Schiff base functionalized Organopropylsilatranes: Synthesis and structural characterization

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Abstract. Synthesis of Schiff bases linked to organopropylsilatranes were performed by condensation reaction of post-functionalized silatranes such as aminopropylsilatrane (**4**), aminopropyl-3,7,10-trimethylsilatrane (**5**) and N-substituted aminopropylsilatrane (**10**) with two different aldehydes *viz.* pyrrole-2-carboxaldehyde and 2-hydroxy-1-naphthaldehyde. The resulting Schiff base substituted silatranes were well characterized by elemental analysis, spectroscopic studies [IR, (¹H, ¹³C) NMR, and MS]. The structures of two silatranes were confirmed by single crystal X-ray diffraction analysis.

Keywords. Schiff base; 3-aminopropylsilatrane; 3-aminopropyltriethoxysilane; pyrrole-2-carboxaldehyde; 2-hydroxy-1-naphthaldehyde.

1. Introduction

Silatranes are cyclic organosilicon ethers of trialkoxyamines which form a unique class of penta-coordinate silicon compounds. The focus of the interest in silatranes arises due to stereo-electronic influence of exocyclic fragment on the shape and reactivity pattern. Since, introduction in 1961 by Frye *et al.*,¹ studies on silatranes have been diversified owing to their potential applications in the field of medicine, agriculture, polymer science and material chemistry.^{2–5} The modification in exocyclic arm of silatrane advances the fundamental properties of a silatrane, such as their response towards hydrolysis, crystal packing and uses in biology and medicine.^{6–15} Only a few silatranes with Schiff base moiety substituted at axial positions have been reported.^{16–18}

Schiff bases form an important class of synthetic organic compounds and are characterized by the presence of azomethine group. Moreover, they form important intermediates in some of the enzymatic reactions.¹⁹ Schiff bases are extensively studied due to pharmacological activity as anti-bacterial, anti-tumor, anti-inflammatory, anti-fungal, anti-HIV, analytical metal ion sensors and as catalysts.^{20–24} Moreover, they have chelating

tendency (bi or tridentate) and form complexes with various transition metals. Owing to their rapidity in synthesis and diversified applications, we herein report the synthesis of Schiff base functionalized silatranes. The resulting organosilatranes can find use as advanced and modified activity centers.

In this manuscript, synthesis of six Schiff base functionalized organopropylsilatranes (**6–9**) and (**12–13**) which were derived from the reaction of aminopropylsilatrane (**4**), aminopropyl-3, 7, 10-trimethylsilatrane (**5**) and N-substituted aminopropylsilatrane (**10**) with two aldehydes *viz.* pyrrole-2-carboxaldehyde and 2-hydroxy-1-naphthaldehyde have been carried out. The molecular structures of silatrane (**6**) and (**12**) were obtained by single crystal X-ray diffraction studies.

2. Experimental

2.1 Materials and methods

2.1a General details: Syntheses of all the compounds were performed under dry nitrogen atmosphere using Schlenk technique. All organic solvents were dried and purified according to standard procedures. 3-aminopropyltriethoxysilane (Aldrich), N-[3-(trimethoxysilyl)propyl]ethylenediamine (Aldrich), triethanolamine

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(Merck), pyrrole-2-carboxaldehyde (Aldrich), 2-hydroxynaphthaldehyde (Aldrich) and trisisopropanolamine (Merck) were distilled prior to use. 3-aminopropylsilatrane (**4**), aminopropyl-3, 7, 10-trimethylsilatrane (**5**) and *N*-substituted aminopropylsilatrane (**10**) were synthesized by the methods reported in literature.^{25,26} The infrared spectra were recorded using Nicolet iS50 FTIR (Fourier Transform Infra-Red) spectrometer. Mass spectral measurements (ESI source with capillary voltage, 2500 V) were carried out on a VG Analytical (70-S) spectrometer. CHN analyses were obtained on a FLASH-2000 Organic Elemental Analyzer. The solution NMR spectra were recorded on Bruker Avance II FT NMR (AL 300 MHz) spectrometers (¹H, ¹³C) using CDCl₃ as the solvent. Chemical shifts in ppm were reported relative to tetramethylsilane (TMS).

2.1b X-ray crystallography: Single crystal diffraction data for compounds **6** and **12** were collected on a Nonius Kappa CCD diffractometer equipped with a CCD detector with graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å). All intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods with the SIR97 program²⁷ and refined on F^2 by full-matrix least-squares methods with anisotropic non-H atoms. In **6**, the N3-H hydrogen atom was located in the difference-fourier map and its coordinates were kept fixed during the refinement. In **12**, the hydrogen atoms linked to N2, N4 and C17 were located in the difference-fourier map and refined isotropically. All other hydrogens of both structures were included on calculated positions, riding on their carrier atoms. In structure of compound **12**, atoms C1, C3 and C5 were found to be disordered over

two almost equivalent positions (60-40%). All other calculations were accomplished using SHELX97²⁸ and WINGX.²⁹ Crystal data and refinement details are given in table 1.

2.2 Synthesis of silatranes

2.2a *N*-((1*H*-pyrrol-2-yl)methylene)-3-(2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3]undecan-1-yl)propan-1-amine (6**):** 3-aminopropylsilatrane (1.00 g, 4.31 mmol) was dissolved in toluene and pyrrole-2-carboxaldehyde (0.41 g, 4.31 mmol) was added to the uniformly stirred pre-dissolved reaction mixture. The mixture was refluxed for 2 h and water formed during the reaction was removed azeotropically from the reaction solution by Dean-Stark assembly. Toluene was evaporated and off-white colored solid appeared which was dried under reduced pressure. Crystals suitable for X-ray diffraction were obtained from chloroform/benzene. Yield: 82%, 1.09 g, M.p.: 156 – 158°C. Anal. Calcd (%) for C₁₄H₂₃N₃O₃Si: C, 54.36; H, 7.44; N, 13.59, Si, 9.06; Found(%): C, 54.37; H, 7.45; N, 13.53; Si, 9.08; IR (KBr pellet, cm⁻¹): $\nu = 579.7$ (Si←N), 751.5 (Si-O), 879.3 (C-N), 937.9 (C-C), 1088.3 (Si-O), 1130.3 (C-O), 1633.9 (C=N), 2873.9 s, 2937.6 (CH₂). ¹H NMR (300 MHz, CDCl₃): $\delta = 0.34$ (2H, m, SiCH₂), 1.66 (2H, m, CCH₂C), 2.71 (6H, t, J_{HH} 5.4 Hz NCH₂), 3.44 (2H, m, CCH₂N), 3.67 (6H, t, J_{HH} 5.1 Hz, OCH₂), 7.97 (s, 1H, N=CH), 6.09-6.78 (3H, m, Ar-H). ¹³C NMR (75 MHz, CDCl₃): $\delta = 13.2$ (SiCH₂), 26.5 (CCH₂C), 51.5 (CCH₂N), 58.0 (NCH₂), 64.1 (OCH₂), ¹³C NMR (75 MHz, CDCl₃): $\delta = 13.2$ (SiCH₂), 26.5 (CCH₂C), 51.5 (CCH₂N), 58.0 (NCH₂), 64.1 (OCH₂), 121.17 (C2, C3-pyrrole), 128.3 (C1, C4-pyrrole), 151.0 (N=CH). MS (309): m/z ; 310[M+H]⁺, 311[M+2H]⁺.

Table 1. Experimental details.

	(6)	(12)
Chemical formula	C ₁₄ H ₂₃ N ₃ O ₃ Si·0.5(C ₆ H ₆)	C ₁₆ H ₂₈ N ₄ O ₃ Si·CHCl ₃
M_r	348.50	471.88
Crystal system, space group	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$
a, b, c (Å)	19.8160 (6), 14.5880 (4), 12.9150 (5)	9.6060 (2), 17.8700 (3), 15.0190 (3)
β (°)	95.3120 (13)	116.3931 (7)
V (Å ³)	3717.4 (2)	2309.42 (8)
Z	8	4
μ (mm ⁻¹)	0.15	0.47
No. of measured, independent and observed [$I > 2s(I)$] reflections	7711, 4039, 2138	18517, 5480, 3582
R_{int}	0.063	0.050
$R[F^2 > 2s(F^2)], wR(F^2), S$	0.076, 0.232, 1.08	0.069, 0.238, 1.02
No. of reflections	4039	5480
No. of parameters	218	292
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	0.60, -0.38	0.48 –0.54

2.2b *N*-((1*H*-pyrrol-2-yl)methylene)-3-(3,7,10-trimethyl-2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3]undecan-1-yl)propan-1-amine (**7**): 3-aminopropyl-3, 7, 10-trimethylsilatrane (1.00 g, 3.65 mmol) was dissolved in toluene and pyrrole-2-carboxaldehyde (0.35 g, 3.65 mmol) was added to pre-dissolved stirred reaction mixture. The mixture was refluxed for 2 h and water formed during the reaction was removed azeotropically from the reaction solution by Dean Stark assembly. Toluene was evaporated and light brown coloured solid appeared which was dried under reduced pressure. Yield: 76%, 0.97 g, M.p.: 160-162°C; Anal. Calcd(%) for C₁₇H₂₈N₃O₃Si: C, 58.29; H, 8.00; N, 12.00; Si, 8.00; Found(%): C, 58.25; H, 8.01; N, 12.01; Si, 8.02; IR (KBr pellet, cm⁻¹): 579.2 ν (Si←N), 750.9 ν (Si-O), 877.6 ν (C-N), 937.2 ν (C-C), 1086.9 ν (Si-O), ν 1178.9 (C-O), 1605.3 ν (C=N), 2873.2 s, 2934.5 (ν_s CH₂); ¹H NMR (300 MHz, CDCl₃): δ = 0.33 (2H, m, SiCH₂), 1.13 (2H, m, CCH₂C), 2.73 (6H, t, J_{HH} 5.4 Hz, NCH₂), 2.91 (2H, m, CCH₂N), 0.92 (9H, dt, CH₃), 2.73(3H, m, OCH), 7.30 (1H, s, N=CH), 5.52-6.82 (3H, m, Ar-H). ¹³C NMR (75 MHz, CDCl₃): δ = 14.0 (SiCH₂), 20.3 (CH₃), 31.5 (CCH₂C), 55.8 (CCH₂N), 56.5 (NCH₂), 67.9 (OCH), 126.6 (C₂, C₃-pyrrole), 128.2 (C₁, C₄-pyrrole), 151.1 (N=CH). MS (350): m/z; 351 [M+H]⁺, 352 [M+2H]⁺.

2.2c 2-((3-(2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3]undecan-1-yl)propylimino)methyl)naphthalen-1-ol (**8**): 3-aminopropylsilatrane (1.00 g, 4.31 mmol) was dissolved in toluene and 2-hydroxy-1-naphthaldehyde (0.62 g, 4.31 mmol) was added pre-dissolved stirred reaction mixture. The mixture was refluxed for 2 h and water formed during the reaction was removed azeotropically from the reaction solution by Dean Stark assembly. Toluene was evaporated and light yellow colored solid appeared which was dried under reduced pressure. Yield: 64%, 1.10 g, M.p.: 164-166°C. Anal. Calcd(%) for C₂₀H₂₅N₃O₄Si: C, 60.15; H, 6.26; N, 10.52; Si, 7.01 Found(%): C, 60.11; H, 6.28; N, 10.50; Si, 7.00. IR (KBr pellet, cm⁻¹): ν = 567.4 (Si←N), 741.2 (Si-O), 864.7 (C-N), 1010.6 (C-C), 1074.5 (Si-O), 1258.7 (C-O), 1591.5 (C=N), 2888.5 s, 2962.0 (CH₂). ¹H NMR (300 MHz, CDCl₃): δ = 0.38 (2H, m, SiCH₂), 1.72 (2H, m, CCH₂C), 2.68 (6H, t, J_{HH} 5.4 Hz, NCH₂), 3.49 (2H, m, CCH₂N), 3.66 (6H, t, J_{HH} 5.4 Hz, OCH₂), 8.55 (1H, s, N=CH), 6.73-7.01 (m, Ar-H). ¹³C NMR (75 MHz, CDCl₃): δ = 12.9 (SiCH₂), 26.8 (CCH₂C), 51.3 (CCH₂N), 55.4 (NCH₂), 57.7 (OCH₂), 157.0 (C1-naphthol), 100.7 (C2-naphthol), 136.9 (C3-naphthol), 126.0 (C4, C5-naphthol), 122.0 (C6-naphthol), 127.6 (C7-naphthol), 129.1 (C8, C9-naphthol), 117.6 (C10-naphthol), 163.8 (N=CH). MS (399): m/z; 422[M+Na]⁺.

2.2d 2-((3-(3,7,10-trimethyl-2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3]undecan-1-yl) propylimino)methyl)naphthalen-1-ol (**9**): 3,7,10 trimethyl substituted amino-propylsilatrane (1.00 g, 4.31 mmol) was dissolved in dry toluene and 2-hydroxy naphthaldehyde (0.44 g, 4.31 mmol) was added to pre-dissolved stirred reaction mixture. The mixture was refluxed for 2 h and water formed during reaction was removed azeotropically from the reaction mixture by Dean Stark apparatus. Toluene was evaporated and yellowish colored solid appeared which was dried under reduced pressure. Yield: 62%, 0.97 g, M.p.: 168-169°C. Anal. Calcd(%) for C₂₃H₃₂N₂O₄Si: C, 64.48; H, 7.47; N, 6.54; Si, 6.54; Found(%): C, 64.49; H, 7.45; N, 6.55; Si, 6.53; IR (KBr pellet, cm⁻¹): ν = 687.2 (Si←N), 1094.7 (Si-O), 1191.9 (C-O), 1631.7 (C=N), 2868.1, 2924.6 (CH₂). ¹H NMR (300 MHz, CDCl₃): δ = 0.63 (2H, m, SiCH₂), 1.28 (2H, m, CCH₂C), 2.76 (6H, t, J_{HH} 5.4 Hz, NCH₂), 3.00 (2H, m, CCH₂N), 0.96 (9H, dt, CH₃), 2.05(3H, m, OCH), 8.30 (1H, s, N=CH), 6.21-7.40 (m, Ar-C). ¹³C NMR (75 MHz, CDCl₃): δ = 14.5 (SiCH₂), 25.5 (CH₃), 38.1 (CCH₂C), 40.1 (CCH₂N), 50.0 (NCH₂), 60.4 (OCH), 152.0 (C1-naphthol), 100.7 (C2-naphthol), 129.9 (C3-naphthol), 128.1 (C4, C5-naphthol), 121.6 (C6-naphthol), 128.1 (C7-naphthol), 129.9 (C8, C9-naphthol), 110.3 (C10-naphthol), 163.4 (N=CH). MS (428): m/z; 429[M+H]⁺, 430[M+2H]⁺.

2.2e *N*¹-((1*H*-pyrrol-2-yl)methylene)-*N*²-(3-(2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3]undecan-1-yl)propyl)ethane-1,2-diamine (**12**): *N*¹-(3-(2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3]undecan-1-yl)propyl)ethane-1,2-diamine (1.00 g, 3.63 mmol) was dissolved in dry toluene and pyrrole-2-carboxaldehyde (0.35 g, 3.63 mmol) was added to pre-dissolved reaction mixture. The mixture was refluxed for 2 h and water formed during reaction was removed azeotropically from the reaction solution by Dean Stark assembly. Toluene was evaporated and light yellow colored solid appeared which was dried under reduced pressure. Crystals suitable for X-ray diffraction were obtained from chloroform/benzene. Yield: 86%, 1.10 g, M.p.: 167-168°C; Anal. Calcd(%) for C₁₆H₂₈N₄O₃Si: C, 54.54; H, 7.95; N, 15.90; Si, 7.95; Found(%): C, 54.52; H, 7.91; N, 15.92; Si, 7.99; IR (KBr pellet, cm⁻¹): 582.3 ν (Si←N), 752.8 ν (Si-O), 877.8 ν (C-N), 941.2 ν (C-C), 1097.3 ν (Si-O), ν 1182.3 (C-O), 1636.0 ν (C=N), 2871.9 s, 2926.7 (ν_s CH₂). ¹H NMR (300 MHz, CDCl₃): δ = 0.39 (2H, m, SiCH₂), 1.59 (2H, m, CCH₂C), 2.63 (2H, m, NCH₂CH₂), 2.77 (6H, t, J_{HH} 5.4 Hz, NCH₂), 3.61 (2H, m, CCH₂N), 3.74 (6H, t, J_{HH} Hz, OCH₂), 8.07 (1H, s, N=CH), 6.21-7.36 (3H, m, Ar-H). ¹³C NMR (100.62 MHz, CDCl₃): δ = 13.4 (SiCH₂), 25.1 (CCH₂C), 49.8 (CCH₂N), 52.9

(NCH₂CH₂), 57.7 (NCH₂), 76.7 (OCH₂), 121.4 (C2, C3-pyrrole), 128.3 (C1, C4-pyrrole), 152.2 (N=CH). MS (352): *m/z* 353[M+H]⁺.

2.2f 2-((2-(3-(2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3]undecan-1-yl)propylamino)ethylimino)methyl)naphthalen-1-ol (13): N¹-(3-(3,7,10-trimethyl-2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3]undecan-1-yl)propyl)ethane-1,2-diamine (1.00g, 3.63 mmol) was dissolved in toluene and 2-hydroxynaphthaldehyde (0.62 g, 3.63 mmol) was added to pre-dissolved reaction mixture. The mixture was refluxed for 2 h and water formed during reaction was removed azeotropically from the reaction solution by Dean Stark assembly. Toluene was evaporated and reddish yellow colored solid appeared which was dried under reduced pressure. Yield: 58%, 0.90 g, M.p.: 170–172°C; Anal. Calcd(%) for C₂₂H₃₁N₃O₄Si: C, 61.53; H, 7.22; N, 9.79; Si, 6.52; Found(%): C, 61.52; H, 7.25; N, 9.80; Si, 6.54; IR (KBr pellet, cm⁻¹): 582.3 ν (Si←N), 749.6 ν (Si-O), 855.4 ν (C-N), 937.8 ν (C-C), 1083.6 ν (Si-O), ν 1178.0 (C-O), 1625.1 ν (C=N), 2872.1 s, 2924.1 (ν_s CH₂), ¹H NMR (300 MHz, CDCl₃): δ = 0.33 (2H, m, SiCH₂), 1.26 (2H, m, CCH₂C), 1.72 (2H, m, NCH₂CH₂), 2.80 (6H, t, J_{HH} 5.4 Hz, NCH₂), 3.61 (2H, m, CCH₂N), 3.75 (6H, t, J_{HH} 5.4 Hz, OCH₂), 8.11 (1H, s, N=CH), 6.13–7.69 (m, Ar-H). ¹³C NMR (75 MHz, CDCl₃): δ = 13.3 (SiCH₂), 26.2 (CCH₂C), 46.4 (CCH₂N), 51.0 (NCH₂CH₂), 57.6 (NCH₂), 76.7 (OCH₂), 163.3 (C1-naphthol), 94.5 (C2-naphthol), 129.0

(C3-naphthol), 128.3 (C4, C5-naphthol), 121.6 (C6-naphthol), 129.7 (C7-naphthol), 129.7 (C8, C9-naphthol), 110.1 (C10-naphthol), 163.3 (N=CH). MS (429): *m/z*; 430[M+H]⁺.

3. Results and Discussion

3.1 Synthetic aspects

The strategic approach towards the synthesis of Schiff bases bearing organosilicon moiety with different structures was based on condensation reaction between 3-aminopropylsilatrane and different aromatic aldehydes. Synthesis of Schiff bases substituted organosilicon complexes have been carried out by the reaction of aminopropylsilatrane (**4**), aminopropyl-3,7,10-trimethylsilatrane (**5**) and N-substituted aminopropylsilatrane (**10**) with various aldehydes *viz.* pyrrole-2-carboxaldehyde, 2-hydroxy naphthaldehyde (scheme 1). These new ‘Schiff modified silatranes’ have been characterized by elemental analysis IR, (¹H, ¹³C) NMR spectroscopy and mass spectrometry.

Synthesis of Schiff base bearing silatranes (**12**, **13**) were also carried out by using N-substituted aminopropylsilatrane (**11**) with increased number of carbon atoms with aromatic aldehydes like pyrrole-2-carboxaldehyde, 2-hydroxy naphthaldehyde as shown in scheme 2. The structure of silatrane (**6**) and (**12**) has been deduced by single crystal X-ray diffraction analysis.

Scheme 1. Synthesis of Schiff bases linked silatranes from 3-aminopropylsilatrane.

Scheme 2. Synthesis of Schiff bases from N-substituted aminopropylsilatrane.

3.2 Spectroscopic Studies

3.2a FT-IR spectroscopy: The formation of the silatranes **6–9**, **12** and **13** was established by FTIR spectroscopy. The most characteristic absorption bands associated with silatrane structure were found in the spectrum of all the silatranes. IR spectra of all compounds (**6–9**, **12**, **13**) exhibit absorption bands characteristic to both C=N of Schiff base and silatranyl moiety. Bands observed in the region of 3200–3400 cm^{-1} are assigned to OH stretching modes, whereas C=N stretching vibrations are observed at 1591–1636 cm^{-1} . The intense bands were present in the region 1086–1094 cm^{-1} and are assigned to asymmetric stretching vibration of the Si–O group. In addition, a Si←N vibration observed in the region 567–687 cm^{-1} is a common feature of silatranes.

3.2b NMR spectroscopy: The multinuclear NMR spectra of all compounds were consistent with the structure of the synthesized complexes (**6–9**, **12**, **13**). The NMR spectra of silatranyl moiety of the synthesized compounds (**6**, **8**, **12**, **13**) were very similar to their parent compounds and consisted of triplets due to protons of OCH₂ δ (3.66–3.74 ppm) and NCH₂ δ (2.68–2.80 ppm)

of Si(OCH₂CH₂)₃N moiety. The ¹H NMR spectra of all the synthesized compounds (**6–9**, **12**, **13**) show singlet in the region δ 7.46–8.55 due to –N=CH moiety of Schiff base bearing silatranes (**6–9**) and (**12**, **13**) which signifies successful condensation reaction. The methyne proton (CH) of the isopropyl group appears at δ 2.05–2.73 ppm since, it is adjacent to six equivalent hydrogens (the two isopropyl CH₃ groups) and the signals for the two (magnetically equivalent) CH₃ groups were ascribed at δ 0.92–0.96 ppm by the adjacent methyne proton (CH). In ¹³C NMR, silatranes (**6**, **8**, **12**, **13**), the resonances due to silatranyl OCH₂ and NCH₂ appears at δ 64.14–76.71 ppm and δ 56.52–58.06 ppm, respectively. In the 3,7,10-trimethylsilatranes (**7**, **9**), the signals ascribed to NCH₂ are at 50.03 and 56.52 ppm, respectively whereas OCH appears slightly downfield at δ 50.03 and 56.52 ppm, respectively. The signals due to the carbon atoms attached to the azomethine groups in compounds (**6–9**) and (**12**, **13**) appear in the range δ 151.00–163.6 ppm, respectively.

3.2c Mass spectrometry: Mass spectra of compounds (**6–9**) and (**12**, **13**) show molecular ion peaks with addition of H⁺, Na⁺ and K⁺ ions and their fragmentation

exhibit common features of silatranes.³⁰ The silatranes reported herein possess considerable stability, as indicated by the continuous observation of a strong $[M + H]^+$ as a base peak.

3.3 Single crystal X-ray structure analysis

Figures 1 and 2 report the ORTEP III diagram³¹ for compounds **6** and **12**, respectively. Relevant geometrical parameters are reported in table 2. In **6**, the asymmetric unit is formed by a silatrane molecule and a half of a benzene molecule, the C15 and C18 atoms of the solvent molecule being positioned on a two-fold rotation

axis, while in **12**, it is composed by a silatrane moiety and one chloroform solvent molecule. In both structures the silicon atom is linked in distorted trigonal bipyramidal geometry (see table 2) to the tripodal triethanolamine ligand, with Si-O and Si-N distances typical for this kind of compounds. Actually, the Si-O and Si-N mean bond lengths calculated on 146 silatrane structures present in CSD are 1.66(1) and 2.15(5) Å, respectively.

The main interactions in both structures are represented by N-H...N hydrogen bonds, which give origin to dimeric units (table 3). Very interestingly, the cocrystallized solvent molecules, benzene in **6** and chloroform

Figure 1. ORTEP III view and atom numbering scheme for compound **6**. Thermal ellipsoids are drawn at the 40% probability level. C-H... π contact is drawn as dashed lines.

Figure 2. ORTEP III view and atom numbering scheme for compound **12**. Thermal ellipsoids are drawn at the 40% probability level. For the sake of clarity, only one set of the disordered part has been considered.

in **12**, are included in the crystalline lattice in such a way to act as linkers among the different dimers. In **6**, C–H... π interactions are formed involving the C10–H atom of two symmetrically related silatrane molecules and the solvent, as shown in figure 3a, with the following geometrical parameters: H...C15–C18 (centroid) = 3.134 Å, C–H...centroid = 148°. Conversely, in **12**, the chloroform acts both as a donor and as an acceptor group, being involved in a C17–H...O3 and in C10–H...Cl3 weak hydrogen bonds with two different silatrane molecules (table 3 and figure 3). This same chloroform silatrane interaction was found in the related compound CABBEN;³² here, DFT calculations have shown the effective importance of the presence of the solvent molecule and the related interactions for the packing energy of the crystal.

Table 2. Selected bond distances and angles (Å, °).

Compound	6	12
Si1 - O1	1.662(3)	1.664(3)
Si1 - O2	1.650(3)	1.660(3)
Si1 - O3	1.656(3)	1.678(3)
Si1 - N1	2.210(4)	2.147(4)
Si1 - C7	1.871(4)	1.876(3)
O1 - Si1 - O2	118.0(2)	119.8(1)
O1 - Si1 - O3	118.6(2)	118.1(1)
O1 - Si1 - C7	97.3(2)	97.0(1)
O2 - Si1 - O3	117.8(2)	117.8(1)
O2 - Si1 - C7	96.8(2)	96.5(2)
O3 - Si1 - C7	99.5(2)	97.3(1)
O1 - Si1 - N1	81.9(1)	83.1(1)
O2 - Si1 - N1	82.3(2)	83.1(1)
O3 - Si1 - N1	82.1(1)	83.0(1)
N1 - Si1 - C7	178.3(2)	179.6(1)

Table 3. Hydrogen bonding parameters (Å, °).

	D-H	D...A	H...A	D-H...A
Compound 6				
N3-H...N2 ⁱ	1.01	2.885(5)	1.90	163
C13-H...O3 ⁱⁱ	0.93	3.375(5)	2.54	150
Equivalent positions: (i) -x,y,-z-1/2; (ii) x-1/2,1/2-y,z-1/2				
Compound 12				
N4-H...N2 ⁱ	0.89(6)	2.912(6)	2.05(6)	162(5)
C4-H...O1 ⁱⁱ	0.97	3.472(5)	2.52	168
C17-H...O3 ⁱⁱⁱ	0.99(5)	3.185(5)	2.22(5)	165(4)
C10-H...Cl3 ^{iv}	0.97	3.680(5)	2.74	162
Equivalent positions: (i) -x-1,-y,-z-1; (ii) 1-x,-y,-z; (iii) x+1,1/2-y,z+1/2; (iv) -x,y-1/2,-z-1/2

Figure 3. Interactions involving the solvent molecules in **6** (a) and **12** (b)

4. Conclusions

A new class of silatrane (**6–9**) and (**12**, **13**) bearing Schiff base moieties were synthesized and characterized by various spectroscopic techniques. These compounds containing azomethine group are bonded to the silicon's axial position through propyl chain. The molecular structures of compounds (**6**) and (**12**) were obtained from single X-ray crystallography.

Supplementary Information (SI)

CCDC 1012013 and 1012014 contain the supplementary crystallographic data for complexes **6** and **12**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at www.ias.ac.in/chemsci.

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