

Silicon (IV) Complexes of Schiff Base : Preparation and Characterization

Gurjaspreet Singh*, Mridula Garg, Pooja, Manu Dabas, Jasbhinder Singh

Department of Chemistry and Centre of Advanced Studies in Chemistry,

Panjab University, Chandigarh, 160014- India

gjsingh@pu.ac.in; gurjaspreet@gmail.com

Abstract : A total of three new silicon (IV) complexes of Schiff base have been synthesized by the reaction of silicon tetrachloride with Schiff base ligands L_1 ($C_{16}H_{16}N_2O_2$), L_2 ($C_{14}H_{12}N_2O_2$) and L_3 ($C_{13}H_{11}NO_2$). The complexes obtained were characterized qualitatively and quantitatively by using micro-elemental analysis, FTIR spectroscopy, 1H and ^{13}C NMR spectroscopy. From the spectral studies we could conclude that all complexes obtained have monomeric structure.

Keywords

Schiff base, silicon tetrachloride, salicylaldehyde, amines, silatranes

Introduction

Schiff Bases derived from N-amino and carbonyl compounds are an important class of ligands that coordinate to metal ions via azomethine nitrogen and have been studied extensively [1]. In azomethine derivatives the C=N linkage is essential for biological activity. Several azomethines have been reported to possess remarkable anti-bacterial, anti-fungal and anti-cancer properties [2-4]. Owing to our interest in the studies of silicon complexes [5,6] we report the synthesis and characterization of new complex derivatives of silicon tetrachloride.

Experimental

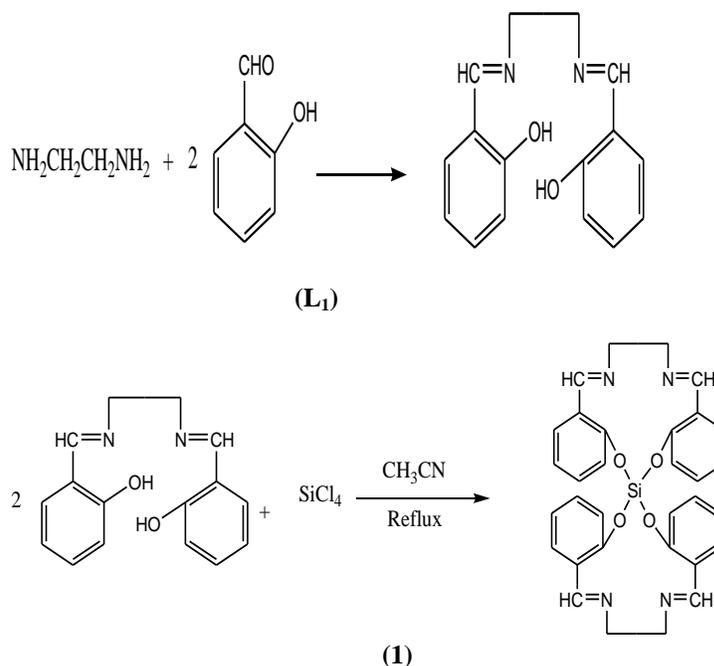
Materials and Equipments

All reactions were carried out under nitrogen atmosphere using vacuum glassline. Solvent was freshly distilled under an inert atmosphere from phosphorus pentoxide (acetonitrile) before use. Ethylene diamine (Qualigens), Salicylaldehyde (CDH), Hydrazine monohydrate (CDH) and o- aminophenol (CDH) were used as supplied.

Infrared spectra were obtained as Nujol mulls and KBr pellet on a Perkin-Elmer RX-I FT IR spectrophotometer. 1H (300 MHz), ^{13}C (75.45 MHz) NMR spectra were recorded on a Jeol and Bruker FT NMR (AL 300 MHz) spectrometer. Chemical shifts in ppm were determined relative to internal standard DMSO and $CDCl_3$ and external standard tetramethylsilane (TMS). C, H and N analysis were obtained on a FLASH-2000 organic elemental analyzer.

Reaction of Silicon tetrachloride with ligand (L_1)

Silicon tetrachloride (0.449g, 2.64mmol) was added dropwise to a stirred solution of (L_1) (0.80g, 2.98mmol) in acetonitrile (30 mL) and the reaction mixture was allowed to stir for 4h. The resulting orange coloured product (**1**) was filtered and dried under vacuum. M. pt: charring above 240°C; Yield: 82%; Anal. Calc. for $C_{32}H_{28}N_4O_4Si$ (Mol mass 560) : C:68.57; H: 5.00; N: 10.00; Si: 5.00; Found: C:68.30; H: 4.87; N: 10.03; Si:4.78; IR (Nujol, KBr, cm^{-1}): $\nu = 562$ (N→Si), 1045 (Si-O(C)), 1258(C-O), 1648 (C=N azomethine); 1H NMR (DMSO): $\delta = 2.01$ (8H, t, N-CH₂); 6.89-7.51 (16H, m, aromatic); 9.90 (4H, s, CH=N); ^{13}C NMR (DMSO): $\delta = 39.22$ (4C, N-CH₂); 117.30-136.52 (24C, aromatic); 160.79 (4C, CH=N).

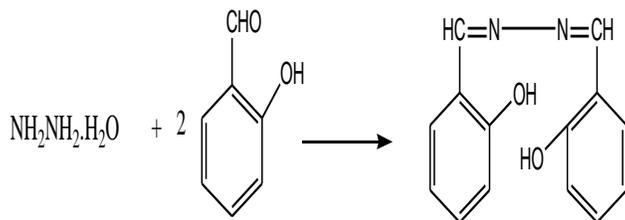


Scheme 1

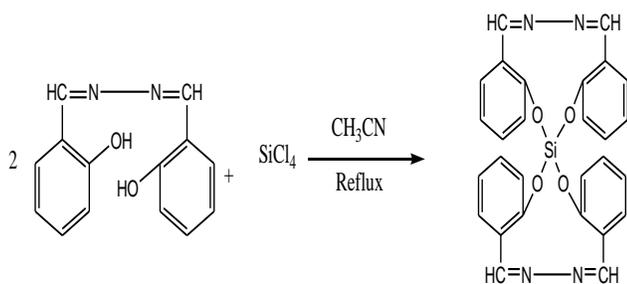
Reaction of Silicon tetrachloride with ligand (L_2)

Silicon tetrachloride (0.192g, 1.13mmol) was added dropwise to a stirred solution of (L_2) (0.50g, 2.08mmol) in acetonitrile (30 mL) and the reaction mixture was allowed to stir for 4h. The resulting off white coloured product (**2**) was filtered and dried under vacuum. M. pt: 240-250°C Yield: 86%; Anal. Calc. for $C_{28}H_{20}N_4O_4Si$ (Mol mass 504) : C:66.66; H: 3.96; N: 11.11; Si: 5.55; Found: C:66.63; H: 3.80; N: 11.00; Si:5.23; IR (Nujol, KBr, cm^{-1}): $\nu = 563$ (N→Si), 1031 (Si-O(C)), 1264(C-O), 1617

(C=N azomethine); ^1H NMR (DMSO): $\delta = 6.91$ (8H, d, aromatic); 7.32 (4H, dd, aromatic); 7.62 (4H, d, aromatic); 8.93 (4H, s, CH=N); ^{13}C NMR (DMSO): $\delta = 116.63$ -158.72 (24C, aromatic); 162.92 (4C, CH=N).



(L₁)

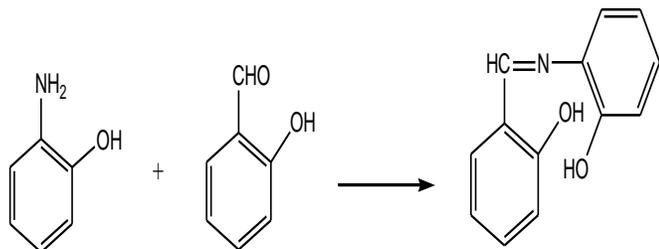


(L₂)

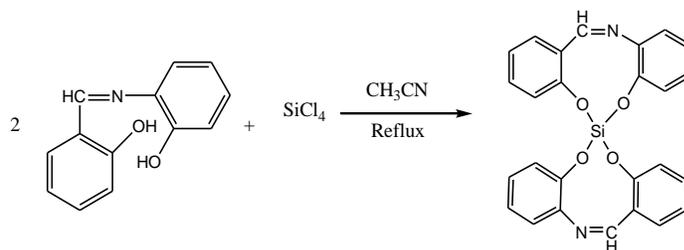
Scheme 2

Reaction of Silicon Tetrachloride with ligand (L₃)

Silicon tetrachloride (0.223g, 1.312mmol) was added dropwise to a stirred solution of (L₃) (0.56g, 2.62mmol) in benzene (30 mL) and the reaction mixture was allowed to stir for 4h. The resulting brown coloured product (3) was filtered and dried under vacuum. M. Pt: 258-262°C Yield: 78%; Anal. Calc. for C₂₆H₁₈N₂O₄Si (Mol mass 450) C:69.33; H: 4.00; N: 6.22; Si: 6.22; Found: C:69.03; H: 3.91; N:5.99; Si:6.03; IR (Nujol, KBr, cm⁻¹): $\nu = 554$ (N→Si), 1119 (Si-O(C)), 1270(C-O), 1625 (C=N azomethine); ^1H NMR (DMSO): $\delta = 5.94$ (4H,dd,aromatic); 6.18 (4H,d,aromatic); 6.51 (2H,dd,aromatic); 6.72 (2H,dd,aromatic); 7.10 (2H,d,aromatic); 7.24 (2H,d,aromatic); 8.50 (2H, s, CH=N). Due to the poor solubility of the compound, ^{13}C spectra could not be recorded.



(L₃)



(3)

Scheme 3

Results and Discussion

Syntheses

The new organosilicon (IV) complexes (C₃₂H₂₈N₄O₄Si) (1), (C₂₈H₂₀N₄O₄Si) (2) and (C₂₆H₁₈N₂O₄Si) (3) were synthesized by the reaction of silicon tetrachloride with Schiff base ligands (L₁), (L₂) and (L₃) as depicted in Scheme 1, Scheme 2 and Scheme 3 respectively. The composition of complexes was confirmed by their analytical data and the structures were suggested by spectroscopic investigations.

IR Spectroscopy

In the IR spectra of ligand, the absence of a band at 1700–1770 cm⁻¹ ruled out keto-enamine C=O stretching. In order to give conclusive idea about the structure of the silicon complexes, the main IR bands were compared with that of the free ligand. The disappearance of band $\nu(\text{O-H})$ at 3306 cm⁻¹ present in the free ligand indicated the deprotonation of the O-H and the consequent coordination of phenolic oxygen atom to silicon metal. This was further substantiated by the appearance of bands in the region 557-563 cm⁻¹ and 1031-1045 cm⁻¹, which were due to $\nu(\text{N} \rightarrow \text{Si})$ and $\nu(\text{Si-O})$ stretching vibrations respectively. In the spectra of analyzed complexes, the absorption band assigned for the $\nu(\text{C=N})$ of azomethine group was shifted to lower region as compared to the spectrum of the free Schiff base ligand which confirmed the coordination of azomethine group through nitrogen atom. This shift could be explained by a reduction of the carbon-nitrogen double bond character in the azomethine group. The C-O (phenolic) stretching frequency of the ligand observed at 1282 cm⁻¹ was shifted to lower value at 1258-1270 cm⁻¹ in the complexes. These shifts were due to coordination of ligand to silicon atom by the azomethine nitrogen and phenolic oxygen. The most significant conclusion drawn from the preceding arguments was that ligand acted as monobasic bidentate ligands towards the central silicon to form higher coordinated complexes.

NMR spectra

Multinuclei (^1H and ^{13}C) NMR spectra were consistent with the structure of synthesized complexes. ^1H -NMR spectra of the ligand showed a multiplet between 6.81-8.42 ppm due to aromatic protons, a singlet at 9.37 ppm due to resonance of the azomethine proton (CH=N) and a broad singlet at 13.44 ppm due

to hydroxyl proton. The downfield shift of the azomethine proton in the silicon complexes indicated shielding which suggested that the most probable binding of the ligand with the silicon was realized through the nitrogen atom of the azomethine group. In the complexes, the absence of a signal due to phenolic proton further supported deprotonation and subsequent involvement of oxygen in coordination. In the $^1\text{H-NMR}$ spectrum of complex (1), N-CH₂ signal appeared at 2.01 ppm. The aromatic protons were observed in the region 6.87-7.51 ppm slightly downfield as compare to the Schiff base ligand while the singlet of the azomethine proton also elucidated downfield shift at 9.90 ppm. In complex (2), the aromatic protons appeared in the region 6.91-7.62 ppm with a well-defined azomethine proton singlet at 8.93 ppm. In complex (3), signals corresponding to aromatic protons appeared in the region 5.9-7.24 ppm whereas the singlet of azomethine proton appeared at 8.50 ppm. The spectra of complexes displayed distinct ^{13}C signals for the aromatic carbon atoms in all the cases.

Conclusion : To examine the versatility of the formation of higher coordinate silicon compounds via silicon-nitrogen donor action, we carried out new synthesis employing the reaction of Schiff base ligands with SiCl_4 . The novel silatranes formed were successfully characterized.

References

- i. Mishra, N.; Poonia, K.; Kumar, D. An overview of biological aspects of Schiff base metal complexes. *International Journal of Advancements in Research & Technology*. **2013**, 2(8), 2013, 52-66.
- ii. Iqbal, A.; Siddiqui, H.L.; Ashraf, C.M.; Ahmad, M.; Weaver, G.W. Synthesis, Characterization and Antibacterial Activity of Azomethine Derivatives Derived from 2-Formylphenoxyacetic Acid. *Molecules*. **2007**, 12, 245-254.
- iii. Cinarli, A.; Gurbuz, D.; Tavman, A.; Birteksoz, A.S. Synthesis, Spectral Characterizations and Antimicrobial Activity of some Schiff Bases of 4-Chloro-2-Aminophenol. *Bull. Chem. Soc. Ethiop.* **2011**, 25(3), 407-417.
- iv. Prakash, A.; Adhikari, D. Application of Schiff bases and their metal complexes-A Review. *Int.J. ChemTech Res.* **2011**, 3(4), 1891-1896.
- v. Singh, G.; Girdhar, S.; Garg, M.; Promila. Synthesis, Characterization and Reactivity of 1-Ethoxysilatrane. *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*. **2013**, 43, 1107-1111.
- vi. Singh, G.; Saroa, A.; Garg, M.; Sharma, R.P.; Gubanov, A.I.; Smolentsev, A.I. 1-Isothiocyanatosilatrane derived from trisopropylamine: Synthesis, characterization, reactivity and theoretical studies. *Journal of Organometallic Chemistry*. **2012**, 719, 21-25.