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Synthesis, Characterization, and Reactivity of 1-Ethoxysilatrane

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Synthesis, Characterization, and Reactivity of 1-Ethoxysilatrane

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The synthesis of four new silatranes with all six-membered rings $N[CH_2(Me_2C_6H_2O)]_3SiR$ [3–6, R = OEt (3); $OCH_2CH_2N(Et)_2$ (4); SPh (5); $OOC(C_5H_4N)$ (6)] using tris(2-hydroxy-3,5-dimethylbenzyl)amine as encapsulating agent is described. Silatranes 4, 5, and 6 have been prepared by transesterifications of ethoxy silatrane 3. Structures of these silatranes have been established by elemental analyses; infrared spectroscopy; ¹H, ¹³C, and ²⁹Si NMR spectroscopy; and mass spectrometry. The results have been correlated with DFT studies using B3LYP basis set at 3–21G level.

Keywords ethoxy silatrane, six-membered ring silatrane, trichloroe thoxysilane, tris(2-hydroxy-3,5-dimethylbenzyl)amine

INTRODUCTION

The amine-tris(phenolate) ligands^[1–4] are typical tetrapodal ligands and there are numerous reports of the wide applicability of their complexes. Among them, tris(2-hydroxy-3,5-dialkylbenzyl)amines are reported to be stable scaffolds for the synthesis of flexible six-membered ring metallatrane systems. For instance, metallatranes^[5] of Al(III), Ga(III), Sn(IV), Sb(III), Zr(IV), and Nb(V) have been reported previously. Fe(III), Ta(IV), W(IV), and Bi(III) complexes^[6–9] have also been documented. Recently, Ti(IV) and V(V) complexes^[10,11] of tris(2-hydroxy-3,5-dialkylbenzyl)amine have been prepared, both finding applications in catalysis of organic reactions. More recently, boratranes with all six-membered rings and with two different ring sizes derived from tris(2-hydroxy-3,5-dimethylbenzyl)amine have been synthesized and characterized by Kim et al.^[12]

With regard to complexes of silicon with aminetris(phenolate) ligands, Holmes et al.^[13–15] reported the synthesis, crystal structures, and dynamic NMR behavior of sixmembered ring silatranes derived from symmetric tetrapodal ligands tris(2-hydroxy-3,5-dimethylbenzyl)amine and tris(2hydroxy-3-*tert*-butyl-5-methylbenzyl)amine. Besides these, 1isothiocyanato six-membered silatrane with Si-NCS linkage and its adducts with Lewis acids and bases have also been reported.^[16]

Six-membered ring silatranes being structurally flexible are of broad theoretical and experimental interest. This flexibility permits changes in the N \rightarrow Si bond lengths as well as ²⁹Si NMR chemical shifts, which are indeed correlated to the electronic influences of the axial or exocyclic substituents. There are ample reports of systematic theoretical studies also on the silatrane systems.^[17–19] These studies have provided vital information regarding the structure and reactivity of such species.

Owing to our interest in such larger rings, in the present context we report the synthesis and structural analysis of novel silatranes 3-6 (Figure 1) with all six-membered rings by employing transesterifications of ethoxy silatrane 3.

The ethoxy silatrane **3** itself has been prepared by the reaction of trichloroethoxysilane **1** with the tetrapodal ligand tris(2hydroxy-3,5-dimethylbenzyl)amine **2**, unlike the conventional method of preparation of alkoxy silatranes by use of tetraalkyl orthosilicates.^[13] Theoretical calculations have also been performed, using density functional theory (DFT) with B3LYP basis set and an account for the parameter of $N \rightarrow Si$ bond length has been given with regard to the electronegativity of the axial/exocyclic substituent.

EXPERIMENTAL

Materials and Physical Measurements

Solvents were freshly dried according to standard procedures. All the reactions involving silanes and silatranes were carried out in dry nitrogen atmosphere. Silicon(IV) chloride (Aldrich, St. Louis, MO, USA), absolute alcohol (CYC China), 2,4-dimethylphenol (Merck, Darmstadt, Germany), hexamethylenetetramine (Aldrich), *p*-toluenesulfonic acid (SDFCL, Chandigarh, India), 2-diethylaminoethanol (CDH, Chandigarh, India), thiophenol (Merck), and 2-picolinic acid (SDFCL) were

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FIG. 1. Structures of silatranes synthesized.

used as supplied. Pyridine (Merck) was refluxed over KOH pellets and vacuum distilled before use. Tris(2-hydroxy-3,5dimethylbenzyl)amine^[13] and trichloroethoxysilane^[20] were prepared according to reported literature methods. Elemental analyses were performed using a Flash Organic Elemental (Model 2000) CHNS-O Analyzer (Panjab University, Chandigarh, India). The % mass compositions of sulfur, silicon and chlorine were determined by standard gravimetric methods. IR spectra were recorded in the range 4000–400 cm⁻¹ in Nujol/KBr plates on a Perkin-Elmer RX1 FTIR Spectrophotometer (Panjab University, Chandigarh, India). ¹H (300 MHz), ¹³C (75.5 MHz), and ²⁹Si (59.6 MHz) NMR spectra were obtained in DMSOd⁶/CDCl₃ on a Jeol AL 300 spectrophotometer (Panjab University, Chandigarh, India). Chemical shifts were reported as positive downfield shifts in ppm, as relative to tetramethylsilane. Mass spectra (ESI, 3500V) were recorded on a Micromass Q-TOF Spectrometer (Panjab University, Chandigarh, India). Computational studies (DFT) were performed on a Gaussian 03 program (Gaussian, Inc., Wallingford, CT, USA) system using B3LYP basis set at 3–21G level.

Synthesis of Silatranes

 $\label{eq:linear} \begin{array}{l} 1-Ethoxysila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4',6'-dimethylbenzo)[4.4.4.0]tricyclotetradecane, N[CH_2 (Me_2C_6H_2O)]_3SiOEt~(\textbf{3}) \end{array}$

A solution of silane 1 (2.60 mL, 14 mmol), tetrapodal ligand 2 (6.10 g, 14 mmol), and pyridine (3.50 mL, 43 mmol) in dry acetonitrile (50 mL) was stirred for 2 h at ambient temperature. Pyridinium chloride formed as white solid was filtered off from the reaction mixture. Removal of solvent from the filtrate in vacuo gave the ethoxy silatrane 3 as a yellow residue which was washed with hexane (5 mL) and dried. Yield: 6.05 g (85%); mp 198–200°C (decomposed). Anal. Calcd. (%) for C₂₉H₃₅NO₄Si (489): C, 71.16; H, 7.16; N, 2.86; Si, 5.72. Found (%): C, 71.00; H, 7.06; N, 2.90; Si, 5.45. IR (KBr, cm⁻¹): 544(N \rightarrow Si), 1108(Si-O), 1244(C-O). ¹H NMR (300 MHz, DMSO-d⁶/CDCl₃): $\delta = 2.20(s, 9H, Ar-CH_3), 2.15(s, 9H, Ar-$ CH₃), 4.14(s, 6H, NCH₂), 6.78(s, 3H, Ar-H), 6.87(s, 3H, Ar-*H*), 3.34(q, 2H, OCH₂CH₃), 1.10(t, 3H, OCH₂CH₃). ¹³C NMR $(75.5 \text{ MHz}, \text{DMSO-d}^{6}/\text{CDCl}_{3}): \delta = 16.41(\text{Ar-CH}_{3}), 20.18(\text{Ar-CH}_{3})$ CH₃), 55.68(NCH₂), 116.45, 126.16, 129.03, 129.47, 133.64, 150.98(Ar-C), 57.73(OCH₂CH₃), 18.20(OCH₂CH₃). ²⁹Si NMR (59.6 MHz, DMSO-d⁶/CDCl₃): $\delta = -94.75$. MS (ESI) m/z [assignment]: 512[M+Na⁺].

(1-(N,N-diethyl)aminoethoxy)sila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4',6'-dimethylbenzo) [4.4.4.0]tricyclo tetradecane, N[CH₂(Me₂C₆H₂O)]₃SiOCH₂CH₂N(Et)₂ (**4**)

To a stirred solution of 3 (1.10 g, 2 mmol) in acetonitrile (30 mL), 2-diethylaminoethanol (0.30 mL, 2 mmol) was added and the contents were heated to reflux for 6 h. Solvent was removed from the reaction mixture by vacuum evaporation and the pale yellow residue was washed with diethyl ether (2 mL), followed by vacuum drying to give 4. Yield: 0.85 g (68%); mp 208-210°C (decomposed). Anal. Calcd. (%) for C33H44N2O4Si (560): C, 70.71; H, 7.86; N, 5.00; Si, 5.00. Found (%): C, 70.05; H, 7.60; N, 4.90; Si, 4.80. IR (KBr, cm⁻¹): $v = 568(N \rightarrow Si)$, 1110(Si-O), 1262(C-O). ¹H NMR (300 MHz, DMSO-d⁶/CDCl₃): $\delta = 2.16(s, 9H, Ar-$ CH₃), 2.22(s, 9H, Ar-CH₃), 4.00(s, 6H, NCH₂), 6.76(s, 3H, Ar-H), 6.87(s, 3H, Ar-H), 3.88(t, 2H, OCH₂CH₂N), 3.29(t, 2H, OCH₂CH₂N), 3.14(q, 2H, NCH₂CH₃), 1.34(t, 3H, NCH₂CH₃). ¹³C NMR (75.5 MHz, DMSO-d⁶/CDCl₃): $\delta = 16.00$ (Ar-CH₃), 19.82(Ar-CH₃), 55.45(NCH₂), 128.86, 150.84(Ar-C), 54.54(OCH₂CH₂N), 53.53(OCH₂CH₂N), 47.12(NCH₂CH₃), 8.28(NCH₂CH₃). MS (ESI) m/z [assignment]: 583[M+Na⁺].

1-Thiophenoxysila-2,10,11-trioxa-6-aza-3,4;8,9;12,13tris(4',6'-dimethylbenzo)[4.4.4.0]tri-cyclotetradecane, $N[CH_2(Me_2C_6H_2O)]_3$ SiSPh (5)

A solution of **3** (1.00 g, 2 mmol) and thiophenol (0.20 mL, 2 mmol) in dry acetonitrile (30 mL) was heated to reflux for 4 h. Solvent was removed by vacuum evaporation; the yellow residue got was washed with hexane (2 mL) and vacuum dried to give **5**. Yield: 0.92 g (81%); mp 218–220°C (decomposed). Anal. Calcd. (%) for C₃₃H₃₅NO₃SiS (553): C, 71.61; H, 6.33; N, 2.53; Si, 5.06; S, 5.79. Found (%): C, 71.00; H, 6.30; N, 2.55; Si, 5.00; S, 5.70. IR (KBr, cm⁻¹): $v = 658(N \rightarrow Si)$, 1072(Si-O), 1296(C-O), 859(Si-S). ¹H NMR (300 MHz, DMSO-d⁶/CDCl₃): $\delta = 2.22(s, 9H, Ar-CH_3), 2.36(s, 9H, Ar-CH_3), 4.10(s, 6H, NCH₂), 6.80(s, 3H, Ar-H), 6.98(s, 3H, Ar-H), 8.28–8.77(m, 5H, SC₆H₅). ¹³C NMR (75.5 MHz, DMSO-d⁶/CDCl₃): <math>\delta = 15.62(Ar-CH_3), 19.36(Ar-CH_3), 54.20(NCH₂), 116.21, 124.83, 126.16, 128.55, 128.67, 132.51, 141.10, 150.22(Ar-$ *C*, SC₆H₅). MS (ESI) m/z [assignment]: 554[M+H⁺].

1-Picolinatosila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris (4',6'-dimethylbenzo)[4.4.4.0]tri-cyclotetradecane, $N[CH_2(Me_2C_6H_2O)]_3SiOOC(C_5H_4N)$ (6)

To a solution of **3** (1.00 g, 2 mmol) in dry acetonitrile (30 mL), 2-picolinic acid (0.25 g, 2 mmol) was added. The contents were stirred and refluxed for 6 h. After removal of solvent *in vacuo*, the yellow residue got was washed with hexane (2 mL) and vacuum dried to yield **6**. Yield: 0.76 g (66%); mp 238–240°C (decomposed). Anal. Calcd. (%) for C₃₃H₃₄N₂O₅Si (566): C, 69.96; H, 6.01; N, 4.95; Si, 4.95. Found (%): C, 69.90; H, 5.98; N, 4.90; Si, 4.50. IR (KBr, cm⁻¹): $\upsilon = 675(N \rightarrow Si)$, 1156(Si-O), 1301(C-O), 1602(C=O). ¹H NMR (300 MHz, DMSO-d⁶/CDCl₃): $\delta = 2.16(s, 9H, 5.9H)$



SCH. 1.

Ar-CH₃), 2.21(s, 9H, Ar-CH₃), 4.08(s, 6H, NCH₂), 6.76(s, 3H, Ar-H), 6.86(s, 3H, Ar-H), 7.46–8.66(m, 4H, NC₅H₄). ¹³C NMR (75.5 MHz, DMSO-d⁶/CDCl₃): δ = 15.52(Ar-CH₃), 19.28(Ar-CH₃), 54.01(NCH₂), 116.18, 116.21, 124.77, 126.39, 128.47, 128.58, 132.40, 140.27, 150.11, 151.71(Ar-C, NC₅H₄), 194.26(C=O). MS (ESI) m/z [assignment]: 566[M⁺], 567[M+H⁺].

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Studies

Silatranes **3–6** were synthesized using two different methods. Silatrane **3** was synthesized by the reaction of the tetrapodal ligand **2** with trichloroethoxysilane **1** in the presence of three equivalents of pyridine (Scheme 1). Silatranes **4–6** were obtained by transesterifications of the preformed silatrane **3** with appropriate ligands like 2-diethylaminoethanol, thiophenol, and 2-picolinic acid respectively, through the replacement of the ethoxy group, as illustrated in Scheme 2.



SCH. 2.

All of the six-membered ring silatranes 3-6 are novel and the ethoxy silatrane 3 was prepared by the reaction of trichloroethoxysilane 1 with tetrapodal ligand 2, rather than by employing the use of tetraalkyl orthosilicate in the presence of a strong fluoride catalyst.^[13] The yields of the prepared silatranes are quite appreciable, ranging from 66% to 85%. The structures of the silatranes 3-6 were analyzed on the basis of spectral data (IR, multinuclei NMR, and mass spectrometry).

IR Spectra

The infrared spectra of the silatranes showed $\upsilon \text{ N} \rightarrow \text{Si}$ absorptions ranging from 544 to 675 cm⁻¹. It was observed that the stretching frequency for N \rightarrow Si increased as the nitrogen donor interaction increased, which is indeed attributed to the increase in electron withdrawing effect of the exocyclic groups while going from **3–6**. Bands at 661, 910, and 945 cm⁻¹ were attributed to typical silatranyl skeletal vibrations.^[21]

NMR Spectra

Multinuclei (¹H, ¹³C, and ²⁹Si) NMR spectra were consistent with the structure of the synthesized compounds. On comparing the ¹H and ¹³C NMR spectra of the silatranes with that of the tetrapodal ligand **2**, a downfield shift for the protons and carbon atoms of the -CH₂N- moiety in all compounds was observed. Also, the ¹H NMR spectra of the silatranes **3–6** were devoid of the signals due to phenolic –OH of **2**, thus confirming complexation. ²⁹Si NMR spectrum of **3** displayed a singlet at –94.75 ppm, the value being in the range of that of a typical pentacoordinate silicon environment.^[22]

Mass Spectral Analysis

The mass spectra (ESI, 3500V) of the compounds clearly revealed molecular ion peaks which were consistent with the molecular masses of the individual compounds.

Computational Study

The structures of the compounds were further correlated with theoretical results as obtained from geometry optimizations by performing DFT calculations (unrestricted, B3LYP) on a Gaussian 03 program system, at 3–21G level. The computed bond lengths for the optimized structures of **3–6** rightly give an

 TABLE 1

 Computational data for silatranes 3–6

Parameter	3	4	5	6
Energy ^a	-1761.92	-1973.35	-2234.91	-2042.18
Dipole moment ^b	5.60	5.43	8.20	6.21
Point group	C1	C1	C1	C1
$N \rightarrow Si^{c}$	2.114	2.110	2.085	2.076

^aCalculated in a.u. ^bCalculated in debyes. ^cComputed in Å.



FIG. 2. Optimized structures of silatranes 3-6 showing TBP arrangement around silicon atom (color figure available online).

insight into the influence of the varying exocyclic substituents on the N \rightarrow Si bond; the variation range being 2.076–2.114 Å, as shown in Table 1. The shortest and hence the most stable bond among **3–6** was observed for **6** due to maximum –I effect of the exocyclic group in this case which not only shortens the N \rightarrow Si bond length but also creates a perfect TBP arrangement around the silicon atom (Figure 2).

CONCLUSION

The formation and reactivity of ethoxy silatrane **3** has been studied. The ethoxy exocyclic group unlike the alkyl counterparts is potentially reactive and opens up the scope for synthesis of further new six-membered ring silatranes without affecting the silatranyl cage. Six-membered ring silatranes exhibit structural flexibility, which allows for the study of effect of exocyclic substituents on the $N \rightarrow Si$ bond lengths as well as infrared stretching frequencies of the bond. This feature of flexible rings is absent in the case of five-membered ring silatranes, which are quite rigid. In the present case, the donor interaction has been found to depend primarily on the electronegativity and electron withdrawing effect of the exocyclic ligands.

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