

**Short Communication****Synthesis and characterization of Si(IV) complexes
with tetradentate Schiff base ligands****Gurjaspreet Singh**Assistant Professor, Department of Chemistry, Panjab University, Chandigarh, **INDIA**Email: gjpsingh@pu.ac.inAccepted on 14th September 2014**ABSTRACT**

Three new silanes derived from tetradentate Schiff base (Z)-2-((2-(2-hydroxy ethylamino)ethylimino)methyl)phenol (**L**) are reported here. Reactions of Schiff base (**L**) with different ethoxy silanes and chlorosilanes have been carried out. The products are characterized by elemental analysis, IR, ¹H NMR and ¹³C NMR spectroscopy.

Keywords: Tetradentate ligand, Silicon complexes, Schiff base, Silane.**INTRODUCTION**

Construction of coordination compounds from multidentate ligands and metal ions is one of the most active areas of material research [1,2]. Ligand design is of great importance in coordination chemistry [3]. One may keep in mind the ligand size, denticity, dipole moment, polarizability and steric factors while developing ligand systems [4]. Schiff base ligands played central role as chelating ligands in the main group and transition metal coordination chemistry [5]. Transition metal complexes of tetradentate Schiff base ligand find applications as model analogues of certain metal enzymes and catalyst in organic reactions [6,7]. In the last decade, a large number of silicon Schiff base complexes of different structural types have been synthesized and characterized [8-18]. These complexes have diverse applications and biological activities. The Schiff base complexes of Si(IV) have been known to possess a range of pharmacological applications [19,20].

MATERIALS AND METHODS

Synthesis: All the syntheses were carried out under dry nitrogen atmosphere using vacuum glass line. Solvents has been dried and purified according to standard procedures [21]. Salicylaldehyde (CDH, India) has been purified by distillation under reduced pressure. Triethylamine have been kept over KOH pellets for a day and collected by simple distillation. 2-(2-aminoethylamino)ethanol (CDH), trichloromethylsilane (Aldrich) and trichlorophenylsilane (Aldrich) were used as such. Ligand **L**, Diethoxy diisothiocyanto silane and triethoxyisothiocyantosilane have been prepared by the procedure as described in the literature [22,23].

Characterization: Infrared spectrum was obtained neat on a Thermo Scientific Fischer spectrometer. CHN analysis was obtained on Perkin Elmer Model 2400 CHNS elemental analyser. Multinuclear NMR (^1H , ^{13}C) spectra were recorded on a Bruker advance II 400 and on a Jeol (AL 300 MHz) spectrometer using CDCl_3 as internal reference and chemical shifts were reported relative to tetramethylsilane. Melting points were uncorrected and measured in a Mel Temp II device using sealed capillaries.

Synthesis of silicon (IV) compounds - Compound 1

Route 1: Ligand **L** (0.83 g, 4.01 mmol) was taken in 30 mL dry benzene and stirred for 10 min at room temperature. Then diethoxydiisothiocyanatosilane (1.00 mL, 4.01 mmol) was added drop wise to the mixture. The mixture was refluxed azeotropically for 4 h at 80°C . The compound formed was filtered and dried under vacuum. The compound was hygroscopic and soluble in dimethyl sulphoxide.

Route 2: Ligand **L** (0.94 g, 4.52 mmol) was taken in 30 mL dry benzene and stirred for 10 min at room temperature. Then triethoxydiisothiocyanatosilane (1.00 mL, 4.52 mmol) was added drop wise to the mixture. The mixture was refluxed azeotropically for 4 h at 80°C . The compound formed was filtered and dried under vacuum. Yield: 71%; mp: $271\text{-}273^\circ\text{C}$. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}_2\text{SSi}$: C, 49.46; H, 4.50; N, 14.42. Found: C, 49.34; H, 4.48; N, 14.24. IR (Nujol, KBr, cm^{-1}): 2053 (ν NCS), 1653 (ν_{as} C=N), 1058 (ν_{as} Si-O), 575 (ν_{as} N \rightarrow Si). ^1H (300 MHz, CDCl_3 , 25°C): δ 2.83 (t, 4H, -NCH₂), 3.67 (t, 2H, =NCH₂), 3.91 (t, 2H, -OCH₂), 6.76-7.45 (m, 4H, Ar-H), 8.11 (s, 1H, CH=N). ^{13}C (75 MHz, CDCl_3 , 25°C): δ 48.2 (-NCH₂), 50.3 (=NCH₂), 65.9 (-OCH₂), 116.0-132.4 (Ar-C), 143.4 (NCS), 157.0 (ArC-O), 163.4 (C=N).

General Synthetic Procedure for compounds 2,3: To the stirred solution of ligand **L** in 50 mL dry THF, slightly excess amount of triethylamine was added. After 20 min of stirring, trichlorophenylsilane and trichloromethylsilane was added drop wise at 0°C to synthesize compounds **2** and **3** respectively. The mixture was stirred for 24 h at room temperature. The desired compound was separated from triethylammonium chloride salt upon solubility basis. The compounds were filtered under vacuum and purified by washing with dichloromethane and hexane for the removal of salt.

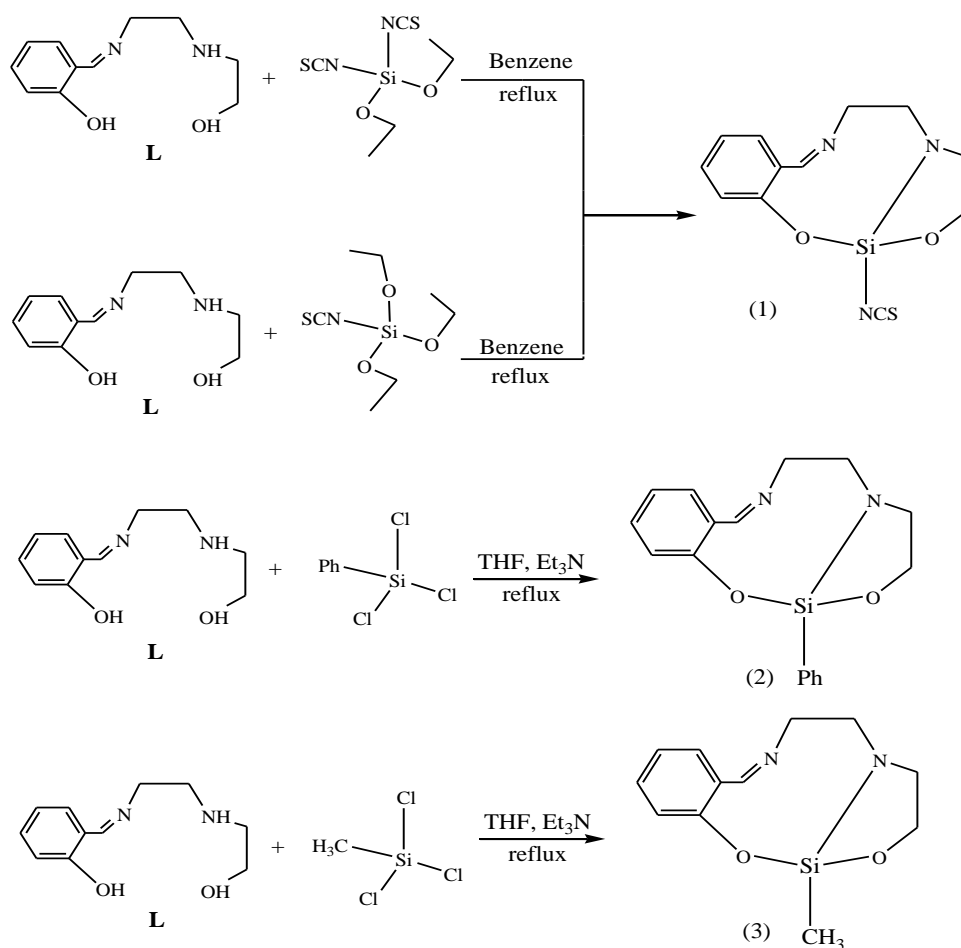
Compound 2: The compound **2** was obtained by the reaction between ligand **L** (0.99 g, 4.78 mmol), triethylamine (2.10 mL, 14.30 mmol) and trichlorophenylsilane (1.0 mL, 4.78 mmol). The compound was hygroscopic. Yield: 78%; mp: $268\text{-}270^\circ\text{C}$. Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2\text{Si}$: C, 65.78; H, 5.84; N, 9.02. Found: C, 65.74; H, 5.78; N, 8.84. IR (Nujol, KBr, cm^{-1}): 1658 (ν_{as} C=N), 1048 (ν_{as} Si-O), 574 (ν_{as} N \rightarrow Si). ^1H (300 MHz, CDCl_3 , 25°C): δ 2.86 (t, 4H, -NCH₂), 3.68 (t, 2H, =NCH₂), 3.89 (t, 2H, -OCH₂), 6.68-7.66 (m, 9H, Ar-H), 8.09 (s, 1H, CH=N). ^{13}C (75 MHz, CDCl_3 , 25°C): δ 48.6 (-NCH₂), 50.5 (=NCH₂), 65.2 (-OCH₂), 114.3-136.5 (Ar-C), 156.7 (ArC-O), 161.7 (C=N).

Compound 3: The compound **3** was obtained by the reaction between ligand **L** (1.41 g, 6.80 mmol), triethylamine (2.90 mL, 20.40 mmol) and trichloromethylsilane (1.0 mL, 6.80 mmol). The compound was hygroscopic. Yield: 74%; mp: $272\text{-}274^\circ\text{C}$. Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_2\text{Si}$: C, 58.03; H, 6.49; N, 11.28. Found: C, 57.97; H, 6.38; N, 11.21. IR (Nujol, KBr, cm^{-1}): 1654 (ν_{as} C=N), 1053 (ν_{as} Si-O), 574 (ν_{as} N \rightarrow Si). ^1H (300 MHz, CDCl_3 , 25°C): δ 0.34 (s, 3H, CH₃), 2.78 (t, 4H, -NCH₂), 3.64 (t, 2H, =NCH₂), 3.87 (t, 2H, -OCH₂), 6.78-7.54 (m, 4H, Ar-H), 8.09 (s, 1H, CH=N). ^{13}C (75 MHz, CDCl_3 , 25°C): δ 12.3 (CH₃), 47.8 (-NCH₂), 50.3 (=NCH₂), 65.9 (-OCH₂), 116.8-133.1 (Ar-C), 154.7 (ArC-O), 160.8 (C=N).

RESULTS AND DISCUSSION

Synthesis: The compounds **1-3** were obtained as yellow color solid in good yield through the reaction of salen-type ligand **L** with silanes as depicted in scheme 1. The compound **1** was synthesized by transesterification reaction of diethoxydiisothiocyanatosilane or triethoxyisothiocyanatosilane with ligand **L** using Dean-stark apparatus without any base. Both the routes gave the same product and it was confirmed gravimetrically by the presence of one sulphur element in the final product. The ligand **L** was

reacted to trichlorophenylsilane (PhSiCl_3) and trichloromethylsilane (MeSiCl_3) at 0°C for the synthesis of silicon (IV) complexes **2** and **3** respectively. The triethylamine base was required in slightly excess amount for the formation of salt as trimethylammonium chloride which was soluble in tetrahydrofuran.



Scheme 1. Synthesis of Si (IV) complexes with salen type ligand.

The reaction mixture was further stirred for 24 h and silicon complexes (IV) **2** and **3** were filtered and dried which were soluble in dimethyl sulphoxide. The structures of complexes were authenticated by various spectroscopic techniques.

Infrared Spectroscopy: In these complexes, the characteristic absorption band for $\text{N}\rightarrow\text{Si}$ is observed in the region $574\text{-}575\text{ cm}^{-1}$ respectively for compounds **1-3**. The absorption band at 2053 cm^{-1} in IR spectra showed the presence of $-\text{NCS}$ group in compound **1**. The stretching band for Si-O bond is observed at $1048\text{-}1058\text{ cm}^{-1}$ for compounds **1-3**. The band assigned to the region $1653\text{-}1658\text{ cm}^{-1}$ showed the presence of azomethine group.

Multinuclear NMR spectroscopy: The multinuclear (^1H and ^{13}C) NMR spectra were in accordance with the synthesized complexes. In ^1H NMR spectra, singlet for azomethine proton ($\text{CH}=\text{N}$) observed in the region $8.09\text{-}8.11\text{ ppm}$ for compounds **1-3** and this singlet appeared downfield as compared to the ligand **L** which supports the coordination of silicon with nitrogen of azomethine group. The aromatic protons for the complexes **1-3** are observed in region $6.68\text{-}7.66\text{ ppm}$ as downfield multiplet signals. The most upfield

protons for methyl group of compound **3** are observed at 0.34 ppm. The peaks due to $-NCH_2$, $=NCH_2$ and $-OCH_2$ protons appear around 2.78-2.86, 3.64-3.68 and 3.87-3.91 respectively in all the compounds. The absence of phenolic $-OH$ at 11.76 ppm justified the formation of bond between oxygen and silicon atom. In ^{13}C NMR, the more shielded peak is observed at 12.3 ppm for methyl group attached directly to silicon of compound **3**. The peak at 143.4 ppm confirmed the presence of NCS group of compound **1**. The peaks in region 160.8-163.4 ppm observed due to azomethine carbon in complexes **1-3** and other aromatic peaks supported the structure of complexes **1-3**.

APPLICATIONS

Hypervalent silicon complexes with Schiff bases have been broadly studied due to their bacteriostatic [24], antimicrobial [25], fungicidal [26], biocidal [27], bactericidal [28] properties. Depending on the respective coordination number and electronic properties of the functional ligands, many of these complexes display novel structural features or reactivity blueprints which give rise to various discoveries during the past decades [29,30].

CONCLUSIONS

Complexes **1-3** containing salen type ligand have been synthesized. The silanes diethoxydiisothio cyanato silane $((C_2H_5O)_2Si(NCS)_2)$, triethoxyisothiocyanatosilane $((C_2H_5O)_3Si(NCS))$, trichlorophenylsilane $(PhSiCl_3)$ and trichloromethylsilane $(MeSiCl_3)$ are used for the production of novel neutral higher coordinated silicon compounds containing salen type ligand **L**. Experimental data supported that silicon atom in **1-3** is hypervalent and $N \rightarrow Si$ bond is dative bond.

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