Synthesis and Characterization of Bis(2-Aminobenzoato)Diphenylsilicate and Bis(2-Aminothiophenoxy)Diphenylsilicate - New Hexacoordinated Silicates Dianions With Seven Membered Rings

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ABSTRACT

Hexacoordinated dianionic silicates $[(C_7H_5O_2N)_2Si(C_6H_5)_2]^{2-}$ $[NHEt_3]_2^{+}$ and $[(C_6H_5NS)_2Si(C_6H_5)_2]^{2}$-$[NHEt_3]_2^{+2}$ are obtained from reaction between tetracoordinate silicon (IV) compound, diphenylsilane, and ligands such as anthranilic acid and o-aminothiophenol. All the compounds are characterized by elemental analysis, molar conductance data as well as IR and ^1H, ^{13}C, ^{29}Si NMR spectroscopy. FAB mass spectra (NBA matrix) of compounds 1 and 2 have identified respective cations and anions of these complexes.

INTRODUCTION

There is well-established chemistry of hypercoordinated silicates, where silicon is bonded to oxygen atom system with SiO_5/SiO_6 or SiO_4R/SiO_5R (where R = F or other alkyl/aryl groups skeletal arrangement). However, there are few reports where silicon is bonded to N, S atoms in this silicon framework /1-3/. In order to understand the effect of these groups/atoms attached to silicon on the structure and reactivity it is desirable to bring variation in the environment around the silicon atom. Hence we have prepared compounds bearing N, S atoms in silicon framework by using ligands like anthranilic acid and o-aminothiophenol respectively.

EXPERIMENTAL

All manipulations were performed under dry nitrogen atmosphere using an all-glass vacuum line. Solvents were dried according to standard procedures reported in literature. Anthranilic acid was dried at 50° C under vacuum for 2-3 days. o-aminothiophenol (Fluka) commercially available was used as such.

Triethylamine was refluxed over potassium hydroxide pellets and distilled under nitrogen atmosphere prior to use. Diphenylsilane (Alfa Aesar) commercially available was used as such. Infrared spectra were routinely obtained as nujol mulls on a Perkin Elmer model 1430 ratio recording spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300MHz instrument operating at 300 MHz for ^{1}H and 75.47 MHz for ^{13}C nuclei respectively. ^{29}Si NMR spectra were carried out on a Bruker AMX-400 spectrometer operating at 74.49MHz. All chemical shift values are reported with respect to TMS as external standard. FAB mass spectra of the samples were obtained on micromass VG-7070 E spectrometer by the SIMS method in 3-nitrobenzyl alcohol (NBA) matrix. C H N analysis of the samples were performed on the Perkin Elmer model 2400 C H N analyzer while S and Si contents were estimated gravimetrically.

PREPARATIONS AND CHARACTERISATIONS

Compound 1:

To the solution of anthranilic acid (1.75 g, 12.8 mmoles) in dry acetonitrile (30 mL), triethylamine (1.8 mL, 12.8 mmoles) was added. The contents were cooled to 0°C and then diphenylsilane (1.17 mL, 6.4 mmoles) was added dropwise. The clear solution obtained was stirred for 3-4 hours. The solvent was evaporated under vacuum from the solution under dry nitrogen atmosphere. On addition of pure dried diethylether to this solution, off white solid was precipitated out. The reaction mixture was again stirred for 1 hour, the solid was filtered, washed with diethylether and dried under vacuum.

Yield:

68%, Melting pt. > 200° C, Λ_M (DMSO Ω^{-1} cm^2 mol^{-1}) 63.1, Anal. Calcd. For $C_{38}H_{52}N_4O_4Si$, C=69.51, H=7.92, N=8.53, Si=4.26. Found: C=68.84, H=7.14, N=7.76, Si= 4.20.

IR (Nujol cm^{1}):

3321.6 (ν_{N-H}), 2703 (ν_{N-H} triethylammonium), 1641 ($\nu_{C=O}$ carboxylate), 1569, 1468, 1360 ($\nu_{C=C}$ aromatic), 1258 (ν_{C-O}), 1119 (ν_{Si-Ph}), 1055 (ν_{C-N}), 8.75 (ν_{Si-O}).

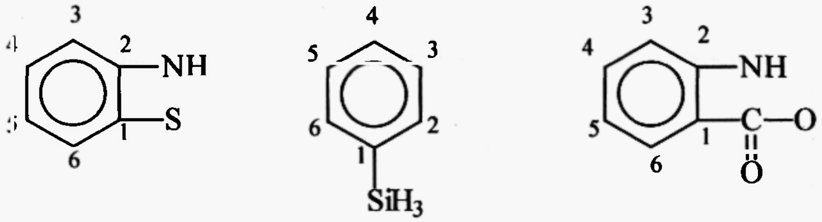
δ ^{1}H NMR ($CDCl_3$ + DMSO-d_6):

4.7 (br, NH, 2H), 2.7 (q, 12H), 1.0 (t, 18H), 6.9 (d, 2H, o-aminobenzoato group), 7.3 (d, 2H, o-aminobenzoato group), 7.9 (t, 2H, o-aminobenzoato), 6.7 (t, 2H, o-aminobenzoato group), 7.0 (d, 2H, Ph ring), 7.3 (t, 2H, Ph ring), 7.2 (t, 1H, Ph ring).

δ ^{13}C NMR ($CDCl_3$ + DMSO-d_6):

172.0 (COO), 113.4 (C_1, o-aminobenzoato group), 150.2 (C_2, o-aminobenzoato group), 115.8 (C_3, o-aminobenzoato group), 132.1 (C_4, o-aminobenzoato group), 117.5 (C_5, o-aminobenzoato group), 131.4 (C_6, o-aminobenzoato group), 126.8 (C_1, Ph ring), 133.2 (C_2/C_6, Ph ring), 127.4 (C_3/C_5, Ph ring), 130.4 (C_4, Ph ring), 45.1 ($-CH_2$), 8.2 ($-CH_3$).

Carbon atom numbering scheme



δ ^{29}Si NMR ($CDCl_3$ + DMSO-d_6):

-111.2 ppm.

Compound 2:

Following the procedure as mentioned above for the preparation of compound 1, compound 2 was prepared by reacting o-aminothiophenol (1.36 mL, 12.8 mmoles), triethylamine (1.8 mL, 12.8 mmoles) with diphenylsilane (1.17 mL, 6.4 mmoles) in dry acetonitrile (30 mL).

Yield:

68%, Melting pt. > 200° C, Λ_M (DMSO Ω^{-1} cm^2 mol^{-1}) 64.1, Anal. Calcd. For $C_{36}H_{52}N_4S_2Si$, C=68.35, H=8.22, N=8.86, S=10.12, Si=4.26. Found: C=67.68, H=7.44, N=8.09, S= 9.34, Si=4.20.

IR (Nujol cm^{-1}):

2923 ($\nu_{C\text{-}H}$ aliphatic), 2657 ($\nu_{N\text{-}H}$ triethylammonium), 1608, 1574, 1448, 1363 ($\nu_{C=C}$ aromatic), 1120 ($\nu_{Si\text{-}Ph}$), 1069 ($\nu_{C\text{-}N}$), 761 ($\nu_{C\text{-}S}$).

δ ^{1}H NMR ($CDCl_3$ + DMSO-d_6):

4.4 (br, NH, 2H), 2.8 (q, 12H), 1.3 (t, 18H), 6.8 (d, 2H, o-aminothiophenoxy group), 7.4 (d, 2H, o-aminothiophenoxy group), 7.8 (t, 2H, o-aminothiophenoxy group), 8.1 (t, 2H, o-aminothiophenoxy group), 7.2 (t, 1H, Ph ring), 7.5 (t, 2H, Ph ring), 7.0 (d, 2H, Ph ring).

δ ^{13}C NMR ($CDCl_3$ + DMSO-d_6):

135.5 (C_1, o-aminothiophenoxy group), 149.2 (C_2, o-aminothiophenoxy group), 114.6 (C_3, o-aminothiophenoxy group), 116.8 (C_4, o-aminothiophenoxy group), 126.5 (C_5, o-aminothiophenoxy group), 133.9 (C_6, o-aminothiophenoxy group), 128.6 (C_1, Ph ring), 136.1 (C_2/C_6, Ph ring), 128.9 (C_3/C_5, Ph ring), 130.8 (C_4, Ph ring), 45.6 (-CH_2), 11.1 (-CH_3).
(Carbon atom numbering, see above).

δ ^{29}Si NMR ($CDCl_3$ + DMSO-d_6):

-54 ppm.

RESULTS AND DISCUSSION

Compounds 1 and 2 are prepared by reaction of diphenylsilane, triethylamine and ligands such as anthranilic acid and o-aminothiophenol respectively in 1:2:2 molar ratio as given in Fig. 1.

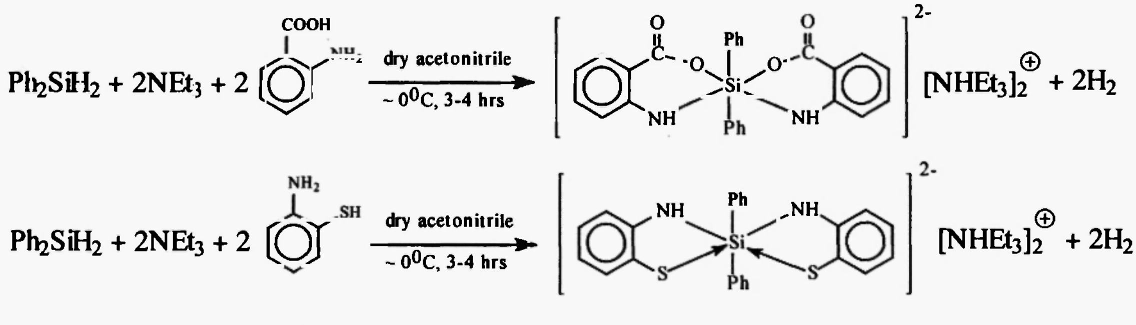


Figure 1.

Complexes 1 and 2 are off-white hygroscopic solids (yield 65-68%) and were found soluble in chloroform and DMSO. These complexes have been characterized by elemental analysis, molar conductance as well as IR and ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy. The FAB mass spectra of 1 and 2 are reported in Table 1.

The IR spectrum of compound 1 reveals a broad band centered at 1641 cm^{-1}, which is ascribed to $\nu_{C=O}$ (carboxylate) of the amino benzoate group. This band has shifted ~ 40 cm^{-1} towards lower frequency as compared to that in the spectrum of free acid ($\nu_{C=O}$ 1680 cm^{-1}) /4/, thereby indicating the chelation of acid to the silicon. The bands at 1569 cm^{-1}, 1468 cm^{-1}, 1360 cm^{-1} are due to $\nu_{C=C}$. The band appearing at 3321 cm^{-1} is attributed to $\nu_{N\text{-}H}$ of aminobenzoate group, which has shifted ~ 51 cm^{-1} towards lower frequency than that of free amino group in aminobenzoic acid ($\nu_{N\text{-}H}$ 3372 cm^{-1}), which confirms that silicon is bonded to N-H of aminobenzoic acid /5/. The band due to $\nu_{Si\text{-}Ph}$ appears at 1119 cm^{-1} /6/. The infrared spectrum of this compound also shows bands at 2930, 2703, 1258, 1055, 875 cm^{-1}, which are assigned to $\nu_{C\text{-}H}$ (aliphatic). $\nu_{N\text{-}H}$ (triethylammonium), $\nu_{C\text{-}O}$, $\nu_{C\text{-}N}$, $\nu_{Si\text{-}O}$ vibrations respectively.

The IR spectrum of compound 2 reveals absorption at 1120 cm^{-1} ($\nu_{Si\text{-}Ph}$). The band at 3110 cm^{-1} has been assigned to N-H group. This absorption is at lower frequency than observed for free NH_2 group of o-aminothiophenol (3300-3200 cm^{-1}), which suggests its chelation to silicon. The bands at 1608, 1574, 1448, 1363 cm^{-1} are attributed to $\nu_{C=C}$ vibrations of the ring. Bands at 2923, 2657, 1069, 761 cm^{-1} are assigned to $\nu_{C\text{-}H}$ (aliphatic). $\nu_{N\text{-}H}$ (triethylammonium), $\nu_{C\text{-}N}$, $\nu_{C\text{-}S}$ respectively.

^{1}H NMR spectrum (300 MHz) of compound 1 in DMSO/$CDCl_3$ exhibits a doublet centred at 7.0 ppm and two triplets centred at 7.2 and 7.3 ppm, which are assigned to ortho, para and meta protons of the phenyl groups attached to silicon atom. The signals due to o-aminobenzoate group appear at 6.9 (d), 7.3 (d), 7.9 (t), 6.7 (t) ppm. A broad signal centred at 4.7 ppm has been assigned to N-H proton of triethylammonium cation. The signal due to $-CH_2$ and $-CH_3$ groups of triethylammonium cation are observed at 2.7 and 1.0 ppm as quartet and triplet respectively. The integrated proton ratio of aromatic group and triethylammonium ion supports the composition as assigned to the compound 1.

^{1}H NMR spectrum of compound 2 gives two triplets centred at 7.5 and 7.2 ppm and one doublet centred at 7.0 ppm due to phenyl group protons attached to silicon. Two doublets at 6.8 and 7.4 ppm and two triplets at 7.8 and 8.1 ppm are due to o-aminothiphenoxy group. Signal at 2.8 (q, 6H) and 1.3 (t, 9H) and broad signal at 4.4 ppm are due to $-CH_2$, $-CH_3$ and -NH group of triethylammonium ion.

^{13}C NMR spectra of these compounds are recorded in DMSO/$CDCl_3$. The carbon atoms are numbered as shown in the experimental section.

^{13}C NMR spectrum of compound 1 gives signals at 126.8, 133.2, 127.4, 130.4 ppm due to C_1, C_2/C_6, C_3/C_5, C_4 of phenyl group. Signals at 113.4, 150.2, 115.8, 132.1, 117.5, 131.4 ppm are attributed to C_1, C_2, C_3, C_4, C_5, C_6 of o-amino benzoate group. The peak at 172.0 ppm is due to –COO carbon of o-aminobenzoate group. The signals due to $-CH_2$ and $-CH_3$ of triethylammonium cation, observed at 45.1 and 8.2 ppm respectively, are upfield relative to those of free base, indicating the protonation of triethylamine base forming the cation.

^{13}C NMR spectrum of compound 2 gives signals at 128.6, 136.1, 128.9, 130.8 ppm due to C_1, C_2/ C_6, C_3/C_5, C_4 of phenyl group. Signals at 135.5, 149.2, 114.6, 116.8, 126.6, 133.9 ppm due to C_1, C_2, C_3, C_4, C_5, C_6 of o-aminothiophenoxy group. Signals due to $-CH_2$ and $-CH_3$ of triethylammonium cation are observed at 45.6 and 11.1 ppm respectively.

In the literature ^{29}Si NMR chemical shifts are used to indicate the coordination number around silicon atom, although variations are largely dependent on factors such as electronegativity of the acyclic substituents and ring size of the fragments /7, 8/. ^{29}Si NMR spectrum of compound 1 in $CDCl_3$ + DMSO-d_6 showed a signal at –111.2 ppm. ^{29}Si NMR spectrum of compound 2 exhibits a sharp signal at –54 ppm.

The access to single crystals of the complexes 1 and 2 was denied as powdery substance precipitated out from the solution each time. However, in the absence of X-ray crystal structure data, FAB mass spectra have been employed to gain evidence for the formation of anionic silicates /9/. Selected FAB mass spectral data are summarized in Table-1.

Table 1

Selected FAB mass spectral data (in 3-nitrobenzyl alcohol, NBA) forcompound 1 and compound 2

Compound	Positive ion mode (m/z)	Negative ion mode (m/z)
1.	$[NHEt_3]_2^+$ (204) $[NHEt_3]^+$.NBA (255)	$[(C_7H_5O_2N)_2Si(C_6H_5)_2]^{2-}$ (452) $[(C_7H_5O_2N)_2Si(C_6H_5)_2]^{2-}$.2NBA (758) $[C_6H_4NH_2COO]^-$ (136) $[(C_6H_4NH_2COOH).OCH_2C_6H_5]^-$ (244)
2.	$[NHEt_3]_2^+$ (204) $[NHEt_3]^+.C_6H_4NH_2SH$ (228) $C_6H_5NH_3^+$.NBA (248)	$[(C_6H_5NS)_2Si(C_6H_5)_2]^{2-}$ (428) $[(C_6H_5NS)_2Si(C_6H_5)_2]^{2-}.C_6H_5CH_2OH$ (536) $[(C_6H_5NS)_2Si(C_6H_5)_2]^{2-}$.NBA (581) $[C_6H_4NH_2S]^-$ (124)

CONCLUSION

The formation of hexacoordinated silicate dianion bearing a seven-membered ring is supported by the above studies. The exact structural details may further be supported from X-ray crystal data, the study of which is in progress .

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