

Preparation and Characterization of New Silicon Mixed Ligand Complexes

Z.F.Dawood¹, S. H. Hussein² and M. A. AL-Shama'a³

¹ Department of Chemistry, College of Education, University of Mosul, Mosul, Iraq

² Department of Chemistry, College of Agriculture, University of Mosul, Mosul, Iraq

³ Department of Chemistry, College of Science, University of Mosul, Mosul, Iraq

Abstract:

Silicon (IV) complexes with mixed ligands: 2-fluorobenzaldehydesemi- carbazone and Schiff-bases (derived from 2- or 3-aminopyridine with 2-hydroxy or 3-methoxy or 2-hydroxy-3-methoxybenzaldehyde) have been prepared. Complexes of the type $[\text{Si}(\text{FSCH})_2(\text{LH})]\text{Cl}_4$ and $[\text{Si}(\text{FSC})_2(\text{L}_n\text{H})]\text{Cl}_2$ or $[\text{Si}(\text{FSC})_2(\text{L})]\text{Cl}$ (where $\text{FSCH} = 2$ -fluorobenzaldehydesemicarbazone, $\text{FSC} =$ deprotonated semi- carbazone ligand, $\text{LH} =$ Schiff-base ligands) have been proposed in neutral and basic medium, respectively. The resulted complexes have been characterized by physical and chemical methods.

Key Words: Silicon complexes, mixed ligands, semicarbazone, Schiff-bases.

Introduction:

There has been a considerable interest in the study of mixed ligand complexes of transition and non transition metals^[1-4] due to their important role in biological processes^[5].

Since d-orbitals of silicon tend to be rather diffused and of higher energy than its s- and p-orbitals^[6], thus its complexes with donor ligands having silicon with coordination number higher than four seems to be somewhat rare^[6]. Recently, it has been shown that silicon can form complexes with penta, hexa and even hepta coordination numbers^[7].

Schiff-bases represent a versatile series of ligands, the metal complexes of which have been widely studied^[8-12]. Semicarbazones are ligands bonding through the nitrogen and oxygen atoms to the central metal ion forming models for metal-ligand bonding sites in several enzymes^[13]. Semicarbazone complexes of some elements have been reported^[14-18].

In view of this, and since mixed ligand complexes with silicon (IV) have not yet been reported. In the present work, new silicon (IV) complexes with mixed ligands 2-fluorobenzaldehyde semicarbazone (FSCH; Figure 1) and Schiff-bases {2-pyridinosalicylidene (L_1H), 2-pyridino-3-methoxysalicylidene (L_2H), 2-pyridino-2-methoxybenzilidene (L_3H), 3-pyridinosalicylidene (L_4H), 3-methyl-2-pyridinosalicylidene (L_5H), 3-iminopyridinosalicylidene (L_6H)} have been synthesized and characterized by physical and chemical methods.

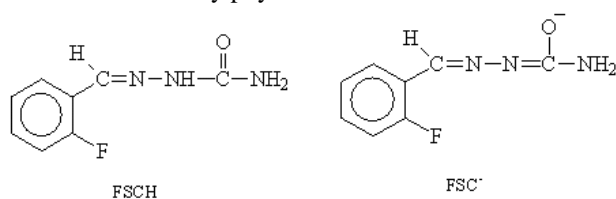


Figure – 1: Model structures of the ligands

Experimental:

I-Analytical and physicl measurement

Elemental analysis for the resulted complexes have been carried out on a CHN Analyzer type 1106 (Carlo-Erba) at Chemisry Department, Science College, Mosul University. Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 10^{-3} M ethanolic solutions at 25 °C. Infrared spectra of the ligands and their complexes have been recorded on Pye-Unicam 1100 spectrophotometer in the $400\text{--}4000\text{ cm}^{-1}$ range using KBr pellets. Electronic spectra have been recorded on Shimadzu UV-Visible Recording Spectrophotometer, UV-160 for 10^{-4} M solutions of the ligands and their complexes in ethanol at 25 °C using a 1 cm cell.

II- Preparation of the ligands

2-Fluorobenzaldehyde semicarbazone ligand has been prepared^[14], by refluxing equimolar quantities of semicarbazide hydrochloride, 2-fluorobenzaldehyde and sodium acetate solutions for about one hour. The precipitated semi- carbazone has been filtered off, washed with cold water and recrystallised from ethanol (decomposition temperature =240 °C).

Schiff-base ligands have been prepared^[8-10] by refluxing equimolar quantities of 2- or 3-aminopyridine and the appropriate aldehyde for about one hour. The formed Schiff-bases have been filtered off from their cold solutions and crystallized from hot methanol (m.p. of $\text{L}_1\text{H}=67\text{--}68$, $\text{L}_2\text{H}=96\text{--}98$, $\text{L}_3\text{H}=136\text{--}140$, $\text{L}_4\text{H}=68$, $\text{L}_5\text{H}=87\text{--}89$, $\text{L}_6\text{H}=50\text{--}54$ °C).

III-Preparation of the complexes

The reaction of SiCl_4 with 7.5-10 ml. ethanolic solutions of 2-fluorobenzaldehyde semicarbazone and Schiff bases ligands in 1:2:1 molar ratio M : FSCH : LH has been carried out. A general procedure has been adopted for the preparation of the complexes in neutral and basic medium as follows:

A-Neutral medium

$[\text{Si}(\text{FSCH})_2(\text{LH})]\text{Cl}_4$ complexes have been prepared by the reaction of 0.5g (0.0059 mole) of SiCl_4 with ethanolic solution of 1.06g (0.0118 mole) 2-fluorobenzaldehydesemicarbazone and (0.0059 mole) Schiff-base ligands (amounts in grams are listed in Table 1). The mixture has been refluxed for 3 hrs., evaporated to about half its volume and cooled. The resulting product has been filtered off, washed with cold ethanol and dried.

Table-1 :Analytical data & physical properties of the complexes

No.	Compounds	Wt. of LH (g)	Colour	M.P. or d* °C	Λ_M^{**} EtOH	% Analysis {Calc./ (Obs.)}		
						C	H	N
1	[Si(FSCH) ₂ (L ₁ H)]Cl ₄	0.5235	Yellowish brown	228-230	154	46.04 (45.66)	3.58 (3.46)	15.34 (15.21)
2	[Si(FSCH) ₂ (L ₂ H)]Cl ₄	0.6706	Brown	239d	145	43.53 (42.88)	3.47 (3.55)	12.08 (11.88)
3	[Si(FSCH) ₂ (L ₃ H)]Cl ₄	0.6235	Brown	282 d	158	46.78 (46.49)	5.79 (5.69)	15.05 (14.96)
4	[Si(FSCH) ₂ (L ₄ H)]Cl ₄	0.5235	Pale yellow	210 –212	146	46.04 (45.66)	3.79 (3.70)	15.34 (15.22)
5	[Si(FSCH) ₂ (L ₅ H)]Cl ₄	0.6235	Pale yellow	244	146	46.78 (46.39)	5.79 (5.42)	15.05 (14.85)
6	[Si(FSCH) ₂ (L ₆ H)]Cl ₄	0.6235	Redish brown	280 d	153	46.78 (46.29)	5.79 (5.66)	15.05 (14.92)
7	[Si(FSC) ₂ (L ₁)Cl	0.5235	Grey	Not melt or d.	32	54.14 (53.77)	3.73 (3.59)	18.04 (17.85)
8	[Si(FSC) ₂ (L ₂ H)]Cl ₂	0.6706	Brown	Not melt or d.	75	49.80 (49.64)	3.58 (3.64)	13.83 (13.65)
9	[Si(FSC) ₂ (L ₃ H)]Cl ₂	0.6235	White	Not melt or d.	88	51.86 (51.49)	3.90 (4.01)	16.68 (16.49)
10	[Si(FSC) ₂ (L ₄)]Cl	0.5235	White	Not melt or d.	30	54.14 (53.77)	3.73 (3.64)	18.04 (17.88)
11	[Si(FSC) ₂ (L ₅)]Cl	0.6235	Pale green	Not melt or d.	30	54.84 (54.39)	3.96 (4.03)	17.64 (17.48)
12	[Si(FSC) ₂ (L ₆)]Cl	0.6235	White	Not melt or d.	51	54.84 (54.55)	3.96 (4.00)	17.64 (17.39)

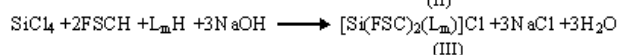
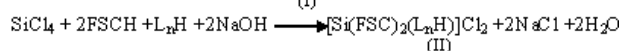
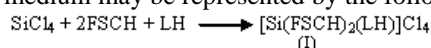
* d = decomposition temperature .

** Λ_M = molar conductivity in ohm⁻¹ cm² mol.⁻¹**B-Basic medium**

[Si(FSC)₂(L_nH)]Cl₂ or [Si(FSC)₂(L)]Cl have been prepared by applying same amounts used in neutral medium after mixing the metal salt with the ligands , ethanolic sodium hydroxide solution (0.0118 or 0.0177 mole) has been added to the mixture until pH of the solution was 9-9.3 The product has been filtered off , washed with cold ethanol and dried .

Results and Discussion :

The reaction of SiCl₄ with 2-fluorobenzaldehyde semicarbazone and Schiff–bases in both neutral and basic medium may be represented by the following reactions :



(where LH =L₁H, L₂H, L₃H, L₄H, L₅H, L₆H; L_nH = L₂H, L₃H; L_m =L₁, L₄, L₅, L₆) .

The resulted complexes are solids, moderately soluble in methanol, soluble in ethanol, dimethylformamide and dimethylsulfoxide . The elemental analysis reveal that the complexes have the composition I, II and III in neutral and basic medium, respectively (Table 1) . The molar conductivities values approached those expected for 1:4, 1:2 and 1:1 electrolytes^[19] for complexes of type I, II and III, respectively .

The infrared spectra(Table 2) of semicarbazone ligand (Figure 2) showed a strong band at about 1675 cm⁻¹ which was attributed to the C=O group^[16,18] . This value shifted towards a lower frequency on coordination, in neutral medium, indicating the formation of a chelation between the oxygen of the C=O group and the metal ion^[14,17] . Meanwhile, in basic medium, this band disappeared in the complexes and a new band was observed at 1335 cm⁻¹ due to C-O group, thereby establishing coordination of the ligand through the enolic oxygen atom^[17,18] .The next strong band at 1580 cm⁻¹ which was attributed to $\nu_{\text{C=N}}$ shifted towards a lower frequency on coordination which was due to the decrease of the bond order as a result of metal nitrogen bond formation^[13-20] . The position of the ligand in the range 3400-3500 cm⁻¹ remained unaltered in the complexes indicating that there is no coordination through the NH group^[14-15] .The spectra of Schiff-bases (Figure 2) showed a strong band in the region 1630-1640 cm⁻¹ as due to C=N stretching vibration^[5,9] . This band shifted towards a lower frequency, which demonstrated that the imine nitrogen was coordinated to the metal ion^[5,9] . The other band in the region 1575-1587 cm⁻¹ as due to $\nu_{\text{C=N(py)}}$ remained unaltered upon coordination^[9,11] . Moreover the shift in the C-O(phenolic, methoxy) vibration band on complexation supported the coordination of phenolic oxygen and methoxy groups to the metal ion^[9,11] .

Table-2: IR spectra of the ligands & their complexes (frequencies expressed in cm^{-1})

Comp.*	$\nu_{\text{C=N}}$ (semi)	ν_{NH} (semi)	$\nu_{\text{C=O}}$ (semi)	δ_{NH_2} (semi)	$\nu_{\text{C-O}}$ (semi)	$\nu_{\text{C=N}}$ (Py)	$\nu_{\text{C=N}}$ (S.B)	$\nu_{\text{C-O}}$ & ν_{OH}	$\nu_{\text{Si-O}}$	$\nu_{\text{Si-N}}$
FSCH & L_1H	1580	3400	1675	1450	-	1575	1630	1280 3100	-	-
1	1535	3400	1650	1450	-	1574	1604	1320 2900	755 650	520 580
7	1540	3400	-	1450	1335	1575	1600	1320	750 700	530 580
FSCH & L_2H	1580	3400	1675	1450	-	1576	1635	1280 3100	-	-
2	1535	3400	1650	1450	-	1575	1595	1320 2700	730 600	520 580
8	1535	3400	-	1450	1335	1575	1595	1320	730 700	530 570
FSCH & L_3H	1580	3400	1675	1450	-	1576	1630	1280	-	-
3	1540	3400	1655	1450	-	1575	1590	1320	730 650	525 575
9	1540	3400	-	1450	1335	1575	1595	1320	740 650	530 575
FSCH & L_4H	1580	3400	1675	1450	-	1587	1640	1280 3100	-	-
4	1540	3400	1650	1450	-	1585	1695	1320 2800	735 650	535 580
10	1540	3400	-	1450	1335	1587	1695	1320	735 600	530 580
FSCH & L_5H	1580	3400	1675	1450	-	1576	1630	1280 3100	-	-
5	1535	3400	1650	1450	-	1575	1600	1320 2700	735 650	530 575
11	1535	3400	-	1450	1335	1575	1595	1320	736 600	530 575
FSCH & L_6H	1580	3400	1675	1450	-	1587	1630	1280 3100	-	-
6	1540	3400	1650	1450	-	1585	1600	1320 2710	735 650	525 575
12	1535	3400	-	1450	1335	1585	1600	1320	740 630	525 575

*Correspond to compounds in table -1 Semi = semicarbazone S.B. = Schiff base Py = pyridine

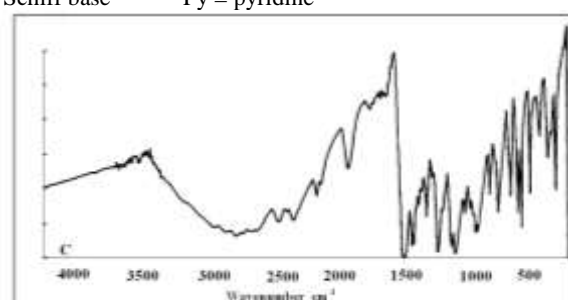
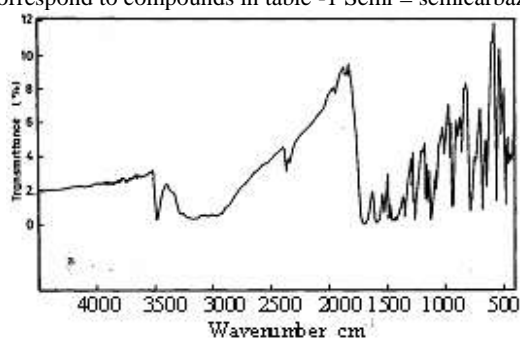
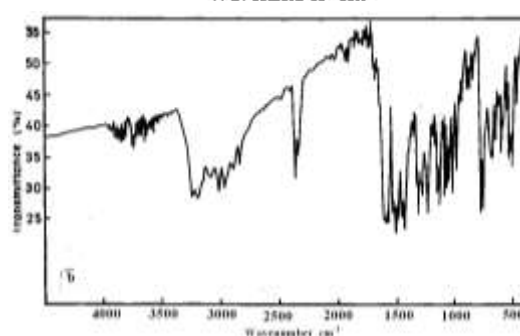


Figure - 2 : Infrared spectra of : a- the ligand FSCH ; b- the ligand L_3H ; c- the complex $[\text{Si}(\text{FSCH})_2(\text{L}_3\text{H})]\text{Cl}_4$



The spectra of all the complexes (Figure 2) showed new bands around 520-580 and 730-755 cm^{-1} due to $\nu_{\text{Si-N}}$ and $\nu_{\text{Si-O}}$, respectively. The presence of these bands strongly supported the coordination of the ligands under investigation with the metal ion^[11,15].

The electronic spectra of the ligands and their complexes in ethanolic solutions have been recorded. The maximum at about 228-233, 260-280 and 320-355 nm which were due to the electronic transition $\pi-\pi^*$ in the

aryl ring, $n-\pi^*$ and $\pi-\pi^*$ in C=N group, respectively^[21,22]. On complexation, a blue shift (305-315 nm) was observed due to the polarization in the C=N bond caused by the metal-ligand electron interaction during the chelation^[21].

Conclusions:

According to the analytical, physical and spectral data, some observations have been achieved that lead to establish the following points:

1. 2-fluorobenzaldehydesemicarbazone acts as bidentate chelating ligand joint to silicon (IV) ion through the azomethine nitrogen and carbonyl oxygen atoms.
2. Schiff base ligands act as bidentate chelating ligands joint to silicon (IV) ion through the imine nitrogen and phenolic or methoxy oxygen atoms.
3. Silicon (IV) ion is probably hexa-coordinated, leading to octahedral geometry (Figure 3).

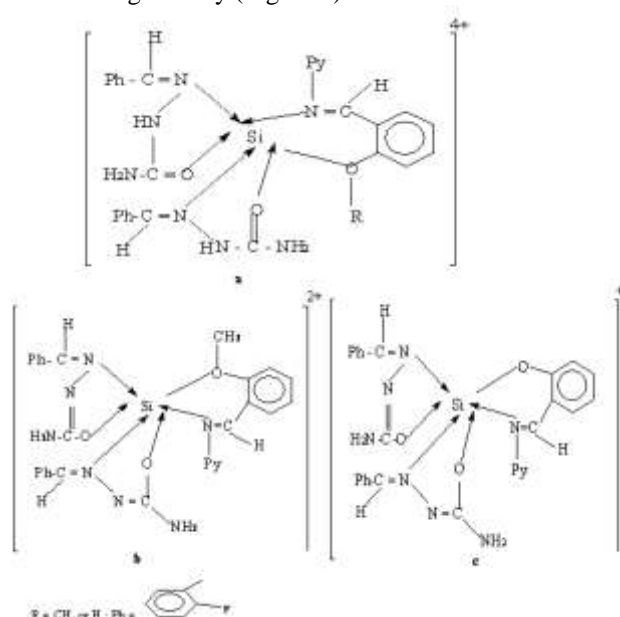


Figure –3 : Model structures of the complexes : a – in neutral medium ; b and c = in basic medium

References:

- 1- P.K. Kanungo, N.K. Sankhla and R.K. Mehta; J. Indian Chem. Soc.; VLIII (3), 335 (1986).
- 2- Z.F. Dawood ; J. Sci. Tekreet Univ.; 7 (2), 33 (2001).

- 3- Z.F. Dawood; Sci. & Tech.; 14, 47 (2000).
- 4- Z.F. Dawood and A.Z. Sheet; J. Sci. Tekreet Univ.; 7 (3), 37 (2001).
- 5- T.A.K. Al-Allaf and M.A. Al-Shamaa and L.J. Rasha; Applied Organomet. Chem.; 10, 545 (1996).
- 6- R.C. Mehrotra and G. Srimstam; Asian J. Chem. Rev.; 1 (1), 17 (1990).
- 7- S.H. Hussein, B.A. Ahmed and M.A. Al-Shamaa; J. Edu. Sci.; 50, 13 (2001).
- 8- T.A.K. Al-Allaf and A.Z.M. Sheet; Asian J. Chem.; 8 (2), 305 (1996).
- 9- T.A.K. Al-Allaf and M.A. Al-Shamaa; Mutah J. Res. & Stud.; 11 (6), 105 (1996).
- 10- T.A.K. Al-Allaf and A.Z.M. Sheet and M.A. Al-Shamaa; Mutah J. Res. & Stud.; 12 (3), 11 (1997).
- 11- G.A. Wilkinson, R.D. Gillard and J.A. McCleverty; Comprehensive coordination chemistry; Pergamon Press, Oxford, England, 1st Ed., Vol. 2, 723 (1987).
- 12- B.B. Wayland, M.F. Abid Elmageed and P. Mohns; Inorg. Chem.; 14, 1456 (1975).
- 13- Y. Kumar and S.P. Tolani; Croat. Chem. Acta; 62 (1), 73 (1989).
- 14- N. Kanoongo, R.V. Singh and J.P. Tandon; Synth. React. Inorg. Met-Org. Chem.; 17 (8&9), 837 (1987).
- 15- C.B. Mahto; J. Indian Chem. Soc.; LVII (5), 553 (1980).
- 16- Z.F. Dawood; Basrah J. Sci.; C, 15 (1), 79 (1997).
- 17- R.A. Buker and Z.F. Dawood; Iraqi J. Chem.; 25 (2), 222 (1999).
- 18- R.R. Shukla, S. Chandra and G. Narain; J. Indian Chem. Soc.; VLIII (3), 333 (1986).
- 19- W.J. Geary; Coord. Chem. Rev.; 7, 81 (1971).
- 20- Z. F. Dawood, S.H. Hussein and M.A. Al-Shama'a; Sci. & Tech. A; 12, 71 (2004).
- 21-10- T.A.K. Al-Allaf, M.A. Al-Shamaa and S. Al-Joburi; Iraqi J. Sci.; 33 (3), 4 (1992).
- 22- E.A.V. Ebsworth; Volatile silicon compounds; Pergamon press, London and Macmillan Co., N.Y. (1963).

تحضير وتشخيص معقدات جديدة للسليكون مع مزيج من الليكاندات

زهرة فتحي داود¹ و سالم حسين² و منال الشماع³

¹ قسم الكيمياء، كلية التربية، جامعة الموصل، الموصل، جمهورية العراق

² قسم الكيمياء، كلية الزراعة، جامعة الموصل، الموصل، جمهورية العراق

³ قسم الكيمياء، كلية العلوم، جامعة الموصل، الموصل، جمهورية العراق

الملخص:

بروتون، LH = ليكاندات قواعد شيف) في الوسط المتعادل والقاعدي على التوالي. شخصت المعقدات الناتجة بطرائق فيزيائية وكيميائية.

الكلمات المفتاحية: معقدات السليكون، مزيج من الليكاندات،

سميكاربازون، قواعد شيف

تم تحضير معقدات للسليكون (IV) مع مزيج من الليكاندات المتضمنة ٢- فلورو بنزالديهايد سميكاربازون وقواعد شيف (المشتقة من ٢- أو ٣- أمينوبريدين مع ٢- هيدروكسي أو ٣- ميثوكسي أو ٢- هيدروكسي-٣- ميثوكسي بنزالديهايد). اقترحت الصيغ $[Si(FSCH)_2(LH)]Cl_4$ و $[Si(FSCH)_2(L)]Cl_4$ (حيث FSCH = ٢- فلورونزالديهايد سميكاربازون، FSC = ليكاند السميكاربازون مزال منه

