PREPARATION OF SI(IV) COMPLEXES WITH MIXED LIGANDS[+]

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Abstract:

Silicon (IV) complexes containing mixed ligands:3-fluorobenzaldehyde semicarba- zone and Schiff-bases (derived from 2- or 3-aminopyridine with 2-hydroxy or 3-methoxy or 2-hydroxy-3-methoxybenzaldehyde) have been synthesized . Complexes of the type $[Si(FBSCH)_2(LH)]Cl_4$, $[Si(FBSC)_2(L_nH)]Cl_2$ and $[Si(FBSC)_2(L)]Cl$ (where LH = Schiff-base ligands , FBSCH = 3-fluorobenzaldehyde semicarbazone , FBSC = deprotonated semicarba- zone , n = 2 or 3) have been proposed . They are characterized by elemental analysis , electrolytic conductivities measurements , infrared and ultraviolet spectra . The results indicate that the ligands FBSCH and Schiff-bases acted as bidentate chelating ligands , and the resulteing complexes have octahedral geometries .

المستخلص:-

تم تحضير معقدات للسليكون (IV) الحاوية على مزيج من الليكندات : ٣- فلوروبنزالديهايد سيميكاربازون وقواعد شيف (المشتقة من ٢- أو ٣- أمينوبريدين مع ٢- هيدروكسي أو ٣- ميثوكسي أو ٢- هيدروكسي-٣- ميثوكسي بنزالديهايد) . أقترحت الصيغ $[Si(FBSCH)_2(LH)]Cl_4$ و $[Si(FBSC)_2(L_nH)]Cl_2$ و $[Si(FBSC)_2(L)]Cl$ للمعقدات المحضرة (حيث LH = ليكاندات قواعد شيف ، FBSCH = ٣- فلوروبنزالديهايد سيميكاربازون ، FBSC = السيميكاربازون مزال منه بروتون ، n =٢ أو ٣) . شخصت المعقدات الناتجة باستخدام التحليل الدقيق للعناصر وقياس التوصيلية الكهربائية وطيف الأشعة تحت الحمراء وطيف الأشعة فوق البنفسجية . أوضحت النتائج أن الليكاندات FBSCH وقواعد شيف تعمل بشكل ليكاندات ثنائية السن كيليتية ، وأن المعقدات الناتجة ذات شكل ثماني السطوح .

Introduction

Since d-orbitals of silicon tend to be rather diffused and of higher energy than its s- and p-orbitals , thus its complexes with donor ligands have silicon with coordination number higher than four seem to be somewhat rare [1] . Recent work shows that silicon can form complexes with penta , hexa and even hepta coordination numbers [2] .

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 [3] Semicarbazone complexes of some elements have been reported [4-6] .

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Schiff-bases represent a versatile series of ligands , the metal complexes of which have been widely studied [7-9] . Recently , there has been considerable interest in the study of mixed ligand complexes due to their important biological processes [10,11] .

Since mixed ligand complexes with silicon (IV) have not yet been introduced , the aim of the present work is , therefore , the preparation and characterization of new silicon (IV) complexes with mixed ligands 3-fluorobenzaldehyde semicarbazone (FBSCH) 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) : Figure 1 } .

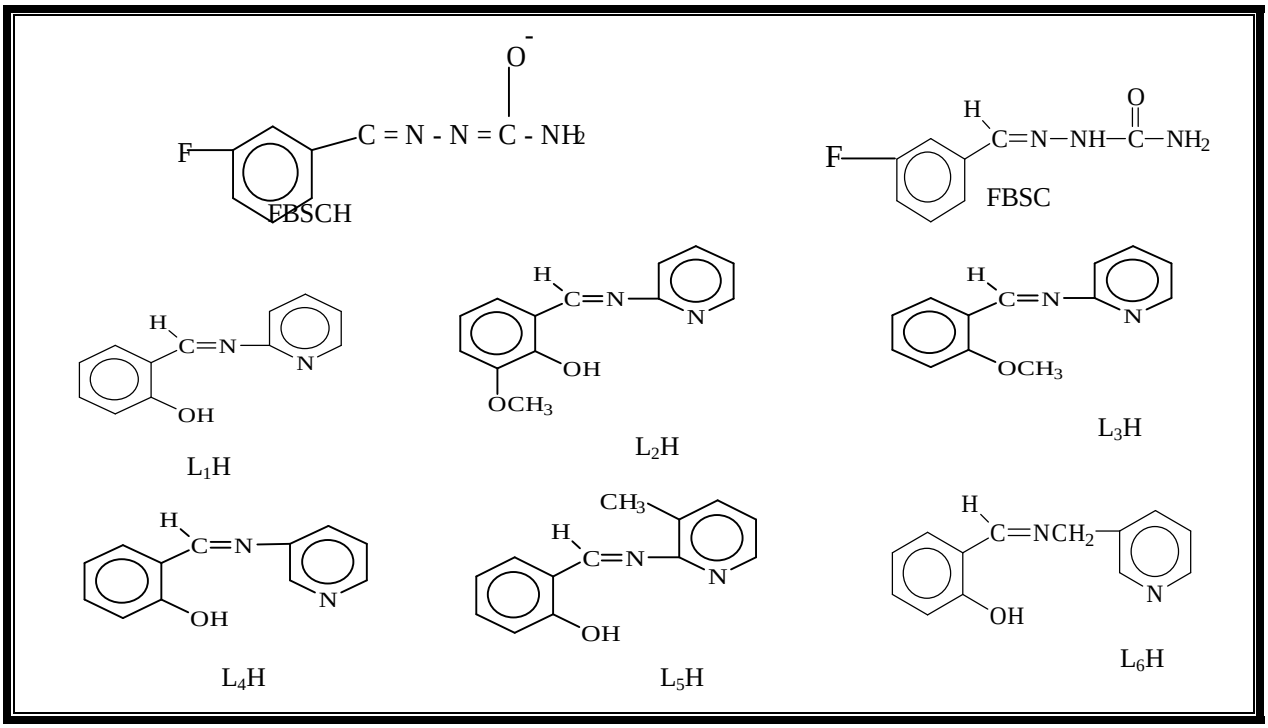

*Figure 1. **Model structures of the ligands***

Experimental

I- Preparation of the Ligands

3-Fluorobenzaldehyde semicarbazone has been prepared [4] by refluxing equimolar quantities of semicarbazide hydrochloride , 3-fluorobenzaldehyde and sodium acetate solutions for about one hour . The precipitated semicarbazone has been filtered off , washed with cold water and recrystallised from ethanol (m.p.=230 ^{0}C)

Schiff-base ligands have been prepared [7] 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 L_1H = 67-67.8 , L_2H = 96-98 , L_3H = 136 -140 , L_4H = 68 , L_5H = 87-89 , L_6H = 50-54 ^{0}C).

II-Preparation of the Complexes :

A-Neutral Medium

Complexes of the type $[Si(FBSCH)_2(LH)]Cl_4$ have been prepared by the reaction of $SiCl_4$ with ethanolic solutions of 3-fluorobenzaldehyde semicarbazone and Schiff-bases ligands in 1:2:1 molar ratio using (7.5-10 ml.) .The mixtures have been refluxed for 3 hrs. , evaporated to about half their volumes and cooled in ice-bath . The resulting products have been filtered off , washed with cold ethanol and dried .

B-Basic medium

Complexes of the type $[Si(FBSC)_2(L_3H)]Cl_2$ or $[Si(FBSC)_2(L)]Cl$ have been prepared by the reaction of $SiCl_4$ with 3-fluorobenzaldehyde semicarbazone and Schiff-bases in 1:2:1 molar ratio . Ethanolic sodium hydroxide solution has been added to the mixtures until pH ~9-9.3 .The products have been filtered off , washed with cold ethanol and dried .

III-Analytical and Physical Measurements

Elemental analysis for the resulted complexes have been carried out on a CHN Analyzer type 1106 (Carlo-Erba) at Department of Chemistry , College of Science , 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 room temperature . Infrared spectra have been recorded on Pye-Unicam 1100 spectrophotometer in the 400-4000 cm^{-1} range as KBr discs . Electronic spectra have been recorded on Shimadzu UV-Visible spectrophotometer , UV 160 for 10^{-4} M solutions of the ligands and their complexes in ethanol at 25 ^{0}C using a 1 cm cell .

Results and Discussion

The reaction of $SiCl_4$ with 3-fluorobenzaldehyde semicarbazone and Schiff–bases in both neutral and basic medium may be represented by the following reactions :

$$SiCl_4 + 2FBSCH + LH \rightarrow [Si(FBSCH)_2 (LH)]Cl_4$$
(I) neutral medium

$$SiCl_4 + 2FBSCH + L_nH + 2NaOH \rightarrow [Si(FBSC)_2(L_nH)]Cl_2 + 2NaCl + 2H_2O$$
(II) basic medium

$$SiCl_4 + 2FBSCH + LH + 3NaOH \longrightarrow [Si(FBSC)_2(L)]Cl + 3NaCl + 3H_2O$$
(III) basic medium

(where LH = L_1H , L_2H , L_3H , L_4H , L_5H , L_6H ; L_nH = L_2H , L_3H ; L = L_1 , L_4 , L_5 , L_6)

The resulting complexes are solids , moderately soluble in methanol , soluble in ethanol and dimethylformamide . The elemental analysis reveals that the complexes have the composition I , II and III in neutral and basic medium , respectively . Ionic nature of the complexes is confirmed by the conductance studies in ethanol medium . The values of the molar conductivities for the complexes prepared in neutral medium are closer to the range reported for 1:4 electrolytes in ethanol solution , whereas the molar conductivities of the complexes prepared in basic medium are closer to the range reported for 1:2 and 1:1 electrolytes in ethanol solution [12], respectively , (Table 1) .

The infrared spectra of semicarbazone ligand (Figure 2) shows a strong band at about 1680 cm^{-1} which was attributed to the C=O group [4,13] . 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 [4,13]. Meanwhile , in basic medium , this band disappears in the complexes and a new band is observed at 1350 cm^{-1} due to C-O group , thereby establishing coordination of the ligand through the enolic oxygen atom [13,14]. The next strong band at 1580 cm^{-1} which is attributed to $\upsilon_{C=N}$ [5,15] shifted towards a lower frequency on coordination [5,13-15] which was due to the decrease of the bond order as a result of metal nitrogen bond formation [5] . The position of the ligand bands in the range 3400-3500 cm^{-1} remains unaltered in the complexes indicating that there is no coordination through the NH group [4,5].

The spectra of Schiff-bases (Figure 2) show a strong band in the region 1630-1644 cm^{-1} is due to C=N stretching vibration [7] . This band shifts towards a lower frequency , which demonstrate that the imine nitrogen is coordinated to the metal ion [7] . The next other band in the region 1576-1587 cm^{-1} is due to $\upsilon_{C=N}$ remained unaltered upon coordination [7] . Moreover the shift in the C-O (phenolic , methoxy) vibration band on complexation supports the coordination of phenolic and methoxy groups to the metal ion [7,16] .

The spectra of all the complexes show new bands around 520-580 ,725-735 cm^{-1} due to υ_{Si-N} and υ_{Si-O} , respectively .The presence of these bands strongly supports the coordination of the ligands under investigation with the metal ion (Figure 2) [4,7,14] .

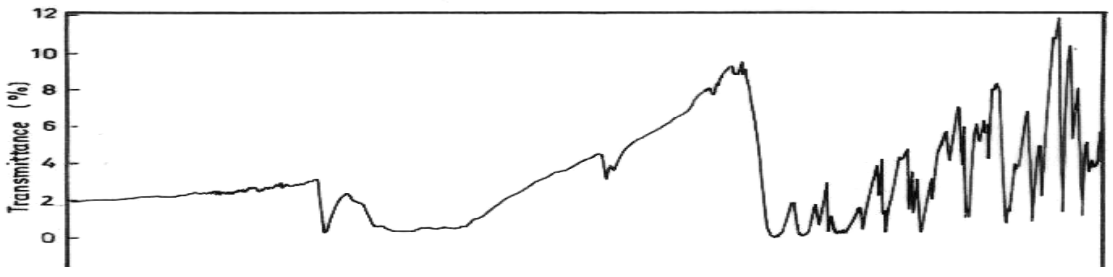

Figure 2 . Infrared spectra of : A = the ligand FBSCH ; B = the ligand L_6H ;
C= the complex $[Si(FBSC)_2(L_6)]Cl$

The electronic spectra (Figure 3) of the ligands and their complexes in ethanolic solutions have been recorded . The maximum is at about 228-235 and 320-360 nm which are due to the electronic transition π - π^* in the aryl ring , π– π^* and n – π^* in C=N group , respectively [4,14,17] . On complexation , a blue shift (305-310 cm^{-1}) was observed due to the polarization in the C=N bond caused by the metal-ligand electron interaction during the chelation [7,17] .

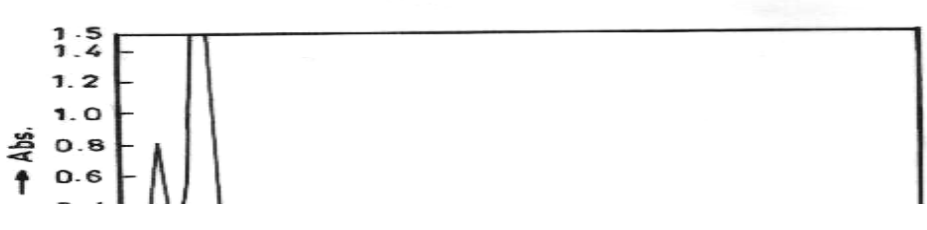

Figure 3 . Electronic spectra of : A = the ligand FBSCH ; B = the ligand L_6H ; C= the complex $[Si(FBSC)_2(L_6)]Cl$

From all the previous study , the proposed geometry of the complexes is shown in Figure 4 .

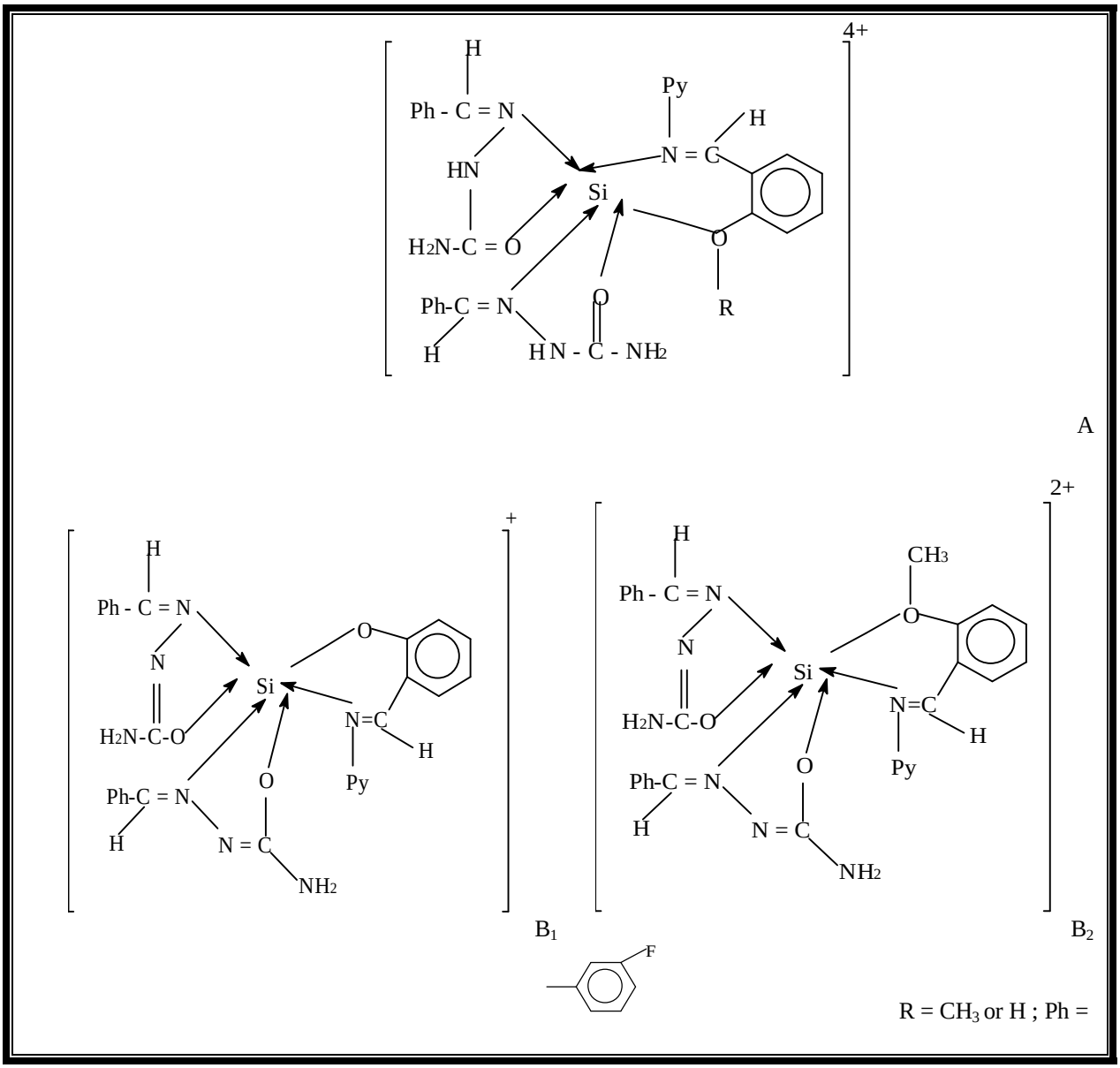

Figure 4 . Model structures of the complexes : A = complexes in neutral medium ; B_1 and B_2 = complexes in basic medium

Table 1 :Analytical data & physical properties of the complexes

No.	Compounds	Colours	M. P. or d.* ^0C	Λ_M **	% Analysis (Calc. /Obs.) C	N	H
1	$[Si(FBSCH)_2(L_1H)]Cl_4$	Grey	246 d	142	46.04 45.79	3.58 3.49	15.34 15.24
2	$[Si(FBSCH)_2(L_2H)]Cl_4$	Brown	Not melt or d.	149	43.53 43.24	3.47 3.38	12.08 11.95
3	$[Si(FBSCH)_2(L_3H)]Cl_4$	Brown	249 d	155	46.78 46.48	5.79 5.68	15.05 14.95
4	$[Si(FBSCH)_2(L_4H)]Cl_4$	Yellow	198 –200	149	46.04 45.66	3.58 3.46	15.34 15.21
5	$[Si(FBSCH)_2(L_5H)]Cl_4$	Green	220 d	149	46.78 46.39	5.79 5.42	15.05 14.85
6	$[Si(FBSCH)_2(L_6H)]Cl_4$	Pale brown	270 d	158	46.78 46.29	5.79 5.66	15.05 14.92
7	$[Si(FBSC)_2(L_1)Cl$	Grey	Not melt or d.	40	54.14 53.86	3.73 3.62	18.04 17.79
8	$[Si(FBSC)_2(L_2H)]Cl_2$	Brown	195 – 197d	78	49.80 48.33	3.58 4.02	13.83 14.11
9	$[Si(FBSC)_2(L_3H)]Cl_2$	White	Not melt or d.	93	51.56 50.98	3.90 4.01	16.68 16.39
10	$[Si(FBSC)_2(L_4)]Cl$	White	Not melt or d.	37	54.14 53.67	3.73 3.87	18.04 17.79
11	$[Si(FBSC)_2(L_5)]Cl$	White	Not melt or d.	43	54.84 54.66	3.96 4.03	17.64 17.55
12	$[Si(FBSC)_2(L_6)]Cl$	White	Not melt or d.	45	54.84 4.45	3.96 4.04	17.64 17.48

* d= decomposition point ; **Λ_M = Molar conductivity in $ohm^{-1} cm^2 mol^{-1}$

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

*Correspond to compounds in Table 1

Comp. *	υC=N (semi)	υNH (semi)	υC=O (semi)	$\upsilon$$NH_2$ (semi)	υC-O (semi)	υC=N (Py)	υC=N (S.B)	υC-O & OH	υSi-O	υSi-N
FBSCH & L_1 H	1580	3400	1675	1450		1575	1630	1280 3100		
1	1540	3400	1655	1450		1575	1600	1320 3000	730 650	530, 580
7	1540	3400		1450	1330	1575	1600	1320	730 655	530, 580
FBSCH & L_2 H	1580	3400	1675	1450		1575	1635	1280 3100		
2	1535	3400	1655	1450		1573	1600	1320 2900	730 650	520, 580
8	1535	3400		1450	1330	1573	1600	1320	730 655	520, 580
FBSCH & L_3 H	1580	3400	1675	1450		1575	1630	1280 3100		
3	1540	3400	1655	1450		1574	1604	1320 2900	750 650	520, 570
9	1540	3400		1450	1330	1574	1604	1320	750 655	520, 570
FBSCH & L_4 H	1580	3400	1675	1450		1587	1640	1280 3100		
4	1540	3400	1650	1450		1585	1600	1325 2850	735 600	530, 570
10	1540	3400		1450	1325	1585	1600	1325	735 605	530, 570
FBSCH & L_5 H	1580	3400	1675	1450		1575	1630	1280 3100		
5	1535	3400	1650	1450		1575	1595	1320 2995	750 600	530, 580
11	1535	3400		1450	1330	1575	1595	1320	750 610	530, 580
FBSCH & L_6 H	1580	3400	1675	1450		1587	1630	1280 3100		
6	1535	3400	1655	1450		1585	1595	1320 2995	730 600	520, 580
12	1540	3400		1450	1300	1585	1595	1320	730 610	520, 580

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