution with $NaB(C_6H_5)_4$ yields $Si(C_9H_6OH)_2(B(C_6H_5)_4)_2$. X-Ray photoelectron spectroscopy was found to yield unequivocal support for the ionic formation proposed for this complex. The chlorine 2p electron binding energy found for $Si(C_9H_6OH)_2Cl_2$ is similar to the value found for chloride ion and 2.5 eV below the binding energy observed for chlorine covalently bound to silicon. Bis(salicylaldehydato)dichlorosilicon(IV), prepared in the reaction of silicon tetrachloride with salicylaldehyde, appears to be a hexacoordinate covalent compound of silicon. This complex is extremely sensitive to moist air. It reacts with alcohol to yield $Si(C_6H_4OCHO)_2(OC_2H_5)_2$. Treatment of $Si(C_6H_4OCHO)_2Cl_2$ with sodium naphthanide yields a disodium salt of a dinegative complex anion of silicon, $Na_2Si(C_6H_4OCHO)_2$.

Introduction

The ability of silicon to form complexes was established early in the study of silicon chemistry. Fluorosilicates[3] containing the octahedral SiF_6^{2-} anion were reported prior to the nineteenth century and Dilthey[4] reported an octahedral β-diketone complex of silicon in 1903. Recently there has been renewed interest in the coordination chemistry of silicon. Tris(acetylacetonato)silicon(IV) chloride has been resolved into its optical isomers[5] confirming the structure proposed by Dilthey. Tris(α,α'-dipyridyl)silicon, a novel uncharged octahedral complex, has been reported.[6] Other octahedral silicon complexes containing phthalocyanine,[7] anions derived from tropolone and *N,N'*-dimethylaminotroponimine,[8] and 2-hydroxypyridine *N*-oxide[9] have been reported. Pike[10,11] has used organocarboxysilanes to prepare neutral nonionic hexacoordinate silicon complexes containing two-coordinate β-diketone ligands. Complexes containing five-coordinate silicon are now well established.[12-16] A large number of four- and six-coordinate adducts of silicon have been prepared and characterized using spectroscopy by Beattie and coworkers. These adducts, as well as others, have been reviewed by Beattie[17] and are included in a more recent review of coordination compounds of silicon by Aylett.[18]

From this brief review it is evident that relatively few complexes of silicon with bi- or multidentate ligands have been studied. In this report, unusual complexes of silicon were found to result from the treatment of silicon tetrachloride with 8-hydroxyquinoline and salicylaldehyde.

The preparation of bis(8-quinolinolato)silicon(IV) dichloride has been reported by Frazer;[19] however, few properties of this compound were given.

Discussion

Treatment of 8-hydroxyquinoline, dissolved in chlorobenzene, with excess silicon tetrachloride results in the formation of yellow solid and gaseous hydrogen chloride. The stoichiometry of this reaction is shown in eq 1.

$$SiCl_4 + 2C_9H_6NOH \rightarrow Si(C_9H_6ON)_2Cl_2 + 2HCl \quad (1)$$

The properties of this compound in the solid state and in solution are best explained assuming the structure illustrated in Figure 1. The silicon atom is four-coordinate with covalent bonds to the oxygen and nitrogen atom of the anion 8-hydroxyquinoline. The complex cation possesses a dipositive charge balanced by two chloride ions in the lattice. This compound does not behave in a fashion typical for silicon chlorides. It is unchanged on exposure to air for 1 month and does not melt or change visibly when heated in air to 360°. It is virtually insoluble in typical organic solvents such as methylene chloride, carbon tetrachloride, chlorobenzene, and ethers. The compound $Si(C_9H_6ON)_2Cl_2$ is moderately soluble in liquid ammonia and can be recovered unchanged from such solutions. The equivalent conductance of a 10^{-3} *M* solution of the complex in liquid ammonia at −23° was determined to be slightly above that found for typical uni-univalent electrolytes in this solvent. The complex dissolves in protonic solvents such as water, alcohol, and dimethylformamide to yield a clear yellow solution. All the chlorine in $Si(C_9H_6ON)_2Cl_2$ can be titrated with silver nitrate immediately after solution. Although there is no visible evidence of chemical reaction upon dissolution in these solvents, the complex cannot be recovered unchanged from these solutions. An indication of the rate of solvolysis of $Si(C_9H_6ON)_2Cl_2$ in various solvents may be obtained by adding ferric chloride to these solutions. Ferric ion forms a deep blue complex with 8-hydroxyquinoline. Such a deep blue color appears immediately when an aqueous solution of ferric chloride is added to a freshly prepared aqueous solution of $Si(C_9H_6ON)_2Cl_2$. Addition of ferric chloride in alcohol to $Si(C_9H_6ON)_2Cl_2$ in alcohol results in the formation of a light blue color. When ferric chloride in dimethylformamide is added to a solution of $Si(C_9H_6ON)_2Cl_2$ in dimethylformamide, a very light blue-green color appears. Addition of 1 drop of water to these alcohol or dimethylformamide solutions results in the immediate formation of the deep blue ferric complex.

Treatment of $Si(C_9H_6ON)_2Cl_2$ with ethanol for 48 hr at room temperature results in alcoholysis of 90% of the complex. This alcoholysis is described in eq 2.

$$Si(C_9H_6ON)_2Cl_2 + 4C_2H_5OH \rightarrow Si(OC_2H_5)_4 + 2C_9H_6ONH\cdot HCl \quad (2)$$

To demonstrate the discrete existence of the $Si(C_9H_6ON)_2^{2+}$ cation in this complex, metathetic reactions of the chloride salt to form salts containing other anions were investigated. The results of these investigations were complicated by the solvolysis of the complex in the solvents used. Conversion of $Si(C_9H_6ON)_2Cl_2$ to the bis(tetraphenylborate) complex in aqueous solution occurred as shown in eq 3. The product $Si(C_9H_6ON)_2(BPh_4)_2$ was isolated as a light yellow precipitate which formed immediately when solutions of the two reactants were mixed at 0°. Since hydrolysis of $Si(C_9H_6ON)_2Cl_2$ can yield 8-hydroxyquinolinium chloride, the tetraphenylborate salt, 8-hydroxyquinolinium tetraphenylborate, was prepared and shown to be different from the product of this reaction,

$$Si(C_9H_6ON)_2Cl_2 + 2KBPh_4 \rightarrow 2KCl + Si(C_9H_6ON)_2(BPh_4)_2 \quad (3)$$

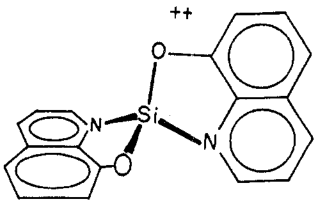

Figure 1. Structure proposed for $Si(C_9H_6ON)_2Cl_2$.

$Si(C_9H_6ON)_2(BPh_4)_2$. The conversion of $Si(C_9H_6ON)_2Cl_2$ to $Si(C_9H_6ON)_2\,Cr(NH_3)_2(SCN)_4)_2$ using Reinicke's salt was attempted but only the hydrolysis product $C_9H_6ONH\text{-}Cr(NH_3)_2(SCN)_4$ could be isolated in this case.

The infrared spectrum of $Si(C_9H_6ON)_2Cl_2$, Figure 2, indicates a chelate structure for this compound. The spectrum is generally similar to that of other complex compounds containing the 8-quinolinolate ligand.[20] A sharp absorption is present at 8.95 μ which is generally attributed to the carbon–oxygen frequency when the oxygen is complexed to a metal.[21] This spectrum is different from that of 8-hydroxyquinoline or 8-hydroxyquinoline hydrochloride and is consistent with a chelate structure rather than a simple ester of silicon. This difference is especially pronounced in the cesium bromide region where 8-hydroxyquinoline does not absorb below 425 cm^{-1}. There are two strong absorptions in the spectrum of $Si(C_9H_6ON)_2Cl_2$ at 343 and 383 cm^{-1}. The frequency of absorptions resulting from the presence of a metal–nitrogen bond is frequently assigned to this region. Thus, these absorptions may be typical for the silicon–nitrogen bond.[15]

X-Ray photoelectron spectroscopy provides good support for the ionic structure proposed for $Si(C_9H_6ON)_2Cl_2$. The binding energy of the 2p electron in chlorine is considerably different in chloride ion and covalently bonded chlorine. The chlorine 2p electron binding energies obtained from $Si(C_9H_6ON)_2Cl_2$ and Ph_3SiCl and two hydrochloride salts containing chloride ion are given in Table I. The chlorine 2p binding energy in $Si(C_9H_6ON)_2Cl_2$ is seen to be close to that obtained for chloride ion and substantially below that observed for Ph_3SiCl. The latter compound contains chlorine covalently bonded to silicon. Its binding energy thus is typical of covalent chlorides of silicon. The chlorine 2p binding energy in $Si(C_9H_6ON)_2Cl_2$ is about 0.8 eV above that observed for chloride ion and probably reflects some deviation from an unperturbed chloride ion. The binding energy shift of about 3.3 eV between covalently bound chlorine and ionic chloride is considerable and binding energy measurements are of great aid in interpreting the structure of adducts and complexes of silicon chlorides as well as other halides.

Table I. Core Electron Binding Energies (eV)

Compd	Si 2p(3/2)	Cl 2p(3/2)
$Si(C_9H_6ON)_2Cl_2$	102.0	197.4
Ph_3SiCl	101.2	199.9
Cys·HCl		196.6
Hist·2HCl		196.6

Since there is no evidence for covalently bonded chlorine in $Si(C_9H_6ON)_2Cl_2$, this compound probably is the first example of a dipositive tetracoordinate complex ion of silicon to be reported. Although a square-planar structure cannot be excluded, the structure of the complex ion $Si(C_9H_6ON)_2{}^{2+}$ is most likely tetrahedral on the basis of the known stereochemistry of tetracoordinate silicon compounds.[18]

$Si(C_9H_6ON)_2Cl_2$ also results from the treatment of 8-hydroxyquinoline with excess hexachlorodisilane. Hydrogen, silicon tetrachloride, trichlorosilane, and a trace of HCl also are produced in this reaction.

Salicylaldehyde dissolved in either chlorobenzene or carbon tetrachloride was found to react with silicon tetrachloride yielding a yellow solid and HCl. The stoichiometry of this reaction is similar to that observed for 8-hydroxyquinoline and silicon tetrachloride

$$SiCl_4 + 2C_6H_4OHCHO \rightarrow 2HCl + Si(C_6H_4OCHO)_2Cl_2 \qquad (4)$$

The yellow solid formed in this reaction was characterized as $Si(C_6H_4OCHO)_2Cl_2$ by its elemental analysis. Although the stoichiometry of this complex is similar to that of $Si(C_9H_6ON)_2Cl_2$, its properties are radically different. The complex formed from salicylaldehyde behaves as a fairly typical covalent silicon chloride. Thus, $Si(C_6H_4OCHO)_2Cl_2$ is hydrolyzed rapidly on exposure to moist air and violently on contact with water. As a consequence of this vigorous reactivity with water, a satisfactory chlorine analysis could be obtained only by treating $Si(C_6H_4OCHO)_2Cl_2$ with alcohol in the vacuum apparatus to determine the amount of HCl evolved. $Si(C_6H_4OCHO)_2Cl_2$ melts sharply at 166° under vacuum. The salicylaldehyde complex is slightly soluble in CH_2Cl_2 and dimethoxyethane. The solubility in either solvent is insufficient to allow determination of the molecular weight or observation of the NMR spectrum.

The infrared spectrum of $Si(C_6H_4OCHO)_2Cl_2$, Figure 3, trace a, indicates carbonyl oxygen bonded to silicon consistent with a chelate structure for the complex. The infrared spectrum contains no carbonyl absorption in the region of 1668 cm^{-1} where the salicylaldehyde carbonyl absorption occurs. After exposure of $Si(C_6H_4OCHO)_2Cl_2$ to air, the spectrum of this compound, Figure 3, trace b, possesses an absorption

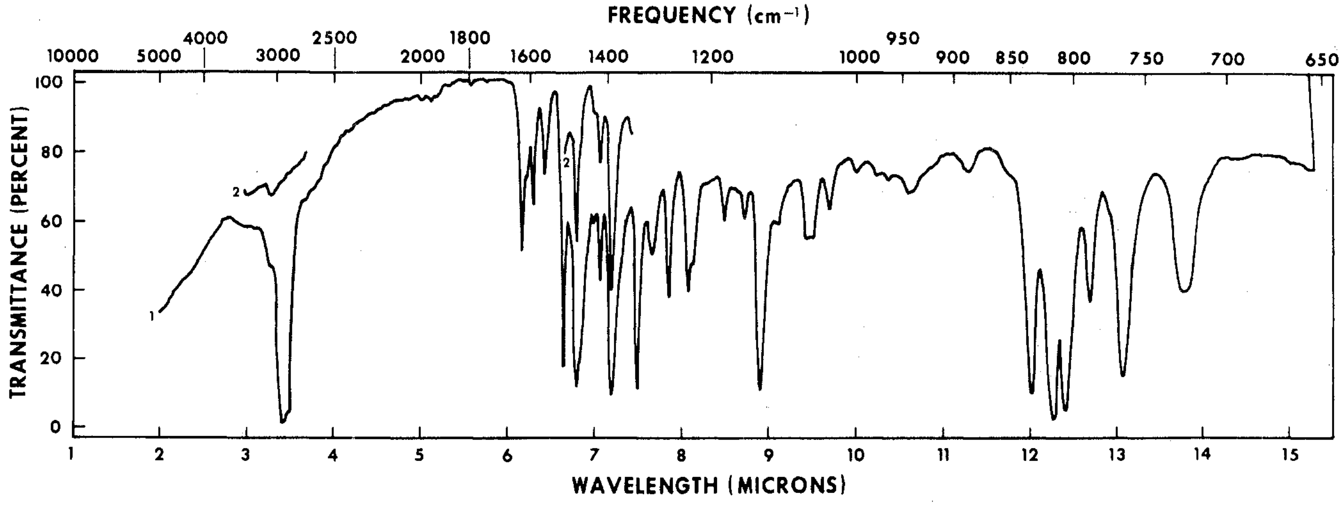

Figure 2. Infrared spectra of $Si(C_9H_6ON)_2Cl_2$: (1) in Nujol; (2) in Fluorolube.

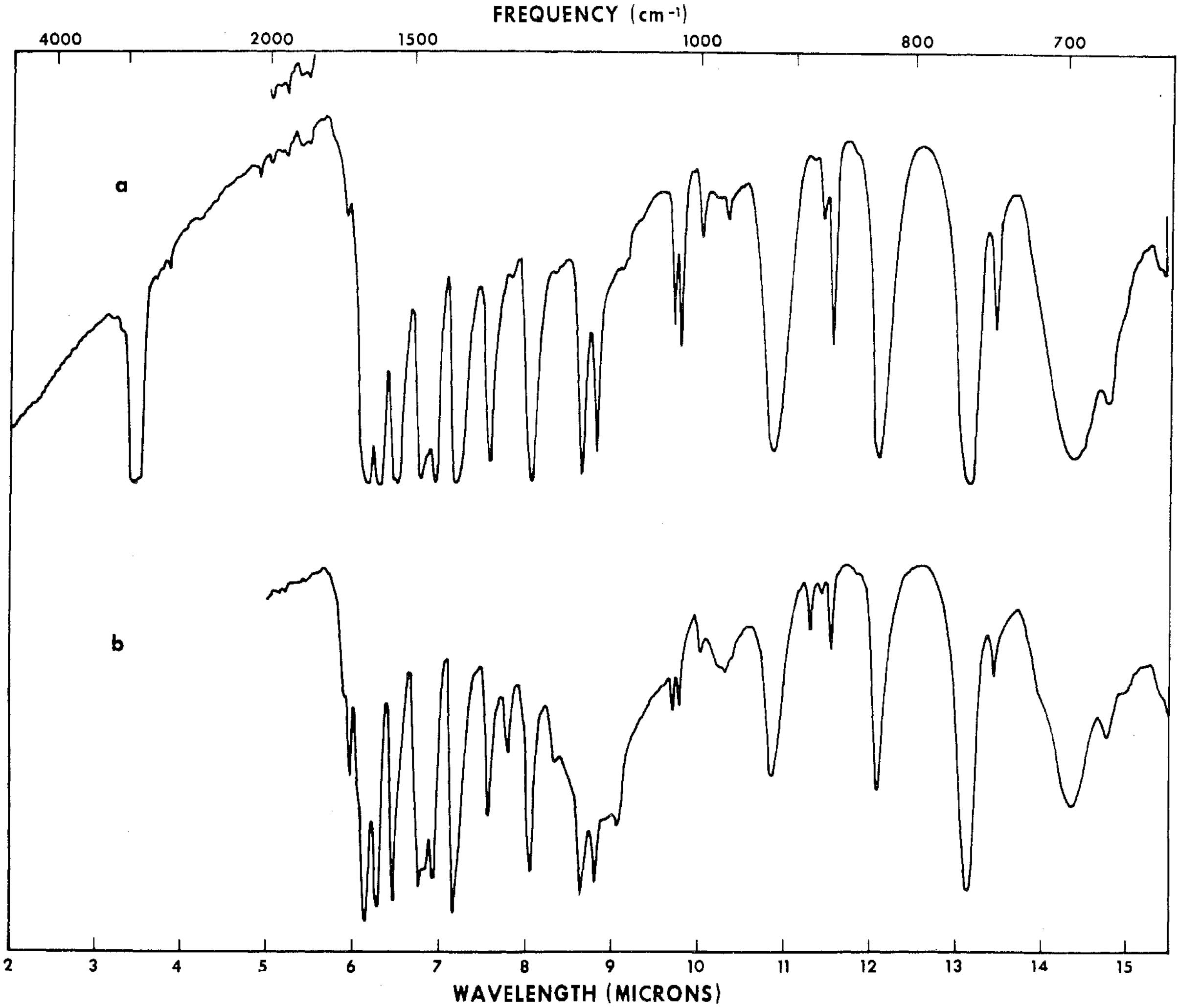

Figure 3. Infrared spectrum of $Si(C_6H_4OCHO)_2Cl_2$ before (a) and after (b) exposure to air.

band for the unshifted carbonyl at 1668 cm^{-1}. The relative intensity of this absorption increases on longer exposure of the compound to air. Similar differences in the carbonyl frequency are observed in the spectrum of complex compounds of salicylaldehyde with transition metals.[23] This evidence strongly suggests that the silicon atom in $Si(C_6H_4OCHO)_2Cl_2$ is covalently bonded to two chlorine atoms and to two salicylaldehydato bidentate ligands. The probable structure of this complex thus is octahedral. Although several stereoisomers are possible for such an octahedral complex, the extreme air sensitivity of the compound together with its low solubility excluded attempts to isolate cis and trans isomers. Since salicylaldehyde and other β-diketones are known to form polymeric complex compounds,[24] the possibility of a polymeric structure cannot be excluded since no molecular weight could be obtained due to the low solubility of this compound.

When $Si(C_6H_4OCHO)_2Cl_2$ is treated with alcohol, a red solid is formed and HCl is evolved. The stoichiometry of this reaction was found to be as in eq 5. The red solid from this

$$Si(C_6H_4OCHO)_2Cl_2 + 2C_2H_5OH \rightarrow 2HCl + Si(C_6H_4OCHO)_2(OC_2H_5)_2 \quad (5)$$

reaction was characterized as $Si(C_6H_4OCHO)_2(OC_2H_5)_2$ by its elemental analysis. The red solid did not change in air when heated to 360°. It is stable in air and does not dissolve or appear to change on contact with nonpolar solvents and dilute acid or alkali. These properties suggest a polymeric structure for $Si(C_6H_4OCHO)_2(OC_2H_5)_2$ which would furnish some support for a polymeric structure for $Si(C_6H_4OCHO)_2Cl_2$.

Treatment of $Si(C_6H_4OCHO)_2Cl_2$ with sodium naphthanide in dimethoxyethane yields a tan amorphous solid. This solid was characterized as $Na_2Si(C_6H_4OCHO)_2$ by its elemental analysis. It is soluble in dimethoxyethane and insoluble in benzene. Assuming that the salicylaldehydato groups are coordinated, this compound is a sodium salt of a dinegative four-coordinate complex ion of silicon. Although this anion is unusual among silicon compounds, similar ions have been reported. Cowell, Urry, and Weissman[25] reported the dinegative ion bis(2,2'-biphenylene)silane as resulting from the treatment of bis(2,2'-biphenyl)silane with potassium metal in dimethoxyethane.

Experimental Section

Apparatus and Reagents. The work described in this paper was carried out using a standard vacuum apparatus and techniques as described in the literature.[26] All of the reactions and subsequent manipulations such as filtrations were carried out in glass apparatus fitted with O-ring joints fitted with Viton-A O rings. **Silicon tetrachloride,** obtained from the Stauffer Chemical Co., Weston, Mich., was repeatedly fractionated through traps maintained at −63, −95, and −196° until the fraction in the −95° trap exerted a vapor tension of 77.5 mm at 0°. The vapor pressure reported for pure silicon tetrachloride at this temperature is 77.0 mm. **8-Hydroxyquinoline,** reagent grade, obtained from Eastman Organic Chemicals, Rochester, N.Y., was used as received. **Chlorobenzene,** obtained from Fisher Scientific Co., Fairlawn, N.J., was dried over calcium hydride and distilled through traps maintained at 0, −45, and −79°. The chlorobenzene retained in the −45° trap had a vapor pressure of 2.8 mm at 0°. **Ethyl alcohol,** absolute, commercial grade, was dried with calcium hydride and distilled through traps maintained at −23, −45, and −79°. Ethyl alcohol retained in the −45° trap had a vapor tension of 12 mm at 0°. The literature value is 12 mm at 0°. ***N,N*-Dimethylformamide,** commercial grade, was dried over calcium hydride and used without further purification. **Ammonia,** commercial grade, was dried over sodium and used without further purification. **Acetonitrile,** obtained from Fisher Scientific Co., Fairlawn, N.J., was dried over calcium hydride and used without further purification. **Silver nitrate,** reagent grade, obtained from Mallinckrodt Chemical Works, St. Louis, Mo., was used as received. **Sodium tetraphenylborate,** reagent grade, obtained from Baker Chemical Co., Phillipsburg, N.J., was used as received. **Salicylaldehyde,** purified, obtained from Fisher Scientific Co., Fairlawn, N.J., was distilled in a simple distillation apparatus at 20 mm. The fraction which distilled at 82° was stored under vacuum and used as needed. It did not change from a clear, colorless liquid when stored in the dark under vacuum. **Carbon tetrachloride,** spectroquality reagent, obtained from Matheson Coleman and Bell, Norwood, Ohio, was dried over calcium hydride and used without further purification. **Disilicon hexachloride,** obtained from the Stauffer Chemical Co., Weston, Mich., was distilled through traps maintained at 0, −23, and −79°. The fraction retained at −23° had a vapor tension of 4.0 mm at 0°. **Dimethoxyethane,** commercial grade, was dried over calcium hydride and distilled through traps maintained at −23, −45, and −196° until the vapor tension of the −45° fraction remained constant. Dimethoxyethane, retained in the −45° trap, exerted a vapor tension of 18.5 mm of mercury at 0°. **Sodium naphthanide,** in solution, was prepared by stirring an equivalent amount of sodium chips and naphthalene in monoglyme under nitrogen. The concentration of the sodium naphthanide solution was determined by titration with a normal solution of alcohol in monoglyme.[27]

Spectral Measurements. The infrared spectra in the sodium chloride region were taken of samples in Nujol mulls on a Perkin-Elmer 221 spectrometer. The spectra in the cesium bromide region were taken of samples in Nujol mulls on a Beckman IR 5A spectrophotometer. Core electron binding energies were measured using a Varian 1EE-15 photoelectron spectrometer. Measurements were made on powders attached to double-back tape in the usual manner. Sample charging effects were minimal and all shifts were referenced to the carbon line assumed to be at 284.0 eV.

Preparation and Properties of $Si(C_9H_6ON)_2Cl_2$. A 50-ml flask, containing 1.655 mmol of 8-hydroxyquinoline and a Teflon-coated stirring bar, was attached to the manifold of the vacuum line and evacuated. About 25 ml of chlorobenzene and 1.775 mmol of silicon tetrachloride were condensed into the bulb. When this mixture was warmed to room temperature, a clear solution and a yellow solid were present. The reactants were stirred for 20 hr at room temperature and the volatile material present at the end of this time was distilled into a trap at −196°. This volatile mixture was separated by distillation into traps maintained at −63, −95, and −196°. The −196° trap contained 1.70 mmol of vapor characterized as HCl by its vapor pressure. The −95° trap contained 0.873 mmol of silicon tetrachloride. The solvent chlorobenzene, was retained in the −63° trap. The yellow solid remaining in the reaction bulb was heated to 200° with pumping. No change took place on heating. The yellow solid did not change visibly when heated to 360° in a capillary in air. Two elemental analyses obtained from different preparations were averaged. Anal. Calcd for $Si(C_9H_6ON)_2Cl_2$: C, 55.85; H, 3.1; N, 7.24; Cl, 18.32; Si, 7.22. Found: C, 55.48; H, 3.34; N, 7.15; Cl, 18.55; Si, 7.09.

The infrared spectrum of a sample of $Si(C_9H_6ON)_2Cl_2$ exposed to air for 1 month was identical with the ir spectrum of a freshly prepared sample. The complex dissolves immediately with no visible evidence of change in water, alcohol, and dimethylformamide to yield clear yellow solutions. Addition of ferric chloride to an aqueous solution of the complex results in the formation of an immediate deep blue color. This color is due to the ferric 8-quinolinolato complex and indicates the rapid hydrolysis of $Si(C_9H_6ON)_2Cl_2$ in solution. All the chloride present in this compound can be titrated with silver chloride immediately after solution of the compound in water. $Si(C_9H_6ON)_2Cl_2$ does not appear to dissolve in the solvents benzene, chlorobenzene, toluene, methylene chloride, chloroform, carbon tetrachloride, acetone, and pyridine. A sample of $Si(C_9H_6ON)_2Cl_2$ was allowed to stand with excess ammonia for 2 hr at −30°. All of the liquid ammonia was recovered and the infrared spectrum of the $Si(C_9H_6ON)_2Cl_2$ was unchanged. The resistance of a solution of $Si(C_9H_6ON)_2Cl_2$ in liquid ammonia was determined with an Aerovox Model 76 capacitance resistance bridge. A solution approximately 10^{-3} *M* exhibited a minimum equivalent conductance of 345 cm^3 ohm^{-1} at −23°. We record this as a minimum value since, due to solubility difficulties, about 5% of the complex remained undissolved.

The infrared absorption spectrum of $Si(C_9H_6ON)_2Cl_2$ in the NaCl region is shown in Figure 2. The infrared spectrum of $Si(C_9H_6ON)_2Cl_2$ in the cesium bromide region contained the following absorptions (wavelength in microns): 12.51 (vs), 13.30 (s), 13.95 (m), 15.15 (w), 15.85 (w), 16.60 (m), 16.90 (m), 17.45 (m), 19.35 (w), 20.25 (vs), 20.55 (vs), 21.10 (w), 24.25 (w), 26.15 (vs), 29.15 (m).

Reaction of $Si(C_9H_6ON)_2Cl_2$ with Ethanol. A 50-ml bulb containing 0.602 mmol of $Si(C_9H_6ON)_2Cl_2$ and a Teflon-coated stirring bar was attached to the vacuum apparatus and evacuated. Ethyl alcohol, 3.13 mmol, was condensed in the bulb and the mixture was allowed to warm to room temperature. The reactants were stirred for 48 hr and appeared unchanged after this time. The material volatile at room temperature was distilled into a trap maintained at −196°. The residue remaining in the reaction flask was heated at 175° for several hours. A bright yellow crystalline material sublimed to the cold surface of the bulb leaving a light yellow solid behind. The yellow sublimate was characterized by its infrared spectrum as 8-hydroxyquinolinium chloride. The nonvolatile yellow solid was characterized as $Si(C_9H_6ON)_2Cl_2$ by its infrared spectrum. Approximately 10% of the complex initially present was recovered unchanged. The volatile material in the −196° trap was separated into two components and identified as alcohol and tetraethoxysilane.

Preparation of $Si(C_9H_6ON)_2(B(C_6H_5)_4)_2$. About 1 mmol of sodium tetraphenylborate in water at 0° was added with stirring to 0.5 mmol of $Si(C_9H_6ON)_2Cl_2$ dissolved in water at 0°. A light yellow precipitate formed immediately when the solutions were mixed. This mixture was allowed to stand at 0° for 10 min. The precipitate was collected on a glass frit and washed several times with ice water. The precipitate was then dried by heating at 50° with pumping in the vacuum apparatus. The results of the elemental analysis of this precipitate were in good agreement with percentages calculated for $Si(C_9H_6ON)_2(B(C_6H_5)_4)_2$. Anal. Calcd for $Si(C_9H_6ON)_2(B(C_6H_5)_4)_2$: C, 83.0; H, 5.45; N, 2.93. Found: C, 82.5; H, 5.55; N, 3.00.

The infrared spectrum of this precipitate, Figure 4, consists of absorptions characteristic of the $Si(C_9H_6ON)_2{}^{2+}$ ion together with absorptions due to the tetraphenylborate ion.

Reaction of Disilicon Hexachloride and 8-Hydroxyquinoline. A 50-ml bulb containing 1.18 mmol of 8-hydroxyquinoline was attached to the vacuum apparatus and evacuated. Disilicon hexachloride (1.03 mmol) and benzene (16.00 mmol) were condensed in the bulb at −196°. The mixture was warmed to room temperature, a light orange-yellow solid precipitated from solution, and a gas evolved slowly from the mixture. After 1 hr, the bulb was cooled to −196° and opened to a manifold leading to a Toepler system. A noncondensable gas, 0.144 mmol, was removed from the reaction mixture. This gas was characterized as hydrogen by combustion over copper oxide at 350–400°. The reaction mixture then was warmed to room temperature and the volatile material present was distilled and separated. A 15.95-mmol amount of benzene, the solvent, was removed in this manner. Two other components were obtained; 0.68 mmol of the lesser volatile component was characterized as silicon tetrachloride. The highly volatile component, 0.59 mmol, was characterized as trichlorosilane by its vapor pressure, molecular weight, and infrared spectrum. A trace of HCl was also present. A light orange-yellow solid remained in the bulb after the volatile material was removed. This solid did not change when heated to 200° under vacuum or 360° in air. Its infrared spectrum was identical with that of $Si(C_9H_6ON)_2Cl_2$, shown in Figure 1. Anal. Calcd for $Si(C_9H_6ON)_2Cl_2$: C, 55.85; H, 3.1; N, 7.24; Cl, 18.32. Found: C, 51.42; H, 3.22; N, 6.69; Cl, 17.61. The discrepancy in these results is probably due to a small amount of orange solid mixed with $Si(C_9H_6ON)_2Cl_2$. No attempt was made to separate these substances.

Preparation and Properties of $Si(C_7H_5C_2)_2Cl_2$. A 50-ml bulb containing 1.98 mmol of salicylaldehyde and a Teflon-coated stirring bar was attached to the vacuum apparatus and evacuated. About 25 ml of chlorobenzene and 1.45 mmol of silicon tetrachloride were condensed into the bulb. On warming the mixture to room temperature the reactants dissolved in the solvent yielding a clear solution. This solution slowly turned yellow and at the end of 2 days a yellow solid had precipitated out of solution. The bulb containing this reaction mixture was opened to the manifold of the vacuum apparatus and the volatile material present was distilled through traps maintained at −63, −112, and −196°. The yellow solid which remained in the

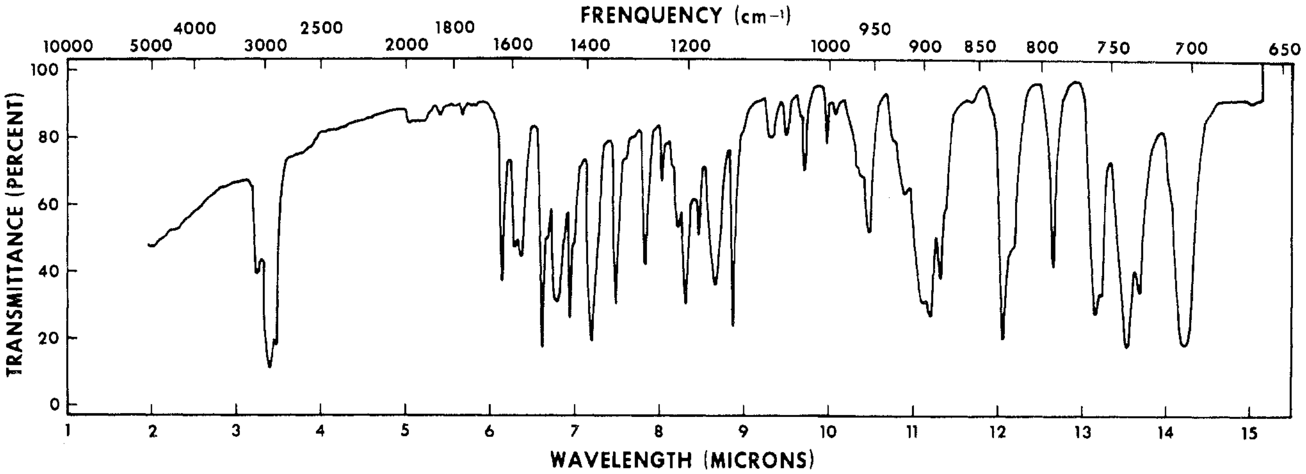

Figure 4. Infrared spectrum of $Si(C_9H_6ON)_2(B(C_6H_5)_4)_2$.

bulb was heated at 90° for 2 hr to remove any entrained solvent. The −196° trap contained 1.99 mmol of vapor characterized as HCl by its vapor pressure. The −112° trap contained 0.463 mmol of silicon tetrachloride. The solvent and a small amount of silicon tetrachloride were retained in the −63° trap. This mixture was condensed in alkaline water and titrated with standard silver nitrate solution. By this method, the solvent was found to contain 0.049 mmol of silicon tetrachloride. From these data 1.99 mmol of salicylaldehyde reacted with 0.96 mmol of silicon tetrachloride to yield a yellow solid of the composition $Si(C_7H_5O_2)_{2.03}Cl_{1.97}$ and 1.99 mmol of HCl was evolved. Anal. Calcd for $Si(C_7H_5O_2)_2Cl_2$: C, 49.3; H, 2.93; Cl, 20.8; Si, 8.2. Found (yellow solid): C, 50.62; H, 3.45; Cl, 18.7; Si, 8.42. A chlorine analysis of this yellow solid was difficult due to its rapid hydrolysis in moist air. The chlorine analysis reported above was obtained as follows. A sample of $Si(C_7H_5O_2)_2Cl_2$ was transferred into a tared 50-ml bulb in the drybox. The bulb was quickly weighed, attached to the vacuum apparatus, and evacuated. Ethanol was condensed into the bulb and the reactants were stirred for 24 hr. The volatile material present after this time was condensed in alkali and the amount of HCl present was titrated with standard silver chloride. An average of several values is given above. A red solid remained in the reaction bulb after ethanolysis. Anal. Calcd for $Si(C_7H_5O_2)_2(OC_2H_5)_2$: C, 60.0; H, 5.52. Found: C, 59.78; H, 5.56. The ethoxide did not melt or change when heated to 330° in air. It is insoluble in ethanol, chloroform, toluene, and water. It is so hard that it cannot be ground fine enough to obtain an infrared spectrum.

$Si(C_7H_5O_2)_2Cl_2$ melted in vacuo at 166° sharply. It was found to be virtually insoluble in toluene, chlorobenzene, and carbon tetrachloride. It was very slightly soluble in methylene chloride and dimethoxyethane. The infrared spectrum of $Si(C_7H_5O_2)_2Cl_2$ in a Nujol mull prepared in an atmosphere of nitrogen in a drybox is shown in the upper part of Figure 3. The lower spectrum in Figure 3 shows the infrared spectrum of the same compound in a mull that was prepared in moist air.

Treatment of $Si(C_7H_5O_2)_2Cl_2$ with Sodium Naphthanide. In the drybox, a sample of $Si(C_7H_5O_2)_2Cl_2$ was placed in a weighed vacuum filtration apparatus containing a thin-walled capillary tube filled with sodium. The apparatus was quickly removed from the drybox and evacuated. In a typical experiment, 0.736 mmol of $Si(C_7H_5O_2)_2Cl_2$, 2.26 mmol of sodium in a capillary tube, and approximately 1 mmol of naphthalene were used. Dimethoxyethane was condensed into the apparatus and the reactants were then warmed to room temperature. The capillary containing the sodium was broken. The color of the sodium naphthanide was visible at the surface of the sodium until the sodium had disappeared. The mixture resulting from this treatment consisted of a flocculant precipitate and a light orange-brown solution. The solution was filtered several times under vacuum. Dimethoxyethane was distilled away from the filtrate. A light brown solid was left behind. This solid was heated at 60° for 24 hr with pumping. During this process a light crystalline solid sublimed to the cold part of the apparatus. This sublimate was identified as naphthalene. The yellow-brown solid resulting from this treatment was washed several times with benzene under vacuum. The solid then was heated at 60° for several hours to remove any benzene entrained in the solid. The compound was characterized as $Na_2Si(C_7H_5O_2)_2$ by its analysis. Anal. Calcd for $Na_2Si(C_7H_5O_2)_2$: C, 53.2; H, 3.17; Na, 14.6. Found: C, 53.5; H, 4.53; Na, 14.75.

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Registry No. $Si(C_9H_6ON)_2Cl_2$, 55124-08-8; $Si(C_9H_6ON)_2(BPh_4)_2$, 55124-10-2; $Si(C_6H_4OCHO)_2Cl_2$, 55124-11-3; $Si(C_6H_4OCHO)_2(OC_2H_5)_2$, 55124-12-4; $Na_2Si(C_6H_4OCHO)_2$, 55124-13-5; C_2H_5OH, 64-17-5.

References and Notes

(1) The work herein reported fulfilled in part the requirements for the degree of Doctor of Philosophy for M. M. Millard at Purdue University, Aug 1963.

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