SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF 2,2’-OXYDIETHANOL COMPLEXES OF SILICON

Gurjaspreet Singh and Sheenam Girdhar
Department of Chemistry and Centre of Advanced Studies in Chemistry, Punjab University, Chandigarh 160-014, India

Abstract A series of 2,5,8-trioxasilocanes–1,1-dietoxy-2,5,8-trioxasilocane (5), 1,1-diisothiocyanato-2,5,8-trioxasilocane (6), 1,1-disocyanato-2,5,8-trioxasilocane (7), 1-phenyl-1-chloro-2,5,8-trioxasilocane (9), and 1-phenyl-1-isothiocyanato-2,5,8-trioxasilocane (10) are prepared starting from diethylene glycol, which acts as a dianionic tridentate ligand. The composition and structures of all novel compounds are established by IR spectroscopy, ¹H and ¹³C NMR spectroscopy, elemental analysis, and thermogravimetric analysis. The structural data obtained from geometry optimizations by DFT calculations correlate with the experimental results.

Keywords 2,5,8-Trioxasilocane; diethylene glycol; thermogravimetric analysis; DFT

INTRODUCTION

Heterosilicones, commonly represented as RR’Si(OCH₂CH₂)₂X (X = O, S, N), are a group of compounds containing nitrogen, oxygen, or sulphur as the donor atoms in which a transannular interaction is possible between the silicon and donor atoms containing an

Received 7 October 2013; accepted 27 May 2014.
Address correspondence to Gurjaspreet Singh, Department of Chemistry and Centre of Advanced Studies in Chemistry, Punjab University, Chandigarh 160-014, India. E-mail: gipsingh@pu.ac.in
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gpss.
unshared electron pair. Donor-functionalized 2,2′-oxydiethanol ligands (Digol) can perfectly surround metals by three coordination sites: an alcololate double function for charge neutralization and a donor function to compensate the electronic demand of the metal. The intramolecular coordination is possible with this ligand for which there exists a favorable conformation aided by the rigid geometry of the ligand allowing interaction between the silicon and the oxygen atom.

The first representative of this class of compounds, Me₂Si(OCH₂CH₂)₂O, was prepared by the reaction of diethylene glycol with dimethyldichlorosilane, dimethyldiethoxysilane, or dimethyldibutoxysilane. The only heterosilocane studied by single-crystal X-ray diffraction is 1,1-diphenyl-2,5,8-trioxasilocane Ph₂Si(OCH₂CH₂)₂O. Surprisingly, the chemistry of diethylene glycol complexes is relatively unexplored; some compounds with lanthanides, alkali, and alkaline-earth metals as well as with yttrium and titanium have been reported. The tri- and tetraethylene glycol complexes of hydrated lanthanides and the triethylene glycol complex of neodymium nitrate have been reported in the literature. The literature also contains reports on some monocyclopentadienyl tantalum complexes with the tridentate diethylene glycolate ligand. The 2,2′-oxydiethanol complex of molybdenum with mer-coordination of the tridentate ligand has also been described.

It is well known that diethanolamine and its N-substituted derivatives (O,N,O-donor ligands, structural analogues of diethyleneglycol) act as tridentate ligands toward silicon. The resulting complexes can be viewed as the corresponding silatranes RSi(OCH₂CH₂)₃N in which one OCH₂CH₂ unit has been removed from the heterocyclic framework and replaced by another substituent. Hypercoordinated group 14 element derivatives display a wide range of biological activity, which makes them interesting for medicinal chemistry and pharmacology. Both silatranes RSi(OCH₂CH₂)₃N and heterosilocanes RR'Si(OCH₂CH₂)₂X (X = O, S, N) are physiologically active.

The aim of the investigations, the results of which are described in this paper, was to synthesize 2,5,8-trioxasilocanes by reaction of diethylene glycol, a tridentate dianionic ligand, with different silanes via silicon-oxygen donor action. The complexes were characterized by elemental analysis, IR, ¹H, and ¹³C NMR spectroscopy and thermogravimetric analysis. The geometries of all complexes reported herein were optimized by density functional theory (DFT) using Becke’s three-parameter exchange functional with Lee, Yang, and Parr’s correlation functional (B3LYP); the total energies, dipole moments, and bond lengths were calculated.

RESULTS AND DISCUSSION

Synthesis

The complexes were synthesized by reaction of diethylene glycol with various silanes (2–4, 8). Diethylene glycol was allowed to react with diethoxydichlorosilane in the presence of triethylamine as a base scavenger to yield complex 5 (Scheme 1). Complexes 6 and 7 were prepared from the transesterification reaction of diethylene glycol with diethoxydiisothiocyanatosilane 3 and diethoxydiisocyanatosilane 4, respectively, following Scheme 2. Similarly, the reaction of diethylene glycol with phenyltrichlorosilane 8 resulted in the formation of compound 9, which further reacted with potassium isothiocyanate to give complex 10 as shown in Scheme 3.
Scheme 1 Synthesis of Complex 5.

Scheme 2 Synthesis of Complexes 6–7.

Scheme 3 Synthesis of Complexes 9–10.

**IR Spectroscopy**

The IR spectra of the new compounds were recorded in the range of 4000–400 cm$^{-1}$. All bands observed were consistent with expected structures. The main absorption peaks of interest were those of Si-O and O$\rightarrow$Si. The stretching vibration $\nu$(Si-O) was assigned to the bands present in the region 1070–1097 cm$^{-1}$. In addition, the symmetric deformational vibration of the 2,5,8-trioxasilocane skeleton with a predominant contribution from the bond O$\rightarrow$Si was observed in the region 547–622 cm$^{-1}$. The IR spectra of complexes 6 and 10 showed strong NCS bands at 2160 and 2066 cm$^{-1}$, respectively. The absorption band corresponding to NCO group was observed at 2288 cm$^{-1}$.

**NMR Spectroscopy**

In the $^1$H NMR spectra of the new complexes, the resonance at 5.08 ppm was absent suggesting deprotonation of aliphatic OH groups of diethylene glycol and indicating involvement of these oxygen atoms in coordination. In the $^1$H NMR spectrum of complex 5 signals for OCH$_2$ and CH$_3$ protons appeared at 3.82 and 1.21 ppm, respectively. The complexes 9 and 10 showed multiplets in the aromatic region (6.62–9.04 ppm) corresponding to phenyl group. The resonances in the $^1$H spectrum at 3.43–3.93 ppm were assigned to the protons of methylene (–CH$_2$–) groups in diethylene glycol.

In the $^{13}$C NMR spectra of all complexes, the signal ascribed to the methylene groups of diethylene glycol carbon atoms appeared at 60.8–72.9 ppm. In complex 5, the
signals corresponding to the OCH$_2$ and CH$_3$ carbon atoms appeared at 59.2 and 18.0 ppm, respectively. The $^{13}$C NMR spectra of compounds 6 and 10 displayed signals at 130.6 and 130.2 ppm, respectively, corresponding to the carbon atom of the NCS groups. The complex 7 showed the signal corresponding to NCO at 117.0 ppm.

**Thermogravimetric Analysis**

The thermal stability of the new complexes was studied by thermogravimetric analysis (Figure 1). The complexes were heated from 25 to 1000°C under nitrogen atmosphere. In the TGA curve of complex 5, initially the loss of both the ethoxy groups occurred (calcd. 41.10%, exp. 40.54%). The next step involved the decomposition of the rest of the compound in the temperature range above 320°C, which continued until the formation of SiO$_2$ residue (calcd. 26.11%, exp. 27.02%).

In complex 6, the first step corresponded to the loss of NCS group in the temperature range below 246°C (calcd. 25.38%, exp. 27.57%), while the second step involved the decomposition of rest of the complex; the residue corresponded to SiO$_2$ (calcd. 24.19%, exp. 25.27%). In the TGA curve of compound 7, the first step observed was the loss of NCO group (calcd. 19.43%, exp. 19.44%) below 235°C, followed by the complete decomposition of the rest of the complex; also in this case, the residue corresponded to the formation of oxides of silicon. The TGA curve of complex 9 revealed the loss of the chlorine atom and of the phenyl ring (calcd. 45.14%, exp. 46.10%) in the first step, while the second step showed the decomposition of the ligand and the formation of a residue corresponding to oxides of silicon. Compound 10 showed the loss of phenyl and NCS groups (calcd. 50.74%,
exp. 49.10%) followed by the decomposition of the rest of the complex resulting in the formation of SiO$_2$ (calcd. 23.75%, exp. 22.47%).

**Computational Study**

The geometries of all structures reported herein (Figure 2) were optimized by Density Functional Theory (DFT)$^{24}$ using B3LYP$^{25}$ along with the 3–21G basis set which has proven its utility for describing accurate geometrical features. All DFT optimizations were preformed with the Gaussian 03 set of programs.

Perhaps the most intriguing aspect of the higher-coordinate 2,5,8-trioxasilocanes is the nature of the silicon-oxygen (O→Si). The intramolecular coordination from a donor group is aided by the rigid geometry of the ligand in which the donor atom is always held in close proximity of the Si center. The ethereal oxygen atom in diethyleneglycol is more likely to coordinate with the silicon atom as there is no steric consideration which needs to be accounted for as in the case of the analogous diethanolamine derivatives. The optimized geometrical parameters of the synthesized compounds are summarized in Table 1.

The silicon-oxygen internuclear distance (O→Si) in all the optimized structures was found in the range of 2.29–2.81 Å. It is important to mention that in the heterosilocane 1,1-diphenyl-2,5,8-trioxasilocane, the distance between oxygen and silicon atoms is 2.98
\begin{table}
\centering
\caption{Parameters of optimized structures of complexes using DFT method}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
 & 5 & 6 & 7 & 9 & 10 \\
\hline
Energy\textsuperscript{a} & $-976.16$ & $-1646.1$ & $-1003.3$ & $-1357.3$ & $-1387.9$ \\
Dipole moment\textsuperscript{b} & 4.12 & 10.80 & 6.64 & 6.67 & 8.01 \\
O$\to$Si & 2.54 & 2.29 & 2.40 & 2.81 & 2.74 \\
Si–O av & 1.68 & 1.68 & 1.66 & 1.68 & 1.67 \\
O–C av & 1.47 & 1.47 & 1.46 & 1.46 & 1.47 \\
\hline
\end{tabular}
\textsuperscript{a} (a.u.). \\
\textsuperscript{b} (Debye). \\
\textsuperscript{c} (Å).
\end{table}

Å as determined by single-crystal X-ray diffraction studies. These distances are considerably shorter than the sum of the van der Waals radii of the O and Si atoms of 3.60 Å, which indicates a weak O$\to$Si transannular coordination interaction in these molecules. The O$\to$Si transannular interaction in these molecules was substantially weaker than the quasisilatranes, which corresponds to a higher donor ability of the nitrogen atom relative to oxygen. The geometry of 2,5,8-trioxasilocanes could be called as crown shaped and is stabilized by the O–Si interaction.

\section*{CONCLUSION}

Bicyclic organosilicon compounds with penta-coordinate silicon atom, 2,5,8-trioxasilocanes, have been synthesized from the reaction of diethylene glycol with diethoxysilanes and phenyltrichlorosilane. The complexes have been characterized by various spectroscopic techniques and thermogravimetric analysis. The experimental observations have been complemented by computational studies, which indicate the existence of O$\to$Si transannular coordination interaction. Systematic studies on compounds of this type could further offer new perspectives for the chemistry of 2,5,8-trioxasilocanes, known as close structural analogues of silatranes.

\section*{EXPERIMENTAL}

\subsection*{Materials and Methods}

All manipulations were carried out in nitrogen atmosphere using vacuum glass line. The solvents were freshly distilled according to standard procedures before use. Silicon tetrachloride (Merck), absolute ethanol (CYC China), phenyltrichlorosilane (Aldrich), triethylamine (SDFCL), potassium thiocyanate (Aldrich), and potassium isothiocyanate (Aldrich) were used as supplied. Diethylene glycol (CDH) was distilled under reduced pressure prior to use. Dichlorodiethoxysilane, diethoxydiisothiocyanatosilane, and diethoxydiisocyanatosilane were synthesized according to a reported procedure\textsuperscript{26} Infrared spectra were routinely obtained as thin films or Nujol mulls and KBr pellet on a Perkin–Elmer RX-I FT IR spectrophotometer. The $^1$H (300 MHz) and $^{13}$C NMR (75.45 MHz) NMR spectra were recorded with a Jeol and Bruker FT NMR (AL 300 MHz) spectrometers. Chemical shifts are given in ppm relative to internal DMSO-d$_6$/CDCl$_3$ and external tetramethylsilane (TMS). The elemental analyses were obtained with a FLASH-2000 Organic Elemental Analyzer. The quantum mechanical calculations were carried out using the GAUSSIAN 03 series
of programs. Geometries were fully optimized at Density Functional Theory level (DFT), using Becke’s three parameter hybrid exchange functional and the correlation functional of Lee, Yang, and Parr (B3LYP) with 3–21G basis set.

**Thermogravimetric Analyses**

The TGA analyses were run on a SDT Q600 V20.9 Build 20 TGA Instrument. The sample was loaded in alumina pans and ramped at 10°C/min over a temperature range of 25–1000°C in dry air at 60 mL/min.

**Synthesis of 2,5,8-Trioxasilocanes**

**1,1-Diethoxy-2,5,8-Trioxasilocane (5).** Diethoxydichlorosilane 2 (1.78 g, 9.43 mmol) was added dropwise to a stirred solution of diethylene glycol 1 (1.00 g, 9.43 mmol) and triethylamine (1.31 g, 9.43 mmol) in tetrahydrofuran and the reaction mixture was allowed to stir for 24 h. The resulting precipitate was filtered off and washed with tetrahydrofuran (2 mL). The solvent of the filtrate (including the wash solution) was removed in vacuo, resulting in viscous oil as the final product. Yield: 1.72 g, 82%; IR (Nujol, KBr): ν = 618 (O→Si); 1097 (Si-O) cm⁻¹. ¹H NMR (CDCl₃/CCl₄): δ = 1.29 (m, 9H, CH₃), 3.04 (m, 6H, OCH₂), 3.44–3.55 (m, 8H, OCH₂). ¹³C NMR (CDCl₃/CCl₄): δ = 18.2 (CH₃), 59.2 (OCH₂), 63.8 (OCH₂CH₂O), 72.0 (OCH₂CH₂O). Anal. Calcd. for C₈H₁₆O₅Si: C: 43.22; H: 8.16; Si: 12.63. Found: C: 43.18; H: 8.12; Si: 12.60.

**Diethyleneglycol (6).** To a dried 100 mL two-neck round-bottom flask fitted with Dean Stark apparatus, diethyleneglycol 1 (1.00 g, 9.43 mmol) and diethoxydiisothiocyanatosilane 3 (2.33 g, 9.43 mmol) were added in acetonitrile (30 mL). The mixture was refluxed for 5 h. The resulting yellow solid was isolated by filtration, washed with diethyl ether (2 mL) and dried in vacuo. Yield: 1.98 g, 85%; mp 260°C (dec.); IR (Nujol, KBr): ν = 636 (O→Si); 1097 (Si-O); 2160 (NCS) cm⁻¹. ¹H NMR (DMSO-d₆/CDCl₃): δ = 3.56–3.70 (m, 8H, OCH₂). ¹³C NMR (DMSO-d₆/CDCl₃): δ = 60.8 (OCH₂CH₂O), 71.9 (OCH₂CH₂O), 130.1 (NCS). Anal. Calcd. for C₆H₈N₂O₃S₂Si: C: 29.02; H: 3.25; N: 11.28; S: 25.82; Si: 11.31. Found: C: 29.00; H: 3.21; N: 11.22; S: 25.78; Si: 11.29.

**1,1-Diisocyanato-2,5,8-Trioxasilocane (7).** To a dried 100 mL two-neck round-bottom flask equipped with Dean Stark apparatus, diethyleneglycol 1 (1.00 g, 9.43 mmol) and diethoxydiisocyanatosilane 4 (1.90 g, 9.43 mmol) were added in acetonitrile (30 mL). The mixture was refluxed for 5 h. The resulting yellow solid was isolated by filtration, washed with diethyl ether (2 mL) and dried in vacuo. Yield: 1.64 g, 81%; mp 220°C (dec.); IR (Nujol, KBr): ν = 547 (O→Si); 1063 (Si-O); 2288 (NCO) cm⁻¹. ¹H NMR (DMSO-d₆/CDCl₃): δ = 3.58–3.71 (m, 8H, OCH₂). ¹³C NMR (DMSO-d₆/CDCl₃): δ = 60.5 (OCH₂CH₂O), 72.2 (OCH₂CH₂O), 117.0 (NCO). Anal. Calcd. for C₆H₈N₂O₅Si: C: 33.33; H: 3.73; N: 12.96; Si: 12.99. Found: C: 33.30; H: 3.70; N: 12.95; Si: 12.95.

**1-Phenyl-1-Chloro-2,5,8-Trioxasilocane (9).** Phenyltrichlorosilane 8 (1.99 g, 9.43 mmol) was added dropwise to a stirred solution of diethyleneglycol 1 (1.00 g, 9.43 mmol) and triethylamine (1.31 g, 9.43 mmol) in tetrahydrofuran (30 mL), and the reaction mixture was allowed to stir for 24 h. Compound 9 was isolated analogous to compound 6. Yield: 1.97 g, 86%; mp 215°C (dec.); IR (Nujol, KBr): ν = 622 (O→Si); 1088 (Si-O).
130 G. SINGH AND S. GIRDHAR

\( \delta = 3.43 - 3.93 \) (m, 8H, OCH\(_2\)), 7.25 - 7.59 (m, 5H, arom-H). \( ^{13} \text{C NMR} \) (CDCl\(_3/\text{CCl}_4\)): \( \delta = 63.9 \) (OCH\(_2\)CH\(_2\)O), 72.9 (OCH\(_2\)CH\(_2\)O), 126.5 (arom-C), 128.9 (arom-C), 129.6 (arom-C), 133.9 (arom-C). Anal. Calcd. for C\(_{10}\)H\(_{13}\)ClO\(_3\)Si: C: 49.07; H: 5.35; Cl: 14.49; Si: 12.63. Found: C: 49.03; H: 5.30; Cl: 14.44; Si: 12.60%.

1-Phenyl-1-Isothiocyanato-2,5,8-Trioxyasiloxane (10). To a stirred solution of 9 (1.00 g, 4.09 mmol) in acetonitrile (30 mL), potassium isothiocyanate (0.39 g, 4.09 mmol) was added and the reaction mixture was allowed to stir for 24 h. The potassium chloride was filtered off and washed with acetonitrile (3 mL). Compound 10 was isolated analogous to compound 6. Yield: 0.87 g, 80%; mp 260°C (dec.); IR (Nujol, KBr): \( \nu = 602 \) (O→Si); 1063 (Si-O); 2066 (NCS) cm\(^{-1}\). \( ^{1} \text{H NMR} \) (CDCl\(_3/\text{CCl}_4\)): \( \delta = 3.54 - 3.70 \) (m, 8H, OCH\(_2\)), 6.92 - 7.45 (m, 5H, arom-H). \( ^{13} \text{C NMR} \) (CDCl\(_3/\text{CCl}_4\)): \( \delta = 61.8 \) (OCH\(_2\)CH\(_2\)O), 72.3 (OCH\(_2\)CH\(_2\)O), 127.6 (arom-C), 128.9 (arom-C), 130.6 (arom-C), 134.2 (arom-C), 130.6 (NCS). Anal. Calcd. for C\(_{11}\)H\(_{13}\)NO\(_3\)SSi: C: 49.41; H: 4.90; N: 5.24; S: 11.99; Si: 10.50. Found: C: 49.39; H: 4.87; N: 5.20; S: 11.95; Si: 10.47%.

FUNDING

Financial support from the University Grants Commission (UGC), New Delhi, is gratefully acknowledged.

SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher’s website at http://dx.doi.org/10.1080/10426507.2014.931400

REFERENCES

1. Selina, A.; Karlov, S. S.; Zaitseva, G. S. Chem. Heterocycl. Compd. 2006, 42, 1097-1100.
2. Voronkov, M. G.; Trofimova, O. M.; Grebneva, E. A.; Albanov, A. I.; Aksamentova, T. N.; Chipanina, N. N.; Soldatenko, A. S. Russ. J. Gen. Chem. 2010, 80, 1276-1282.
3. Urtane, I. P.; Zelchans, G. I.; Lukevics, E. Z. Anorg. Allg. Chem. 1985, 520, 179-185.
4. Wilson, A. J.; Penfold, B. R.; Wilkins, C. J. Acta. Crystallorg., Sect. C: Cryst. Struct. Commun. 1983, C39, 329-330.
5. Zyla, G.; Cholewa, M.; Witek, A. RSC Adv. 2013, 3, 6429-6434.
6. Kriebel, R. H.; Burkhard, C. A. J. Am. Chem. Soc. 1947, 69, 2689-2692.
7. Voronkov, M. G.; Romadan, Yu. P. Khim. Geterotsikl. Soedin. 1966, 2, 671-674.
8. Dyakov, V. M.; Kireyana, A. N.; Kireeva, L. N.; Chernyshev, A. E.; Bochkarev, V. N.; Androsenko, S. I. Zh. Obschh. Khim. 1988, 58, 539-541.
9. Gusev, A. I.; Chuklanova, E. B.; Dyakov, V. M.; Zhdanov, A. S.; Alekseev, N. V.; Kireeva, L. N.; Kireyana, A. N. Dokl. Akad. Nauk SSSR 1986, 291, 608-611.
10. Sobota, P.; Utko, J.; Sztajnowska K.; Jerzykiewicz L. B. New J. Chem. 1998, 22, 851-855.
11. White, J. P.; Deng, H.; Boyd, E. P.; Gallucci, J.; Shore, S. G. Inorg. Chem. 1994, 33, 5366-5366.
12. Hirashima, Y.; Tsutsui, T.; Shiiokawa, J. Chem. Lett. 1982, 55, 1405-1408.
13. Rogers, R. D.; Voss, E. J.; Ettenhouser, R. D. Inorg. Chem. 1988, 27, 533-542.
14. Bo, C.; Fandos, R.; Feliz, M.; Hernandez, C.; Otero, A.; Rodriguez, A.; Ruiz, M. J.; Pastor, C. Organometallics 2006, 25, 3336-3339.
15. Karlov, S. S.; Yakubova, E. K.; Gauchenova, E. V.; Selina, A. A.; Churakov, A. V.; Howard, J. A. K.; Tyurin, D. A.; Lorberth, J.; Zaitseva, G. S. Z. Naturforsch. 2003, 58, 1165-1170.
16. Voronkov, M. G.; Korlyukov, A. A.; Zelbst, E. A.; Grebneva, E. A.; Trofimova, O. M.; Antipin, M. Yu. Dokl. Chem. 2008, 418, 27-29.
17. Voronkov, M. G.; Korlyukov, A. A.; Zelbst, E. A.; Grebneva, E. A.; Trofimova, O. M.; Antipin, M. Yu. J. Struct. Chem. 2008, 49, 378-381.
18. Kemme, A.; Bleidelis, J.; Urtane, I.; Zelchan, G.; Lukevics, E. J. Organomet. Chem. 1980, 202, 115-121.
19. Daly J. J.; Sanz, F. J. Chem. Soc., Dalton Trans. 1974, 26, 2051-2054.
20. Corey, J. Y.; Rath, N. P.; John, C.- S.; Corey, E. R. J. Organomet. Chem. 1990, 399, 221-233.
21. Loginov, S. V.; Zharikova, S. A.; Simakina, N. E. J. Polym. Sci., Part D: Macromol. Rev. 2011, 4, 236-241.
22. Lukevics, E.; Germane, S.; Ignatovich, L. Appl. Organomet. Chem. 1992, 6, 543-564.
23. Kemme, A.; Bleidelis, J.; Urtane, I.; Zelchan, G.; Lukevics, E. J. Organomet. Chem. 1980, 202, 115-121.
24. Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652.
25. Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785-789.
26. Anderson, H. H. J. Am. Chem. Soc. 1949, 71, 1801-1803.