

Synthesis and Characterization of Si (IV) Complexes with Salen-Type Ligand

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ABSTRACT: The silicon(IV) compounds possessing SiN_4O_2 (**1**), $\text{SiN}_2\text{O}_2\text{C}_2$ (**2,4**) and $\text{SiN}_2\text{O}_2\text{CCl}$ (**3**) coordinating frameworks have been synthesized in high yield by the reaction of the O,N,N,O- donor salen-type ligand **L** with different silanes i.e. diethoxydiisocyanatosilane $(\text{C}_2\text{H}_5\text{O})_2\text{Si}(\text{NCO})_2$, dichlorodiphenylsilane $(\text{Ph}_2\text{SiCl}_2)$, trichlorophenylsilane (PhSiCl_3) and dichloromethylphenylsilane (MePhSiCl_2) . The compounds **1-4** have been characterized by elemental analysis, IR, ^1H NMR and ^{13}C NMR spectroscopy.

KEYWORDS: Schiff base, Silane, Silicon (IV) compound.

I. INTRODUCTION

Higher coordinate silicon(IV) complexes have received considerable attention over the last three decades [1,2]. Most of these compounds have been synthesized from silicon precursors whereas it is rare to find higher coordinate silicon complexes themselves used as starting materials. The assorted chemistry of these compounds is varied in both structure and reactivity and generated a flurry of innovative research endeavors in recent years. Numerous articles on the silicon complexes with salen-type ligands bearing tridentate O,N,O- and tetradentate O,N,N,O- skeleton have been published frequently in recent years [3-11].

The Schiff base complexes of higher-coordinate silicon can be found at key points in connection with the disclosure of a multitude of pharmacological applications [12,13]. Several schiff base chelates are known with most transition metal ions which form a useful basis for the development of effective, selective and environmental friendly insecticides.

II. EXPERIMENTAL

Syntheses: All the syntheses were carried out under dry nitrogen atmosphere using vacuum glass line. Solvents has been dried and purified according to standard procedures [14]. 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. Hydrazine hydrate (CDH), Dichlorodiphenylsilane (Aldrich), Dichloromethylphenylsilane (Aldrich) and Trichlorophenylsilane (Aldrich) were used as such. Ligand **L** and Diethoxydiisocyanatosilane have been prepared by the procedure as described in the literature [15,16].

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: Ligand **L** (1.18 g, 4.95 mmol) was taken in 30 mL dry benzene and stirred for 10 min at room temperature. Then diethoxydiisocyanatosilane (1.00 mL, 4.95 mmol) was added dropwise to the mixture. The color of solution changes from light yellow to dark yellow. 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

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sulfoxide. Yield: 71%; mp: 260-262 °C. Anal. Calcd for $C_{16}H_{10}N_4O_4Si$: C, 54.85; H, 2.88; N, 15.99. Found: C, 54.74; H, 2.68; N, 15.84. IR (Nujol, KBr, cm^{-1}): 2248 (ν NCO), 1631 (ν_{as} C=N), 1040 (ν_{as} Si-O), 560 (ν_{as} N→Si). 1H NMR (400 MHz, $CDCl_3/DMSO-d_6$, 25°C): 7.58-7.62 (m, 4H, Ar-H), 7.98-8.05 (m, 4H, Ar-H), 9.20 (s, 2H, CH=N). ^{13}C NMR (101 MHz, $CDCl_3/DMSO-d_6$, 25°C): 115.8, 117.7, 130.9, 131.6 (Ar-C), 159.2 (NCO), 166.1 (CH=N).

General Synthetic Procedure for compounds (2-4)

To the stirred solution of ligand **L** in 70 mL dry THF, slightly excess amount of triethylamine was added. After 20 min of stirring, respective silane was added dropwise at 0 °C to synthesize compounds (**2-4**). The mixture was stirred for 24 h at room temperature. The desired compound was separated from triethylammonium chloride salt upon solubility basis. The compounds (**2-4**) were filtered under vacuum and purified by washing with dichloromethane and hexane for the removal of salt.

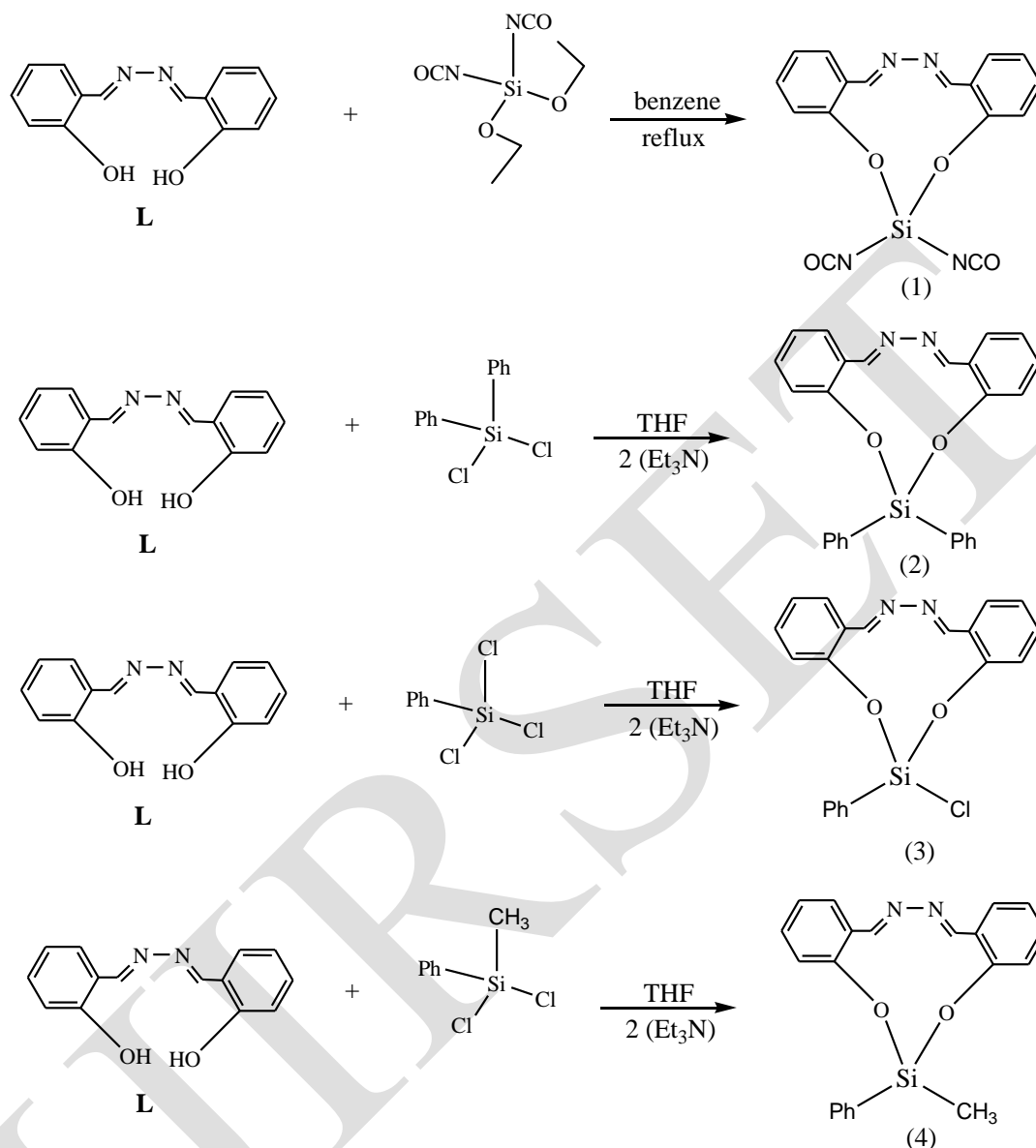
Compound 2: The compound **2** was obtained by the reaction between ligand **L** (0.95 g, 3.96 mmol), triethylamine (1.10 mL, 7.93 mmol) and dichlorodiphenylsilane (1.0 mL, 3.96 mmol). The compound was hygroscopic. Yield: 62%. mp: 266-268 °C. Anal. Calcd for $C_{26}H_{20}N_2O_2Si$: C, 74.26; H, 4.79; N, 6.66. Found: C, 74.18; H, 4.68; N, 6.58. IR (Nujol, KBr, cm^{-1}) 1630 (ν_{as} C=N), 1040 (ν_{as} Si-O), 560 (ν_{as} N→Si). 1H NMR (400 MHz, $CDCl_3/DMSO-d_6$, 25°C): 6.74-7.72 (m, 18H, Ar-H), 7.94 (s, 2H, CH=N). ^{13}C NMR (101 MHz, $CDCl_3/DMSO-d_6$, 25°C): 114.9-145.8 (Ar-C), 160.7 (CH=N).

Compound 3: The compound **3** was obtained by stirring the solution of ligand **L** (1.14 g, 4.76 mmol), triethylamine (1.33 mL, 9.52 mmol) and trichlorophenylsilane (1.0 mL, 4.76 mmol). Yield: 70%. mp: 258-260 °C. Anal. Calcd for $C_{20}H_{15}ClN_2O_2Si$: C, 63.40; H, 3.99; N, 7.39. Found: C, 63.28; H, 3.87; N, 7.28. IR (Nujol, KBr, cm^{-1}) 1639 (ν_{as} C=N), 1034 (ν_{as} Si-O), 556 (ν_{as} N→Si). 1H NMR (400 MHz, $CDCl_3/DMSO-d_6$, 25°C): 6.76-7.78 (m, 13H, Ar-H), 8.06 (s, 2H, CH=N). ^{13}C NMR (101 MHz, $CDCl_3/DMSO-d_6$, 25°C): 116.3-149.1 (Ar-C), 166.5 (CH=N).

Compound 4: The compound **4** was obtained by stirring the solution of ligand **L** (1.26 g, 5.26 mmol), triethylamine (1.47 mL, 10.52 mmol) and dichloromethylphenylsilane (1.0 mL, 5.26 mmol). Yield: 71%. mp: 260-262 °C. Anal. Calcd for $C_{21}H_{18}N_2O_2Si$: C, 70.36; H, 5.06; N, 7.81. Found: C, 70.16; H, 4.98; N, 7.67. IR (Nujol, KBr, cm^{-1}) 1639 (ν_{as} C=N), 1036 (ν_{as} Si-O), 557 (ν_{as} N→Si). 1H NMR (400 MHz, $CDCl_3/DMSO-d_6$, 25°C): 0.86 (s, 3H, CH_3), 6.65-7.45 (m, 13H, Ar-H), 7.80 (s, 2H, CH=N). ^{13}C NMR (101 MHz, $CDCl_3/DMSO-d_6$, 25°C): 5.38 (CH_3), 114.9-134.0 (Ar-C), 160.7 (CH=N).

III. RESULTS AND DISCUSSION

Synthesis: The compounds **1-4** 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 diethoxydiisocyanatosilane with ligand **L** using Dean-stark apparatus without any base. The ligand **L** was reacted to dichlorodiphenylsilane (Ph_2SiCl_2), trichlorophenylsilane ($PhSiCl_3$) and dichloromethylphenylsilane ($PhMeSiCl_2$) at 0 °C for the synthesis of silicon(IV) complexes **2**, **3** and **4** respectively. The triethylamine base was required in slightly excess amount for the formation of salt as triethylammonium chloride which was soluble in tetrahydrofuran. The reaction mixture was further stirred for 24 h and silicon(IV) complexes **2-4** were filtered and dried which were soluble in dimethylsulfoxide. The structures of complexes were authenticated by various spectroscopic techniques.



Scheme 1. Synthesis of Silicon(IV) complexes.

Infrared Spectroscopy: In these complexes, the characteristic absorption band for N→Si is observed in the region 556-560 cm^{-1} respectively for compounds 1-4. The absorption band at 2248 cm^{-1} in IR spectra showed the presence of –NCO group in compound 1. The stretching band for Si-O bond is observed at 1034-1040 cm^{-1} for compounds 1-4. The band assigned to the region 1630-1639 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 (CH=N) observed in the region 7.80-9.20 ppm for compounds 1-4 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 1-4 are observed in region 6.65-8.05 ppm as downfield multiplet signals. The most upfield protons for methyl group of compound 4 are observed at 0.86 ppm. The absence of phenolic –OH at 11.79 ppm justified the formation of bond between oxygen and silicon atom. In ^{13}C NMR, the more shielded peak is observed at 5.38 ppm for methyl group attached directly to silicon

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of compound **4**. The peak at 159.2 ppm confirmed the presence of NCO group of compound **1**. The peaks in region 160.7-166.5 ppm observed due to azomethine carbon in complexes **1-4** and other aromatic peaks supported the structure of complexes **1-4**.

IV. CONCLUSIONS

We have synthesized Si(IV) complexes **1-4** containing salen type ligand. The silanes diethoxydiisocyanatosilane ((C₂H₅O)₂Si(NCO)₂), Dichlorodiphenylsilane (Ph₂SiCl₂), Trichlorophenylsilane (PhSiCl₃) and Dichloromethylphenylsilane (MePhSiCl₂) are used for the production of novel neutral higher coordinated silicon compounds containing salen type ligand **L**. From experimental data, we have concluded that silicon atom in **1-4** is hypervalent and N→Si bond is dative bond.

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