Synthesis and reactivity of novel 3-isothiocyanatopropylsilatrane derived from aminopropylsilatrane: X-ray crystal structure and theoretical studies

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ABSTRACT

A novel silatrane $\overset{\frown}{N(CH_2CH_2O)_3}SiCH_2CH_2CH_2NCS$ (**3**) containing Si ← N bond (2.160 Å), has been synthesized by the reaction of 3-aminopropylsilatrane (**1**), dicyclohexylcarbodiimide (**2**) and CS_2. The structure was established by elemental analysis, spectroscopic methods (IR, ^1H NMR, ^{13}C NMR and Mass spectroscopy) and X-ray crystallography. It was correlated with theoretical studies such as semiempirical (AM1, PM3, PM3MM and MNDO), Density Functional Theory (B3LYP) and Hartree–Fock at 3-21+G^* and 6-31G^*(d) levels. The reactivity of compound **3** was studied with some Lewis acids and bases that showed the formation of corresponding adducts (**4–7**), which were characterized by elemental analysis, IR and NMR (^1H, ^{13}C) spectroscopy.

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1. Introduction

Silatranes, cyclic organosilicon ethers of tris(2-oxyalkyl)amine, have been the subject of intense study since their discovery in 1961 [1]. Perhaps the most intriguing aspect of these hypercoordinate silicon compounds is the nature of the silicon–nitrogen interaction and the variation in the transannular Si–N distance as a function of change in the axial silicon substituent [2–9]. Aminopropylsilatranes are potential precursor materials for the synthesis of a number of N-derivative silatranes [10–15]. These derivatives of aminopropylsilatranes find applications as fungicides [13,14], anticancer and antitumour agents [15,16]. The aminopropylsilatranes have also been used for immobilization of DNA due to less reactivity, extremely resistant behavior to hydrolysis and polymerization at neutral pH [17]. They can also function as additives of water-based metalworking fluids due to their tribological properties. Semenov et al. reported the coordination of metal salts with aminopropylsilatrane to form various metal complexes [18].

The X-ray structure and reactivity of a five membered 1-isothiocyanatosilatrane with a direct Si–NCS bond was reported by Narula et al. [19] and the structure was compared with ab initio and DFT calculations to examine the precise structure by Chung et al. [20]. Recently, we have reported the synthesis and reactivity of six membered 1-isothiocyanatosilatrane, prepared by transetherification reaction of triethoxyisothiocyanatosilane with tris-(2-hydroxy-3,5-dimethylbenzyl)amine [21].

As discussed above, aminopropylsilatranes have captured contemporary interest of chemists due to their involvement in the synthesis of some novel silatranes by the derivatization of amino group. In the context of these studies, we aimed at a novel synthesis of 1-(3-isothiocyanatopropyl)-2,8,9-trioxa-5-aza-1-sila-bicyclo[3.3.3]undecane (**3**) from aminopropylsilatrane (**1**) with the structural characterization in solid state by X-ray crystallography, multinuclear NMR (^1H, ^{13}C), IR and mass spectroscopy. Theoretical methods such as DFT and HF theory as well as their extensions are very important for computing a molecular structure. So, the experimental studies were complemented by computational studies such as semiempirical (AM1, PM3, PM3MM and MNDO), DFT and Hartree–Fock methods. The newly synthesized compound **3** was found to be reactive due to the presence of –NCS moiety and reactivity of the compound towards some of Lewis acids and Lewis bases to form adducts is also reported in the present paper.

2. Results and discussion

2.1. Synthesis

Amines can be converted into isothiocyanates by reacting primary amines with thiophosgene or by the decomposition of 1,3-disubstituted thiourea with acids [22]. Isothiocyanates can also be accessed by the decomposition of dithiocarbamates from primary amines and CS_2 in the presence of heavy metal salts [23] or dicyclohexylcarbodiimide (DCC) [24], dicyandiamide [25] or cyanamide [26]. The use of DCC in nonaqueous systems is advantageous over other methods.

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In the present work, 3-isothiocyanatopropylsilatrane (**3**) is synthesized from 3-aminopropylsilatrane (**1**) and DCC (**2**) as a white substance which is stable in air and soluble in common organic solvents such as diethylether, chloroform and carbon tetrachloride. The general reaction scheme for the synthesis of **3** is given below (Scheme 1). Based on the previous reports [19], reactions of **3** with some Lewis acids and bases were carried out to yield corresponding adducts (**4–7**) and the routes followed are summarized in Scheme 2.

2.2. Spectroscopic data

The IR spectrum of **3** was recorded in the range 4000–400 cm^{-1}. The absorption bands were assigned on the basis of literature [19,25,26]. The IR absorption frequencies are in accordance with the structure of prepared complex. The absorptions of interest are those of NCS, Si–O and Si–N bonds. IR spectrum in Nujol/KBr plates show ν_{as} NCS absorption at 2121 cm^{-1} for **3**.

Multinuclear (^{1}H and ^{13}C) NMR spectra are consistent with the structure of synthesized compound. On comparing ^{1}H NMR spectra of **3** with those of **1**, a downfield shift for the OCH$_2$ and NCH$_2$ protons of Si(OCH$_2$CH$_2$)$_3$N moiety in **3** is observed. Correspondingly, triplet due to –CH$_2$–NCS protons is also shifted to downfield as compared to –CH$_2$NH$_2$ which can be justified on the basis of electron withdrawing effect of –NCS group. All protons in the compound **3** have been identified and the total number of protons calculated from the integration curve was found to be equal to expected number.

In the ^{13}C NMR, δ N**C**S appeared at 177.0 ppm. The effect of –NCS moiety on the ^{13}C spectra is observed on the signals due to –**C**H$_2$NCS and –CH$_2$**C**H$_2$CH$_2$ which are shifted downfield and up-

field, respectively. The peaks appearing at 55.0 and 48.0 ppm in **1** due to δ O**C**H$_2$ and N**C**H$_2$ are observed at the same position as in **3**.

The most common feature of mass spectrum of C-substituted silatrane is the fragmentation of X–Si bond. Besides the molecular ion (M+Na, 297) and (M+K, 313), a silatranyl ion (174) peak was also observed in the mass spectrum. The molecular ion peak was more abundant as compared to silatranyl ion peak.

2.3. Crystal structure

The molecular structure of compound with atom numbering scheme is depicted in Fig. 1. The X-ray data, selected bond distances and angles of compound **3** are listed in Tables 1 and 2, respectively. The compound possesses usual skeleton containing
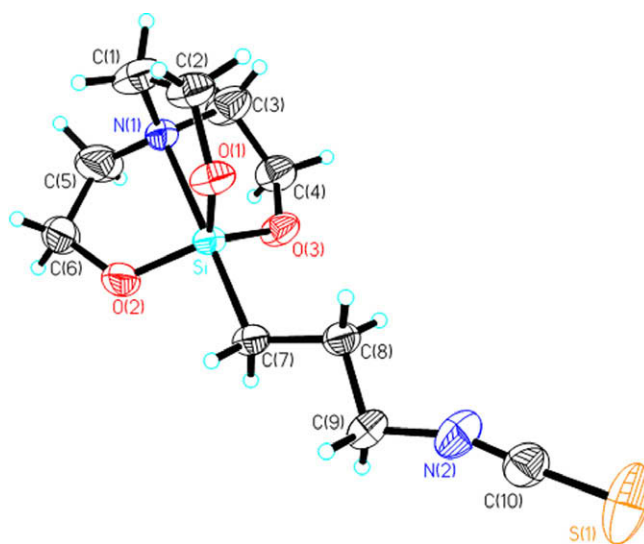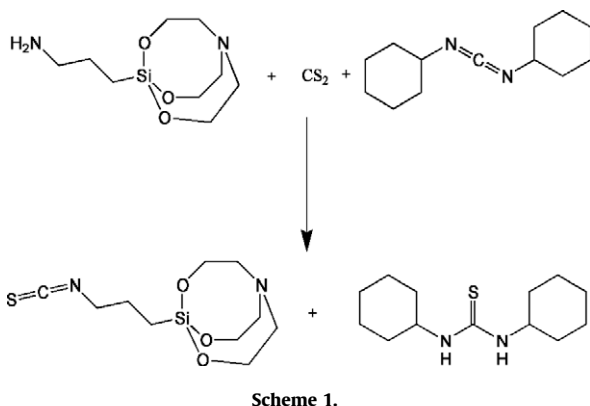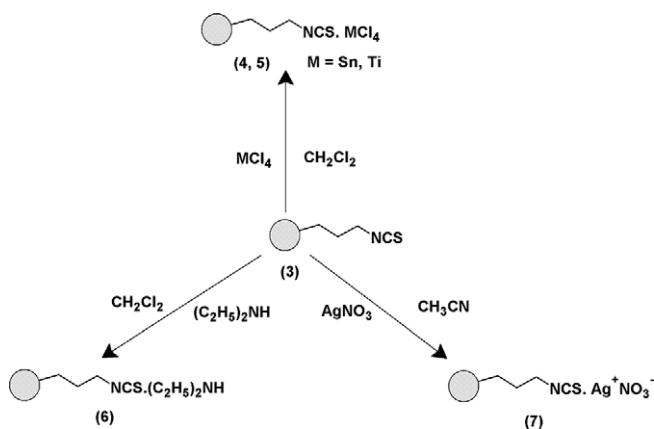

Fig. 1. Perspective view of **3** showing atom numbering scheme (thermal ellipsoids are at 45% probability level).

Scheme 1.

Scheme 2.

Table 1
X-ray crystal data and structure refinement of 3-isothiocyanatopropylsilatrane.

Empirical formula	C$_{10}$H$_{18}$N$_2$O$_3$SSi
Formula weight	274.41
T (K)	293(2)
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	
a (Å)	7.955(1)
b (Å)	13.204(1)
c (Å)	12.9492(10)
β (°)	90.150(1)
V (Å^3)	1360.1(2)
Z	4
Density (calculated) (Mg/m^3)	1.340
Absorption coefficient (mm^{-1})	0.325
Theta range for data collection (°)	2.20–24.99
Index ranges	$-9 \leqslant h \leqslant 0$, $-15 \leqslant k \leqslant 0$, $-15 \leqslant l \leqslant 15$
Reflections collected	2555
Independent reflections [$R_{(int)}$]	2376 [0.0270]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2376/0/154
Goodness-of-fit (GOF) on F^2	1.039
Weighting scheme	$1/[\sigma^2(F_o^2) + (0.0719P)^2 + 0.83P]$, $P = (\text{Max}(F_o^2, 0) + 2 * F_c^2)/3$
Final R indices, 1631 reflections [$I > 2\sigma(I)$]	$R_1 = 0.0586$, $wR_2 = 0.1444$
R indices (all data)	$R_1 = 0.0929$, $wR_2 = 0.1590$
Largest difference peak and hole (e Å^{-3})	0.527 and −0.272

Table 2
Selected bond lengths (Å) and angles (°) of 3-isothiocyanatopropylsilatrane.

N(1)–Si	2.160(3)	O(1)–Si–O(2)	118.17(15)
C(7)–Si	1.882(3)	O(1)–Si–O(3)	118.06(14)
C(9)–N(2)	1.447(5)	O(2)–Si–O(3)	119.47(16)
C(10)–N(2)	1.138(5)	C(8)–C(7)–Si	117.7(2)
O(1)–Si	1.663(3)	O(1)–Si–C(7)	97.92(12)
O(2)–Si	1.655(3)	O(2)–Si–C(7)	95.51(14)
O(3)–Si	1.659(3)	O(3)–Si–C(7)	97.36(14)
C(10)–S(1)	1.575(5)	C(9)–C(8)–C(7)	109.8(3)
N(2)–C(9)–C(8)	112.5(3)	C(10)–N(2)–C(9)	159.9(4)
N(2)–C(10)–S	176.7(4)	C(7)–Si–N(1)	178.34(14)

a five-coordinate silicon atom. The stereochemistry of silicon is distorted trigonal bipyramidal. A comparison with the 1-isothiocyanatosilatrane showed a slight lengthening of Si–O bonds with the contraction of C–C, N–C and O–C bonds. The influence of electron withdrawing effect of –NCS on the transannular Si–N bond was found to be less as compared to the silatrane with direct Si–NCS bond. The reduced electron withdrawing inductive effect of –NCS due to the intervening –CH$_2$–CH$_2$–CH$_2$– alkyl chain might be responsible for the longer Si–N distance 2.160(3) Å in **3** when compared with 1-isothiocyanatosilatrane, which has the shortest Si–N distance, 2.007(3) Å. The SiO$_3$ pyramid is flattened, the average values of both O–Si–C and O–Si–N angles being closer to perfectly flattened 90° value. This bond angle is an important factor to illustrate the deviation in the geometry around the Si atom from a pentacoordinated trigonal bipyramidal structure. The silicon atom deviates to an extent of −0.20 Å from the best least square plane defined by the three O atoms (O1, O2 and O3) that also indicates that the hypercoordination induces significant structural deviations in the molecule.

Compound **3** crystallizes in a monoclinic crystal system (space group = $P2_1/c$) with four molecules in a unit cell. Although there are strong hydrogen bond acceptors like O and N atoms in the molecule, there are no strong hydrogen bond donors like –OH or –COOH moieties. Besides this, the hydrogen atom to non-hydrogen atom ratio is relatively low to a value of 1 that prompts the molecules to adopt a packing that utilizes the interactions with hydrogen atoms that are most acidic in the structure. These hydrogen atoms are the one at C9 (bonded to the –NCS group) (Fig. 2) and indeed both the hydrogen atoms participate in C–H⋯O hydrogen bonding that play a significant role in the lattice stabilization. Within the centrosymmetrically related molecules, both O1 and O3 act as C–H⋯O hydrogen bond acceptors of these hydrogen atoms (C9–H9A⋯O1 = 2.516 Å, C9–H9B⋯O3 = 2.490 Å) that generates a zig–zag corrugated ribbon like arrangement that run parallel to the 'a' axis of the unit cell. Such an arrangement is depicted in the Fig. 2. The molecules in the corrugated sheet like arrangement are further linked to c glide related molecules through another C–H⋯O hydrogen bond involving the third oxygen atom, O2 and H1B (C1–H1B⋯O2 = 2.637 Å). The resulting arrangement of the molecules viewed down 'b' axis is shown in the Fig. 3. It is to be noted that CH$_2$CH$_2$CH$_2$NCS moiety attached to the silatrane ring is like an appendage protruding out of a sphere and their closest packing arrangement is achieved if they are arranged in a head to tail fashion. This indeed happens in the lattice ($P2_1/c$ space group, centrosymmetric arrangement). Thus, the Kitaigorodsky model of close packing is achieved in the lattice and within this arrangement the C–H⋯O hydrogen bonds anchor the molecule to their respective positions. There are no other significant short contacts observed in the molecular packing.

2.4. Theoretical studies

The limited literature on computational studies on silatranes is due to the large size of these molecules which restricts largely
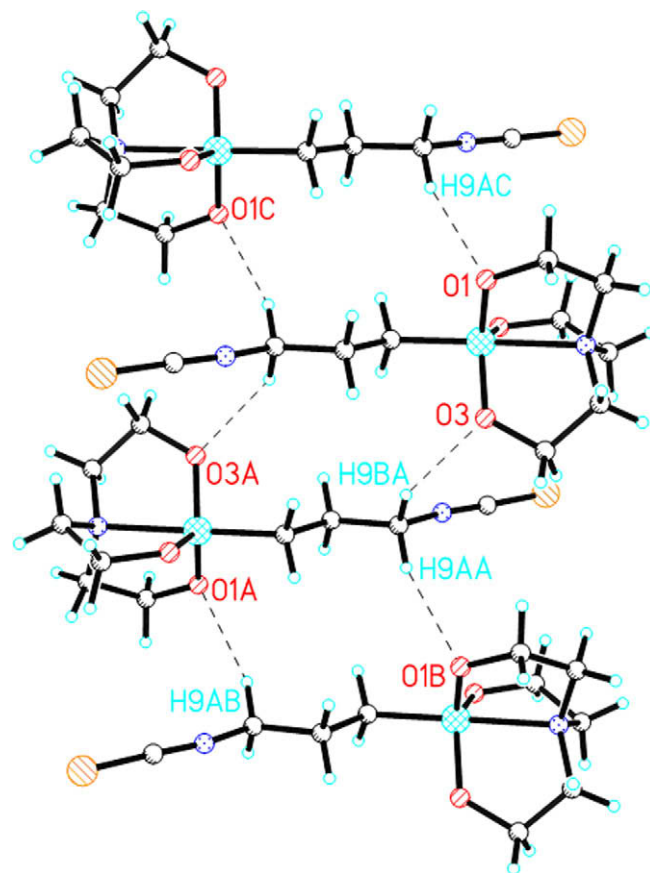

Fig. 2. The corrugated sheet formation through C–H⋯O hydrogen bonding involving most acidic hydrogen atoms (H9AA and H9BA). The third oxygen atom links these sheets through a third C–H⋯O hydrogen bond (see Fig. 3).

these studies to semi empirical methods, but a few reports using ab initio methods have been appeared in the last decade [27–31]. Initially, quantum chemical calculations of **3** were performed by using semiempirical methods (AM1, PM3, PM3MM and MNDO) but the accuracy of these methods was found insufficient to describe transannular N → Si interaction and appeared to be of little use. Therefore, optimization of geometry parameters was carried out by using DFT/B3LYP and HF methods with different basis sets. The optimized geometrical parameters of 3-isothiocyanatopropylsilatrane with various levels of DFT and RHF methods are summarized in Table 3, respectively.

The Density Functional Theory and Hartree–Fock calculations were performed at 3-21+G* and 6-31+G(d) basis sets for **3** and the results were compared with crystal data. The most important geometrical parameter, N → Si distance, examined with RHF method at 3-21+G* and 6-31+G(d) basis sets was found to be significantly longer than the crystal data, the values are lower than other methods when computed with B3LYP at 3-21+G* and 6-31+G(d) basis sets. The X-ray studies demonstrate the bond angle N–C–S at around 176.8° which is accordance with the theoretical value obtained with DFT/B3LYP/6-31G*(d). The variation in other bond angles is attributed to the denser packing of molecules which promotes the intensification of crystal field and, hence, compression of the molecules. As a result, the N → Si bond length decreases with the increase of crystal density and packing coefficient. Probably, stringent packing requirements involving large number of cooperative C–H⋯O hydrogen bonds may compress the molecule through the N → Si vector leading to a smaller value (2.16 Å) than the same observed in an isolated molecule (2.54–2.70 Å) through theoretical means. However, this bond length is sensitively af-
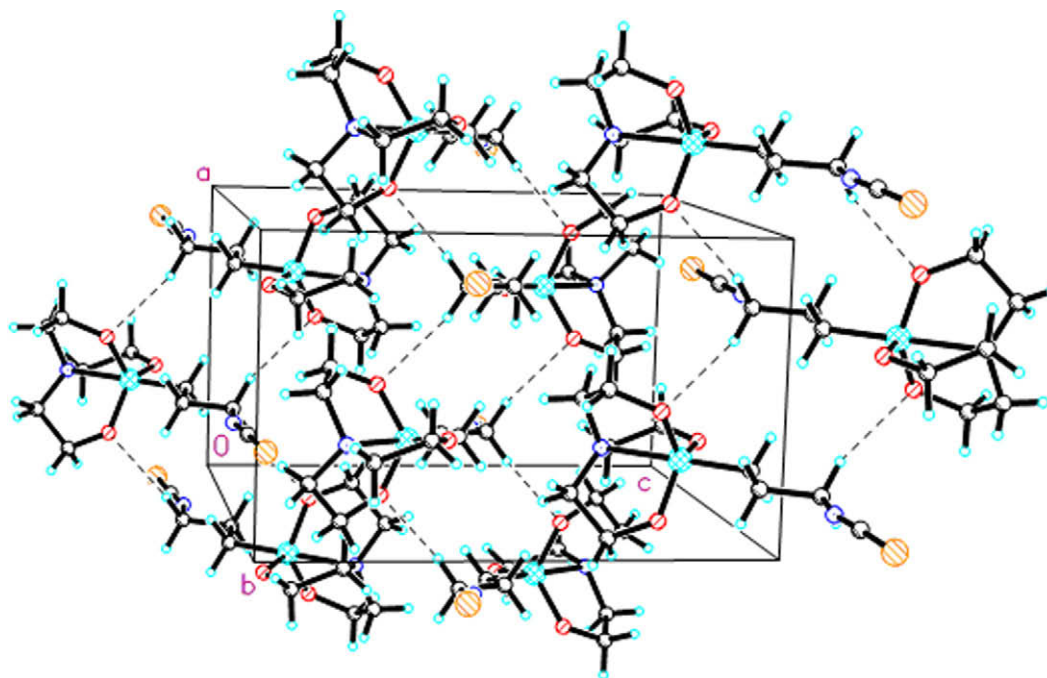
Fig. 3. Close packing of compound **3** viewed down '*b*' axis of the unit cell. All the dotted lines show C–H···O type hydrogen bonding within the centrosymmetric arrangement of the molecules.

Table 3
DFT and HF studies of 3-isothiocyanatopropylsilatrane.

Parameters	DFT, B3LYP 3-21+G*	DFT, B3LYP 6-31G*(d)	RHF, 3-21+G*	RHF, 6-31G*(d)
Total energy (a.u.)	−1407.77	−1414.89	−1402.09	−1409.21
Dipole moment	9.8	8.10	9.76	8.74
N(1) → Si	2.54	2.59	2.70	2.67
Si–C(7)	1.87	1.87	1.86	1.87
Si–O av.	1.68	1.67	1.65	1.65
N(1)–C(2,4,6) av.	1.48	1.46	1.46	1.45
N(2)–C(10)	1.18	1.18	1.15	1.15
C(7)–S(1)	1.60	1.60	1.61	1.61
N(2)–C(10)–S(1)	179.30	176.49	179.85	179.98
C(9)–N(2)–C(10)	174.24	157.41	179.29	179.55
C(7)–C(8)–C(9)	112.91	113.76	112.87	113.91
C(8)–C(7)–Si(1)	113.22	115.12	112.69	114.66
O(1)–Si(1)–O(2)	114.10	114.74	111.16	112.08
O(2)–Si(1)–O(3)	115.38	114.67	112.31	112.90
O(3)–Si(1)–O(1)	115.38	113.96	112.06	113.06
C(2)–N(1)–C(4)	116.75	117.70	118.15	118.49
C(4)–N(1)–C(6)	116.68	117.72	118.16	118.48
C(6)–N(1)–C(2)	116.67	117.72	118.12	118.47

fected by adding the electron correlation effect at the B3LYP levels and showed an increase in the value. The computed Si–C(7) bond lengths at both RHF and B3LYP levels are equal to the crystallographic value. Other parameters like Si–O bond length computed from RHF levels are almost same with the values obtained in the X-ray crystallographic studies. The slight change observed in other bond lengths might be because of either the crystal packing forces in the solid state or an experimental unreliability.

The optimized structure of **3**, when compared with the optimized structure of 1-isothiocyanatosilatrane depicted structural changes in silatrane ring on decreasing the inductive effect of X moiety [20]. The most drastic change was found in Si–N1 bond distance for 1-isothiocyanatosilatrane (2.33 Å) at the B3LYP/6-31G* level which was very less than the **3** due to direct bond of electron withdrawing –NCS with silicon.

3. Reactivity

Compound **3** is stable towards atmospheric moisture as compared to **1**. It was found that compound **3** readily reacts with Lewis acids to produce corresponding adducts. The reactions (Scheme 2) were carried out in accordance with the literature [19] and the products were analyzed with spectroscopic studies. The reaction of **3** with equimolar amounts of SnCl$_4$ and TiCl$_4$ leads to the formation of **4** and **5**, respectively. IR spectra suggested the bonding of adducts **4** and **5** through N atom of NCS. The decrease observed in the ν_{as} NCS absorption band in case of **4** and **5** adducts is due to the coordination of Lewis acids through N atom of NCS group. Reaction of **3** with diethylamine yielded the desired product **6**. However, the obtained white product was hygroscopic. The decrease in the ν NH in **6** indicated the formation of adduct of **3** with

diethylamine. A reaction of **3** with AgNO₃ gave **7** in which Ag⁺ is coordinated to S atom of NCS group. The shift of band towards the higher frequency in adduct **7** supports the bonding through S. IR spectrum showed ν_{as} NCS absorption in the range of 1990–2190 cm⁻¹ for adducts. In addition, investigation of adducts for structural fragment of Si–O–C–C is shown by the characteristic frequencies appearing in the region 1480–575 cm⁻¹. The characteristic spectra for pentacoordinated molecular structure and Si ← N coordinative bond are observed as medium intensity band in the region of 570–590 cm⁻¹.

4. Experimental

4.1. General details

4.1.1. Synthesis

All the syntheses were carried out under a dry nitrogen atmosphere using vacuum glassline. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. 3-Aminopropyl(triethoxy)silane (Aldrich), triethanolamine (Merck) and DCC (Merck) were used as such. Diethylamine (Merck) was distilled by refluxing over KOH pellets under dry nitrogen atmosphere. CS₂ (Qualigens) was purified by distillation prior to use.

4.1.2. Characterization

Infrared spectra were routinely obtained as thin films or Nujol mulls on a Perkin–Elmer RX-I FT IR Spectrophotometer. Mass spectral measurements (EI, 70 eV) were carried out on a VG Analytical (70-S) spectrometer. C, H and N analyses were obtained on a Perkin–Elmer Model 2400 CHN elemental analyzer. Cl, S and Si were estimated by gravimetric methods. The solution ¹H and ¹³C NMR spectra were recorded at 25 °C on a Jeol FT NMR (AL 300 M Hz) spectrometer using CDCl₃ as the solvent. Chemical shifts in ppm were determined relative to internal CDCl₃ and external tetramethylsilane (TMS).

4.1.3. X-ray crystallography

Single crystals of compound **3** suitable for X-ray structure determination were obtained from its saturated solution in diethylether and a crystal with dimensions 0.41 × 0.22 × 0.31 mm was mounted along the largest dimension and used for data collection. Diffraction measurements were carried out on a Siemens P4 single X-ray crystal diffractometer equipped with molybdenum sealed tube ($\lambda = 0.71073$ Å) and highly oriented graphite monochromator. The lattice parameters and standard deviations were obtained by least-squares fit to 30 reflections. The data were collected by $2\theta-\theta$ scan mode with a variable scan speed ranging from 2° to a maximum of 60° min⁻¹. The stability and orientation of the crystal were monitored by three reflections and remeasured after every 97 reflections. The intensities showed only statistical fluctuations during data collection. The corrections in the data were made for Lorentz and polarization factors.

The crystal structure was determined by direct methods using SHELX-86 and refined by full matrix least-squares using SHELX-97 package [32]. Non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were fixed at their ideal positions with their isotropic U values varying 1.2 times to that of their respective non-hydrogen atoms and were riding. A weighing scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $a = 0.0719$ and $b = 0.83$ was used. The refinement converged to a final R value of 0.0586 for 1631 reflections [$I > 2\sigma(I)$]. The final difference map was featureless.

4.1.4. Theoretical studies

The quantum mechanical calculations were carried out using the GAUSSIAN 03 series of programs. Geometries were fully optimized at both the Restricted Hartree–Fock (RHF) and Density Functional Theory level (DFT), using Becke's three parameter hybrid exchange functional and the correlation functional of Lee, Yang, and Parr (B3LYP) with 3-21+G* and 6-31G*(d) basis sets.

4.2. Synthesis of 3-aminopropylsilatrane (1)

The starting material **1** was synthesized according to the method reported in literature [14,15]. 3-Aminopropyl(triethoxy)silane (5.00 g, 22.5 mmol) was added to triethanolamine (3.36 g, 22.5 mmol) at room temperature in a two-necked flask which was fitted with a Dean Stark trap. The resulting mixture was refluxed to remove the ethanol formed during the reaction. After the complete removal of ethanol, when the reaction mixture was kept in refrigerator for 5 h, white solid was obtained. Dry hexane was added, stirred for one hour and the solid was filtered and dried under vacuum.

4.3. Synthesis of 3-isothiocyanatopropylsilatrane (3)

3-Aminopropylsilatrane (2.00 g, 8.62 mmol) and DCC (1.76 g, 8.62 mmol) dissolved in 50 mL of dry diethylether were taken in a two-necked round bottom flask. The contents were stirred at 0–5 °C in an ice bath for 15 min and 4 mL of CS₂ was added dropwise at low temperature. The temperature was allowed to increase to 20 °C during the stirring for 5 h. The mixture was kept at room temperature overnight and filtered. The residue was washed with diethylether and the filtrate was evaporated under reduced pressure. The product obtained was recrystallized from diethylether. Yield: 1.6 g, 69.6%. Anal. Calc. for C₁₀H₁₈N₂O₃SSi: C, 43.77; H, 6.61; N, 10.21; S, 11.69; Si, 10.23. Found: C, 43.70; H, 6.59; N, 10.20; S, 11.63; Si, 10.17%. IR (Nujol, cm⁻¹): 2121 vs ν (C=N), 456 m δ (NCS), 576 m ν (Si ← N), 670 m ν (C=S), 625 m δ_s (SiO3), ν_s (Si–C), 725 vs, 770 s δ_{as} (SiO₃), 938 s, 975 s, 1085 s, 1115 s, 1152 s ν (Si–O–C–C), 1175 m τ (CH₂O), 1270 m ω (CH₂O), 1370 m, 1342 m ω (CH₂N); ¹H NMR (CDCl₃): δ 3.76 (t, OCH₂), 2.82 (t, NCH₂), 0.42 (t, CH₂Si), 1.82 (q, CCH₂C), 3.44 (t, CH₂NCS). ¹³C NMR (CDCl₃): δ 55.47 (OCH₂), 48.91 (NCH₂), 11.35 (SiCH₂), 24.29 (CCH₂C), 45.88 (CH₂NCS), 177.05 (NCS); MS (m/z, assignment): 297 (M+Na), 313 (M+K), 174 (silatranyl ion).

4.4. Synthesis of adducts

Compound **4**: To the stirred solution of **3** (0.25 g, 0.90 mmol) in dry CH₂Cl₂, tin(IV) chloride (0.1 mL, 0.88 mmol) was added dropwise. A white solid was appeared immediately and the contents were allowed to stir at 25 °C for 4 h. The solid obtained was filtered and washed with 15 mL of CH₂Cl₂. The white solid was dried under vacuum and analyzed with spectroscopic methods. Yield: 0.38 g, 79.2%. Anal. Calc. for C₁₀H₁₈Cl₄N₂O₃SSiSn: C, 22.45; H, 3.39; Cl, 26.51; N, 5.24; S, 5.99; Si, 5.25. Found: C, 21.98; H, 3.28; Cl, 26.60; N, 5.25; S, 5.83; Si, 5.23%. IR (Nujol, cm⁻¹): 2011, 1995 s ν (C=N), ¹H NMR (CDCl₃): δ 3.75 (t, OCH₂), 2.80 (t, NCH₂), 0.45 (t, CH₂Si), 1.80 (q, CCH₂C), 3.40 (t, CH₂NCS). ¹³C NMR (CDCl₃): δ 55.40 (OCH₂), 48.90 (NCH₂), 11.20 (SiCH₂), 24.20 (CCH₂C), 45.71 (CH₂NCS), 177.01 (NCS).

Compound **5**: In 25 mL dry CH₂Cl₂, **3** (0.25 g, 0.9 mmol) was taken in a round bottom flask and titanium(IV) chloride (0.1 mL, 0.9 mmol) was added dropwise. The contents were stirred for 4 h at room temperature. The precipitated solid was filtered and washed with 10 mL CH₂Cl₂ three times. The solid was dried under vacuum and characterized. Yield: 0.31 g, 73.8%. Anal. Calc. for C₁₀H₁₈Cl₄N₂O₃STi: C, 25.88; H, 3.91; Cl, 30.56; N, 6.04; S, 6.91; Si,

6.05. Found: C, 24.88; H, 3.89; Cl, 30.51; N, 6.01; S, 6.81; Si, 5.98%. IR (Nujol, cm^{-1}): 2013 s, 1990 s v (C=N), ^{1}H NMR (CDCl$_3$): δ 3.72 (t, OCH$_2$), 2.81 (t, NCH$_2$), 0.47 (t, CH$_2$Si), 1.79 (q, CCH$_2$C), 3.41 (t, CH$_2$NCS). ^{13}C NMR (CDCl$_3$): δ 55.43 (OCH$_2$), 48.88 (NCH$_2$), 11.25 (SiCH$_2$), 24.23 (C**C**H$_2$C), 45.79 (**C**H$_2$NCS), 177.01 (NCS).

Compound **6**: Excess diethylamine (0.5 mL, 4.5 mmol) was added to a solution of **3** (0.25 g, 0.9 mmol) in dry CH$_2$Cl$_2$. The solution was heated to reflux for 12 h. After removal of all volatile components under reduced pressure, diethylether was added and the obtained white solid was filtered, dried and stored under nitrogen due to its highly hygroscopic nature. Yield: 0.25 g, 78.1%. Anal. Calc. for C$_{14}$H$_{29}$N$_3$O$_3$SSi: C, 48.38; H, 8.41; N, 12.09; S, 9.23; Si, 8.08. Found: C, 48.21; H, 8.34; N, 12.05; S, 9.12; Si, 8.00%. IR (Nujol, cm^{-1}): 3215 s v (NH), 2083 s, v (C=N), ^{1}H NMR (CDCl$_3$): δ 3.02 (t, OCH$_2$), 2.11 (t, NCH$_2$), 0.40 (t, CH$_2$Si), 1.60 (q, CCH$_2$C), 3.15 (t, CH$_2$NCS), 2.89 (q, CH$_2$), 1.28 (t, CH$_3$), 8.5 (br, NH); ^{13}C NMR (CDCl$_3$): δ 12.5 (CH$_3$), 42.12 (CH$_2$), 54.23 (OCH$_2$), 46.58 (NCH$_2$), 11.28 (SiCH$_2$), 24.21 (C**C**H$_2$C), 45.81 (**C**H$_2$NCS), 177.01 (NCS).

Compound **7**: To a solution of **3** (0.25 g, 0.9 mmol) in dry CH$_3$CN (20 mL), was added AgNO$_3$ (0.15 g, 0.9 mmol) and the mixture was stirred for 4 h under diffused light. The solution was concentrated to 20 mL under reduced pressure. The solid obtained was filtered and dried under vacuum. Yield: 0.30 g, 73.2%. Anal. Calc. for C$_{10}$H$_{18}$AgN$_3$O$_6$SSi: C, 27.03; H, 4.08; N, 9.46; S, 7.22; Si, 6.32. Found: C, 26.98; H, 4.05; N, 9.35; S, 7.12; Si, 6.40%. IR (Nujol, cm^{-1}): 2183 s v (C=N), ^{1}H NMR (CDCl$_3$): δ 3.69 (t, OCH$_2$), 2.75 (t, NCH$_2$), 0.36 (t, CH$_2$Si), 1.75 (q, CCH$_2$C), 3.42 (t, CH$_2$NCS). ^{13}C NMR (CDCl$_3$): δ 55.30 (OCH$_2$), 48.78 (NCH$_2$), 11.20 (SiCH$_2$), 24.20 (C**C**H$_2$C), 45.85 (**C**H$_2$NCS), 177.01 (NCS).

Acknowledgement

Appendix A. Supplementary material

CCDC 742997 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.013.

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