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Preliminary communication

Synthesis and characterization of (4S)-1-chloroalkylsilatrane-4-carboxylic acids; crystal structures of (3R,4S)-1-chloromethyl-3-methylsilatrane-4-carboxylic acid and (3R,4S)-1-(3-chloropropyl)-3-methylsilatrane-4-carboxylic acid

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Abstract

(4S)-1-(chloromethyl)silatrane-4-carboxylic acid **1** and (3R,4S)-1-chloromethyl-3-methylsilatrane-4-carboxylic acid **2** were synthesized by the transesterification of chloromethyltriethoxysilane with L-*N*,*N*-bis(2-hydroxyethyl)serine or L-*N*,*N*-bis(2-hydroxyethyl)threonine in the presence of pyridine. (4S)-1-(3-chloropropyl)silatrane-4-carboxylic acid **3** and (3R,4S)-1-(3-chloropropyl)-3-methylsilatrane-4-carboxylic acid **4** were similarly synthesized from the reaction of 3-chloropropyltrimethoxysilane with the chiral ligands. The compounds were characterized by elemental analyses, IR spectra, ^{1}H and ^{13}C NMR spectra and mass spectra. The structures of compounds **2** and **4** were determined by X-ray single crystal diffraction. It is shown that the silatranyl carboxylic acids are linked by the intermolecular hydrogen bonds to give linear polymer in the crystals, and the equatorial Si–O oxygens behave as proton acceptors. It seems that the influence of the carboxylic group on the Si–N dative bond of compound **4** is greater than that of compound **2**.

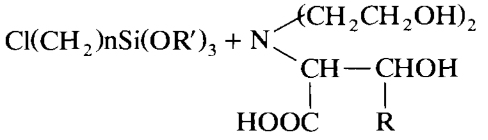
Keywords: Silicon; Silatrane compounds

1. Introduction

The peculiar pentacoordinate structure of silatrane compounds, in which the central silicon atom is bound to the nitrogen atom to form a transannular three-center four-electron bond, has received much attention in recent years [1]. The transannular Si–N dative bond distances are variable according to the properties of the apical substituent on silicon. The relationship between the Si–N distance and the axial substituent is well understood, a stronger electron-withdrawing substituent generally resulting in a shorter Si–N distance [2]. However, the effect of other functional groups, such as the acidic carboxyl group, on the rings of silatrane is virtually unexplored. Previously, we reported a novel class of silatrane compounds, (4S)-1-substituted silatrane-4-carboxylic acids, and found that the presence of an acidic carboxyl group weakens the transannular Si–N dative bonding interaction, and the axial nitrogen atom could be partially protonated [3]. In order to further investigate the influence of the carboxyl group on the Si–N dative bond, (4S)-1-(chloroalkyl)silatrane-4-carboxylic acids **1–4** were synthesized. In this paper, we report their synthesis, the X-ray crystal structures of (3R,4S)-1-chloromethylsilatrane-4-carboxylic acid **2** and (3R,4S)-1-(3-chloropropyl)silatrane-4-carboxylic acid **4** and the inductive effect of chlorine atom on the Si–N dative bond in the presence of an acidic carboxyl group.

2. Results and discussion

Synthesis of chloroalkylsilatrane-4-carboxylic acids



$$\mathrm{Cl(CH_2)nSi(OR')_3} + \mathrm{N}\begin{cases}\mathrm{(CH_2CH_2OH)_2} \\ \mathrm{\underset{HOOC}{CH}-\underset{R}{CHOH}}\end{cases}$$

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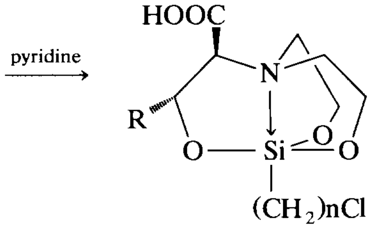

Compound	n	R′	R
1	1	Et	H
2	1	Et	Me
3	3	Me	H
4	3	Me	Me

(4S)-1-(chloromethyl)silatrane-4-carboxylic acid **1** and (3R,4S)-1-(chloromethyl)-3-methylsilatrane-4-carboxylic acid **2** were synthesized by the reaction of chloromethyltriethoxysilane with L-*N*,*N*-bis(2-hydroxyethyl)serine or L-*N*,*N*-bis(2-hydroxyethyl)threonine in the presence of pyridine. The preparation of (4S)-1-(3-chloropropyl)silatrane-4-carboxylic acid **3** and (3R,4S)-1-(3-chloropropyl)-3-methylsilatrane-4-carboxylic acid **4** from 3-chloropropyltriethoxysilane is a little more difficult than that of chloromethylsilatranyl carboxylic acids, and the reaction produces mainly sticky polymeric products with a rather low yield of desired products. When 3-chloropropyltrimethoxysilane was used instead of 3-chloropropyltriethoxysilane, the reaction with the chiral reagents in the presence of pyridine gives compound **3** or **4** in relatively high yield.

All compounds are colorless crystalline substances. They are very stable in the presence of moisture in the crystals, but less stable than the corresponding chloroalkylsilatranes since the presence of an acidic carboxyl group might accelerate their hydrolysis. Chloromethylsilatranyl carboxylic acids are more stable than (3-chloropropyl)silatranyl carboxylic acids. This may be attributable to the stronger negative induction effect of the chloromethyl group which enhances the transannular Si–N dative bond of silatrane.

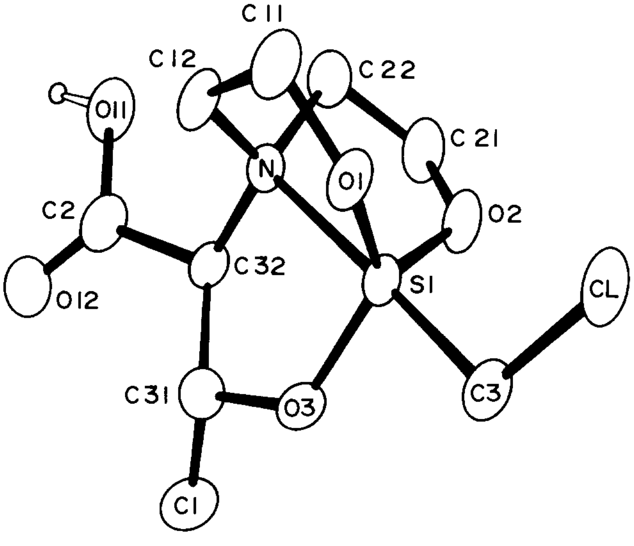

Fig. 1.

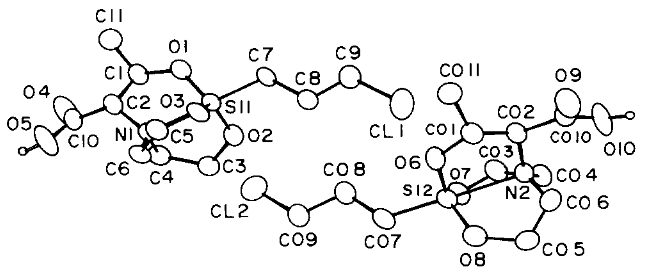

Fig. 2.

2.1. Molecular and crystal structure

The perspective views, positional parameters, bond distances and bond angles of compounds **2** and **4** appear in Figs. 1 and 2 and in Tables 1–6 respectively.

In the solid state, (3R,4S)-1-chloromethyl-3-methylsilatrane-4-carboxylic acid **2** and (3R,4S)-1-(3-chloropropyl)-3-methylsilatrane-4-carboxylic acid **4** are present as linear polymer linked by the intermolecular hydrogen bonding interactions between the carboxyl group of one molecule and one of the equatorial Si–O oxygens of the other molecule. The equatorial Si–O oxygens behave as proton acceptors. The intermolecular hydrogen bonding interaction between the carboxyl groups, present in most cases of carboxylic acid, does not occur in this case because the equatorial oxygen has a stronger Lewis base than the carboxyl oxygen. For compound **2**, the hydrogen bond (O11–H03...O1′; 2.72 Å, 164.6°) is formed between the carboxyl group of

Table 1
The atomic positions and estimated deviations of **2**

Atom	*x*	*y*	*z*	*B* (A2)
Si	0.50497(9)	0.97327(6)	0.4661(2)	1.93(2)
C1	0.6252(1)	0.80282(7)	0.3479(2)	4.54(2)
O1	0.5614(2)	0.9427(2)	0.6749(4)	2.50(5)
O2	0.5909(2)	1.0121(2)	0.2985(4)	2.81(5)
O3	0.3668(2)	0.9959(2)	0.4567(4)	2.73(5)
O11	0.4645(3)	1.2809(2)	0.6645(5)	3.63(6)
O12	0.2853(3)	1.2352(2)	0.7170(5)	3.93(7)
N	0.5189(3)	1.1022(2)	0.5821(4)	1.78(5)
C1	0.2166(4)	1.0995(3)	0.3993(8)	4.1(1)
C2	0.3777(4)	1.2247(2)	0.6496(6)	2.49(7)
C3	0.4890(4)	0.8590(2)	0.3640(6)	3.05(8)
C11	0.6023(4)	1.0046(2)	0.8106(6)	2.94(8)
C12	0.5335(3)	1.0889(2)	0.7889(5)	2.46(8)
C21	0.6207(4)	1.1026(2)	0.2871(6)	2.97(8)
C22	0.6209(3)	1.1391(2)	0.4868(6)	2.57(7)
C31	0.3158(3)	1.0749(2)	0.5262(6)	2.49(7)
C32	0.4100(3)	1.1452(2)	0.5289(5)	1.98(7)
HO3	0.5566	0.8339	0.7929	5

Table 2
Bond distances of **2**

Si–O1	1.678(3)	Si–O2	1.658(3)	Si–O3	1.646(3)
Si–N	2.136(3)	Si–C3	1.895(4)	C1–C3	1.806(4)
O1–C11	1.426(5)	O2–C21	1.425(4)	O3–C31	1.430(4)
O11–C2	1.328(5)	O12–C2	1.187(5)	N–C12	1.482(5)
N–C22	1.475(5)	N–C32	1.475(4)	C1–C31	1.508(6)
C2–C32	1.528(5)	C11–C12	1.522(5)	C21–C22	1.515(6)
C31–C32	1.533(5)				

one silatrane and the Si–O3) oxygen of other silatrane. In the crystal of compound **4**, there are two crystallographically different molecules, and the crystallographically equivalent molecules are linked by the intermolecular hydrogen bonds (O5–H01...O3: 2.66 Å, 166.6°; O10–O011...O7: 2.62, 165.5° respectively). The hydrogen bonding interaction causes the protonated Si–O bond in both compounds to be slightly longer than the unprotonated Si–O bonds.

The transannular Si–N dative bond distances of compounds **2** and **4** are longer than that of the corresponding chloroalkylsilatrane. The Si–N dative bond distance of compound **2** is 2.136(3) Å, longer than that of chloromethylsilatrane (2.120 Å) [4] by 0.016 Å. The Si–N dative bond distances of compound **4** are 2.198(3) Å and 2.244 Å, longer than that of 3-chlorosilatrane (2.180 Å) [5] by 0.018 A and 0.064 Å respectively. The increase of Si–N bond distance might not arise from the hydrogen bonding interaction since the protonation of the equatorial oxygen could reduce the electron density on the central silicon atom, and might shorten the Si–N bond distance [6]. It has been reported that the presence of a methyl group in the 3-position does not affect the degree of Si–N interaction [1a]. The weakening of Si–N interaction might be attributed to the presence of the acidic carboxyl group. It is notable that the degree of the increase of the Si–N bond distance of compound **4**, as compared with that of 3-chloropropylsilatrane, is greater than that of compound **2** compared with the corresponding chloromethylsilatrane. This suggests that if the subsituent on the ring is the same, the influence of the carboxyl group on the Si–N interaction depends on the electronegativity of apical substituents. With the decreasing-I-effect of the apical group of compounds **2** to **4**, the effect of the carboxyl group on Si–N interaction increases. This is

Table 3
Bond angles of **2**

O1–Si–O2	119.2(2)	O1–Si–O3	118.4(2)
O1–Si–N	83.7(1)	O1–Si–C3	96.7(2)
O2–Si–O3	119.1(2)	O2–Si–N	84.2(1)
O2–Si–C3	96.7(2)	O3–Si–N	84.1(1)
O3–Si–C3	94.7(2)	N–Si–C3	178.7(2)
Si–O1–C11	122.4(2)	Si–O2–C21	122.2(2)
Si–O3–C31	124.6(2)	Si–N–C12	105.0(2)
Si–N–C22	103.8(2)	Si–N–C32	104.2(2)
C12–N–C22	114.1(3)	C12–N–C32	114.2(3)
C22–N–C32	114.0(3)	O11–C2–O12	124.8(4)
O11–C2–C32	111.7(3)	O12–C2–C32	123.5(3)
Si–C3–C1	111.9(2)	O1–C11–C12	108.4(3)
N–C12–C11	106.0(3)	O2–C21–C22	107.7(3)
N–C22–C21	106.4(3)	O3–C31–C1	108.9(3)
O3–C31–C32	107.2(3)	C1–C31–C32	112.4(3)
N–C32–C2	115.0(3)	N–C32–C31	107.9(3)
C2–C32–C31	112.7(3)		

Table 4
The atomic positions and estimated deviations of **4**

Atom	*x*	*y*	*z*	*B* (Å2)
Cl1	0.5542(2)	−0.068	0.1318(2)	7.93(4)
Cl2	0.8738(2)	0.16179(9)	0.3671(2)	6.28(3)
Si1	0.78565(9)	0.24603(7)	−0.0479(1)	2.37(2)
Si2	0.69530(9)	−0.16508(7)	0.5838(1)	2.48(2)
O1	0.7942(3)	0.2872(2)	−0.2148(3)	3.18(5)
O2	0.6784(2)	0.2814(2)	0.0632(3)	3.37(5)
O3	0.9191(2)	0.2054(2)	0.0276(3)	2.97(5)
O4	0.8710(3)	0.5592(2)	−0.1873(5)	6.71(9)
O5	1.0335(3)	0.5318(2)	−0.0409(4)	5.12(7)
O6	0.7777(2)	−0.2117(2)	0.4568(3)	3.28(5)
O7	0.5556(2)	−0.1216(2)	0.5353(3)	3.20(5)
O8	0.7117(3)	−0.2004(2)	0.7542(3)	3.55(6)
O9	0.6965(3)	−0.4841(2)	0.3981(4)	5.71(8)
O10	0.4982(3)	−0.4529(2)	0.4283(4)	5.42(8)
N1	0.8733(3)	0.3737(2)	0.0126(3)	2.48(5)
N2	0.5868(3)	−0.2920(2)	0.5568(3)	2.37(5)
C1	0.8320(4)	0.3753(3)	−0.2497(4)	2.91(7)
CO1	0.7695(4)	−0.3025(3)	0.4130(5)	3.34(8)
C2	0.9200(3)	0.4075(2)	−0.1253(4)	2.53(6)
CO2	0.6344(4)	−0.3306(2)	0.4226(4)	2.80(7)
C3	0.6892(4)	0.3596(3)	0.1496(5)	3.67(8)
CO3	0.4554(4)	−0.1728(3)	0.4724(5)	3.57(8)
C4	0.7707(4)	0.4257(3)	0.0708(5)	3.39(8)
CO4	0.4554(3)	−0.2632(3)	0.5450(5)	3.13(7)
C5	1.0211(3)	0.2595(3)	0.0799(4)	3.17(7)
CO5	0.6426(4)	−0.2725(3)	0.8103(4)	3.61(8)
C6	0.9713(4)	0.3497(3)	0.1229(4)	2.97(7)
CO6	0.6218(4)	−0.3409(3)	0.6917(4)	3.09(7)
C7	0.7108(4)	0.1364(3)	−0.0983(5)	3.41(8)
CO7	0.7845(4)	−0.0587(3)	0.6049(5)	3.48(8)
C8	0.6618(4)	0.0827(3)	0.0297(5)	3.85(9)
CO8	0.7948(4)	0.0017(3)	0.4734(5)	3.26(8)
C9	0.6180(7)	−0.0070(3)	−0.0155(6)	6.9(1)
CO9	0.8664(5)	0.0856(3)	0.5161(5)	4.4(1)
C10	0.9378(4)	0.5082(3)	−0.1232(5)	3.35(8)
CO10	0.6150(4)	−0.4320(2)	0.4142(5)	3.32(8)
C11	0.8936(4)	0.3762(3)	−0.3937(5)	3.92(9)
CO11	0.8161(5)	−0.3093(4)	0.2609(6)	5.8(1)

Table 5
Bond distances (A) of **4**

Cl1–C9	1.791(6)	Cl2–CO9	1.788(5)	Si1–O1	1.658(3)
Si1–O2	1.657(3)	Si1–O3	1.683(3)	Si1–N1	2.198(3)
Si1–C7	1.884(4)	Si2–O6	1.648(3)	Si2–O7	1.681(3)
Si2–O8	1.655(3)	Si2–N2	2.244(3)	O1–C1	1.425(5)
O2–C3	1.420(5)	O3–C5	1.432(5)	O4–C10	1.190(5)
O5–C10	1.302(5)	O6–CO1	1.425(5)	O7–CO3	1.428(5)
O8–CO5	1.422(5)	O9–CO10	1.188(5)	O10–CO10	1.306(5)
N1–C2	1.471(5)	N1–C4	1.470(5)	N1–C6	1.478(5)
N2–CO2	1.471(5)	N2–CO4	1.477(5)	N2–CO6	1.476(5)
C1–C2	1.532(5)	C1–C11	1.502(6)	CO1–CO2	1.519(6)
CO1–CO11	1.505(7)	C2–C10	1.525(5)	CO2–CO10	1.540(5)
C3–C4	1.525(6)	CO3–CO4	1.512(6)	C5–C6	1.515(5)
CO5–CO6	1.509(6)	C7–C8	1.535(6)	CO7–CO8	1.517(6)
CO8–CO9	1.521(6)	C8–C9	1.481(7)	Si2–CO7	1.870(4)

consistent with the results from IR spectroscopic studies.

2.2. IR spectroscopy

It has been observed previously that the alkylsilatranyl carboxylic acids might be present as two tautomers, acid form and salt form, because of the protonation of axial nitrogen atom [3]. The IR spectra of the chloroalkylsilatranyl carboxylic acids **1–4** indicate that the property of the apical substitute group might affect the protonation of the axial nitrogen atom. It is observed that there is a strong absorption in the region 1740–1730 cm^{-1} (the absorption of acid form) in the spectra of all these compounds, and a weak absorption in the region 1630–1650 cm^{-1} (the absorption of salt form) in the spectra of compounds **1** and **3**, but no such absorption in the spectra of compounds **2** and **4**. For the investigation of the protonation of the axial nitrogen in the absence of intermolecular hydrogen bonding, we studied the IR spectroscopy of compounds **1–4** in dried tetrahydrofuran solution in which the intermolecular hydrogen bonding interaction is very weak. It is found that, in the dried tetrahydrofuran solution, there is a weak absorption in the region 1630–1650 cm^{-1} in the spectra of compounds **1**, **2** and **4**, but not in the spectrum of compound **2**. The weak absorption in the spectrum of compound **4** suggests that the protonation of the axial nitrogen in solution is easier than in crystal, and it depends mainly on the properties of the apical substituent on silicon.

Table 6
Bond angles of **4**

O1–Si1–O2	120.9(2)	O1–Si1–O3	116.0(2)
O1–Si1–N1	82.5(1)	O1–Si1–C7	97.9(2)
O2–Si1–O3	117.7(2)	O2–Si1–C7	97.5(2)
O3–Si1–N1	82.1(1)	O3–Si1–C7	97.7(2)
N1–Si1–C7	179.6(2)	O6–Si2–O7	118.5(2)
O6–Si2–O8	119.5(2)	O6–Si2–N2	81.5(1)
O6–Si2–CO7	98.6(2)	O7–Si2–O8	115.8(2)
O7–Si2–CO7	98.3(2)	O8–Si2–N2	82.4(1)
O7–Si2–N2	81.1(1)	O8–Si2–CO7	98.1(2)
N2–Si2–CO7	179.4(2)	Si1–O1–C1	125.5(2)
Si1–O2–C3	124.5(3)	Si1–O3–C5	124.2(2)
Si2–O6–CO1	125.3(3)	Si2–O7–CO3	123.3(3)
Si2–O8–CO5	123.3(3)	Si1–N1–C2	104.0(2)
Si1–N1–C4	103.6(2)	Si1–N1–C6	104.3(2)
C2–N1–C4	114.6(3)	C2–N1–C6	114.6(3)
C4–N1–C6	114.0(3)	Si2–N2–CO2	103.4(2)
Si2–N2–CO4	104.5(2)	Si2–N2–CO6	102.5(2)
CO2–N2–CO4	114.7(3)	CO2–N2–CO6	114.8(3)
CO4–N2–CO6	114.8(3)	O1–C1–C2	107.4(3)
O1–C1–C11	110.2(3)	C2–C1–C11	111.8(3)
O6–CO1–CO2	107.3(3)	O6–CO1–CO11	107.9(3)
CO2–CO1–CO11	112.9(4)	N1–C2–C1	108.1(3)
N1–C2–C10	112.2(3)	C1–C2–C10	113.3(3)
N2–CO2–CO1	107.7(3)	N2–CO2–CO10	112.4(3)
CO1–CO2–CO10	113.5(3)	O2–C3–C4	108.0(3)
O7–CO3–CO4	108.6(3)	N1–C4–C3	106.2(3)
N2–CO4–CO3	106.2(3)	O3–C5–C6	108.7(3)
O8–CO5–CO6	108.8(3)	N1–C6–C5	106.8(3)
N2–CO6–CO5	106.9(3)	Si1–C7–C8	115.3(3)
Si2–CO7–CO8	118.8(3)	CO7–CO8–CO9	110.0(4)
C7–C8–C9	112.2(4)	Cl1–C9–C8	112.3(4)
Cl2–CO9–CO8	111.8(3)	O9–CO10–O10	124.8(4)
O9–CO10–CO2	124.0(4)	O10–CO10–CO2	111.2(3)
O4–C10–O5	124.0(4)	O4–C10–C2	124.0(4)
O5–C10–C2	111.9(3)	O2–Si2–N1	82.3(1)

3. Conclusion

The presence of the carboxylic group in the silatranes leads to a slightly increased transannular Si–N dative bond distance; the degree of the increase of the Si–N bond distance depends on the property of the apical substituent on silicon. In a silatrane with a weaker electron-withdrawing apical substituent, the lengthening of the Si–N bond distance is greater and the protonation of axial nitrogen is easier, as shown by the IR spectroscopy. The equatorial Si–O oxygens of the silatranyl carboxylic acids behave as proton acceptors to form intermolecular hydrogen bonds with carboxylic groups of other molecules giving a linear polymer in crystal. It seems that the intermolecular hydrogen bonding between the carboxylic group and the equatorial oxygen has no contribution to the increase of the Si–N dative bond distance.

4. Experimental details

Solvents were purified by standard methods. IR spectra were recorded with a Nicolet FT-IR spectrometer, ^{1}H and ^{13}C NMR spectra with a Varian XL-200 NMR spectrometer, EI mass spectra with a VG ZAB-HF-3F spectrometer and elemental analyses with a Carlo-Erba 1106 elemental analyzer. L-*N*,*N*-bis(2-hydroxyethyl)serine and L-*N*,*N*-bis(2-hydroxyethyl)threonine were synthesized from the reaction of 2-chloroethanol with L-serine and L-threonine respectively [6].

Preparation of 1. A mixture of chloromethyltriethoxysilane (2.2 g, 10 mmol), L-*N*,*N*-bis(2-hydroxyethyl)serine (1.9 g, 10 mmol) and a catalytic amount of pyridine was stirred at 80°C for 8 h. After the solid was completely dissolved, the ethanol formed was distilled off under vacuum. The residue was dissolved in tetrahydrofuran (THF) and precipitated by petroleum ether (30–60°C). The product was recrystallized from THF and petroleum ether to give white crystals 2.3 g, 87%. M.p., 180°C (dec). Anal. found: C, 35.93; H, 5.36; N, 5.65; calc. C, 35.60; H, 5.23; N, 5.23%. IR (cm^{-1}, KBr): 3200–2400, 1738vs, 1647w, 1450m, 1398m, 1267s, 1224s, 1175m, 1115vs, 1066s, 937s, 900s, 815s, 782vs, 737s, 651vs. ^{1}H NMR (δ, ppm/TMS, DMSO-d_6, 200 MHz): 2.38 (s, 2H, CH$_2$Cl), 2.80–3.20 (m, 4H, NCH$_2$), 3.60–3.80 (m, 6H, OCH$_2$), 3.97 (m, 1H, NCH). ^{13}C NMR: 31.87, 48.4, 49.5, 57.3, 57.4, 58.4, 60.0, 170.3. EI-MS (*m/e*, %): 267 (M$^+$, 1.7), 222 ([M-COOH]$^+$, 4.8), 218 ([M-CH2Cl)]$^+$, 100).

Preparation of 2. Compound **2** was prepared from chloromethyltriethoxysilane with L-*N*,*N*-bis(2-hydroxyethyl)threonine according to the procedure described for **1**. Yield, 76%. M.p., 150°C (dec). Anal. found: C, 38.04; H, 5.56; N, 4.63; calc. C, 38.37; H, 5.68; N, 4.97%. IR (cm^{-1}, KBr): 3290–2800, 1746vs, 1461s, 1380s, 1271s, 1189vs, 1120vs, 1075vs, 979s, 946s, 892s, 802s, 784vs, 737s, 655s, 641vs. ^{1}H NMR (δ, ppm/TMS, DMSO-d_6, 200MHz): 2.38 (s, 2H, CH$_2$Cl), 2.85–3.25 (m, 4H, NCH$_2$), 3.60–3.70 (m, 1H, OCH), 3.65–3.80 (m, 4H, OCH$_2$), 3.95 (m, 1H, NCH), 1.41 (d, 3H, CH$_3$). ^{13}C NMR: 21.4 32.0, 48.9, 49.8, 57.0, 57.2, 64.9, 65.8, 170.3. EI-MS (*m/e*, %): 281 (M$^+$, 1.0), 237 ([M-COO]$^+$, 15.7) 232 ([M-CH$_2$Cl]$^+$, 100).

Preparation of 3. Compound **3** was synthesized from (3-chloropropyl)trimethoxysilane and L-*N*,*N*-bis(2-hydroxyethyl)serine according to the procedure described for **1**. Yield, 70%. M.p., 132–133°C. Anal. found: C, 40.31; H, 6.25; N, 4.83; calc. C, 40.60; H, 6.13; N, 4.73%. IR (cm^{-1}, KBr): 3200–2400, 1732s, 1635w, 1460m, 1364w, 1254s, 1225s, 1178s, 1123vs, 1081s, 1018s, 930s, 894s, 805s, 752vs, 681s, 626s. ^{1}H NMR (δ, ppm/TMS, DMSO-d_6, 200MHz): 0.26 (m, 2H, SiCH$_2$), 1.68 (m, 2H, CH$_2$), 2.65–3.16 (m, 4H, NCH$_2$), 3.49 (t, 2H, CH$_2$Cl), 3.55–3.75 (m, 6H, OCH$_2$), 3.80 (m, 1H, NCH). ^{13}C NMR: 14.7, 29.4, 48.2, 48.6, 49.4, 57.5, 57.6, 58.7, 67.4, 168.9. EI-MS (*m/e*, %): 295 (M$^+$, 2.4), 250 ([M–COOH]$^+$, 13.8), 218 ([M–C$_3$H$_6$Cl]$^+$, 100).

Preparation of 4. Compound **4** was synthesized from (3-chloropropyltrimethoxysilane with L-*N*, *N*-bis(2-hydroxyethyl)threonine according to the procedure described for **1**. Yield, 50%. M.p., 100–102°C. Anal. found: C, 42.85; H, 6.61; N, 5.34, calc. C, 42.65; H, 6.51; N, 5.52%. IR (cm^{-1}, KBr): 3000–2400, 1728vs, 1443w, 1361w, 1262m, 1206s, 1172m, 1123vs, 1049m, 1009s, 961m, 895m, 796s, 742vs, 684s, 632m. ^{1}H NMR (δ, ppm/TMS, DMSO-d_6, 200MHz): 0.25 (m, 2H, SiCH$_2$), 1.68 (m, 2H, CH$_2$), 2.72–3.20 (m, 4H, NCH$_2$), 3.50 (t, CH$_2$Cl), 3.60–3.74 (m, 1H, OCH), 3.68–3.80 (m, 4H, OCH$_2$), 3.85 (m, 1H, NCH), 1.21 (d, 3H, CH $_3$); ^{13}C NMR: 14.7, 21.3, 29.5, 48.6, 49.3, 49.6, 57.3, 57.5, 64.9, 65.9, 171.2. EI-MS (*m/e*, %): 309 (M$^+$, 1.4), 265 ([M–COO]$^+$, 22.9), 232 ([M–C$_3$H$_6$Cl]$^+$, 100).

4.1. X-ray structure determination

The X-ray diffraction data were collected on a computer controlled CAD4 (Enraf-Nonius) diffractometer at room temperature. Crystal data, data collection and least-squares parameters for compounds **2** and **4** are listed in Table 7.

The structures of (3R,4S)-1-chloromethyl-3-methylsilatrane-4-carboxylic acid and (3R,4S)-1-(3-chloropropyl)silatrane-4-carboxylic acid were solved by direct methods using the MULTAN program and refined anisotropically by full-matrix least-squares for non-hy-

Table 7
The crystal data, data collection and least-squares parameters of **2** and **4**

Empirical formula	SiO$_5$C$_9$H$_{16}$ClN	SiO$_5$C$_{11}$H$_{20}$ClN
M	281.77	309.82
Crystal system	orthorhombic	monoclinic
a (Å)	7.051(2)	10.7514(6)
b (Å)	11.638(4)	15.0253(38)
c (Å)	15.247(3)	9.1813(9)
β (°)		92.25(6)
Space group	$P2_12_12_1$	$P2_1$
Z	4	4
D_x (g cm^{-1})	1.496	1.388
λ (Mo Kα) (Å)	0.71073	0.71073
μ (Mo Kα) (cm^{-1})	4.049	3.483
θmax (°)	25	28
Scan technique	$\theta/2\theta$	$\theta/2\theta$
No. of unique data	1310	3713
Reflections used in least squares (NO)	1118 ($I > 3\sigma(I)$)	3068 ($I > 3\sigma(I)$)
Number of variables	154	343
$R1$	0.030	0.035
$R2$	0.035	0.038

drogen atoms. Positional parameters of the hydrogen atoms were located from difference Fourier syntheses and refined isotropically. All calculations were performed by PDP 11/44 computer using the SDP program.

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