

PREPARATION AND CHARACTERIZATION OF SOME SILICON (IV) COMPLEXES

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Résumé

Des complexes de silicium (IV) complexes contenant un mélange de ligands: Schiff-bases (AH) {dérive par la 2- or 3-amino= pyridine sur le 2-hydroxy- or 3-methoxy or 2-hydroxy-3-methoxy-benzaldehyde} et les benzaldehyde semicarbazone (BSCH), ont été préparés, puis caractérisés par différentes méthodes: analyse élémentaire, conductance molaire, spectroscopies infra-rouge et électronique. Des complexes de type $[\text{Si}(\text{BSCH})_2(\text{AH})]\text{Cl}_4$, $[\text{Si}(\text{BSC})_2(\text{A}_n\text{H})]\text{Cl}_2$ et $[\text{Si}(\text{BSC})_2(\text{A})]\text{Cl}$ (ou $n=2$ or 3 , A=deprotonated Schiff-base ligands, BSC=deprotonated semicarbazone ligand) sont proposés dans des solutions respectivement neutre et basique.

Mots clés: Mélange de ligands, benzaldehyde semicarbazone, Schiff-bases, silicium.

Abstract

Silicon(IV) complexes containing mixed ligands: Schiff-bases (AH) {derived from 2- or 3-amino-pyridine with 2-hydroxy- or 3-methoxy- or 2-hydroxy-3-methoxy-benzaldehyde} and benzaldehyde semicarbazone (BSCH), have been prepared. The resulted complexes have been characterized by elemental analysis, molar conductance values, infrared and electronic spectral data. Complexes of the type $[\text{Si}(\text{BSCH})_2(\text{AH})]\text{Cl}_4$, $[\text{Si}(\text{BSC})_2(\text{A}_n\text{H})]\text{Cl}_2$ and $[\text{Si}(\text{BSC})_2(\text{A})]\text{Cl}$ (where $n=2$ or 3 , A=deprotonated Schiff-base ligands, BSC= deprotonated semicarbazone) have been proposed in neutral and basic medium, respectively.

Key words: Mixed ligands, benzaldehyde semicarbazone, Schiff-bases, silicium.

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ملخص

تمّ تحضير معقدات السليكون (IV) الحاوية على مزيج من الليكاندات: قواعد شيف (مشتقة من 2- أو 3-أمينو-بيريدين مع 2-هيدروكسي أو 3-هيدروكسي أو 2-هيدروكسي-3-ميثوكسي-بنزالدهيد) و بنزالدهيد سميكاربازون (BSCH). شخّصت المعقدات الناتجة بالتحليل الدقيق للعناصر و قيم التوصيلية المولارية و أطيف الأشعة تحت الحمراء والالكترونية. اقترحت الصيغ $[\text{Si}(\text{BSCH})_2(\text{AH})]\text{Cl}_4$ و $[\text{Si}(\text{BSC})_2(\text{A}_n\text{H})]\text{Cl}_2$ و $[\text{Si}(\text{BSC})_2(\text{A})]\text{Cl}$ (حيث $n=2$ أو 3 و A = ليكاندات قواعد شيف مزال منها بروتون و BSC = بنزالدهيد سميكاربازون مزال منه بروتون) في الوسط المتعادل والقاعدي على التوالي.

الكلمات المفتاحية: مزيج من الليكاندات، بنزالدهيد سميكاربازون، قواعد شيف، سليكون.

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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 having silicon with coordination number higher than four seems to be somewhat rare[1]. Recent works show that silicon can form complexes with penta, hexa and even hepta coordination number- s[2]. Schiff-bases represent a versatile series of ligands, the metal complexes of which have been widely studied[3-7]. Semicarbazone complexes of some metal ions have been reported[8-12]. There has been considerable interest, recently, in the study of mixed ligands complexes of transition and non-transition metal ions due to their important role in biological processes [13-21].

In the present work, new silicon(IV) complexes with mixed ligands benzaldehyde semicarbazone (BSCH) and Schiff-bases (AH) {2-pyridinosalicylidene (A₁H), 2-pyridino-3-methoxysalicylidene (A₂H), 2-pyridino-2-methoxybenzilidene (A₃H), 3-pyridinosalicylidene (A₄H), 3-methyl-2-pyridinosalicylidene (A₅H), 3-iminopyridinosalicylidene (A₆H): Figure-1} have been synthesized and characterized physicochemically.

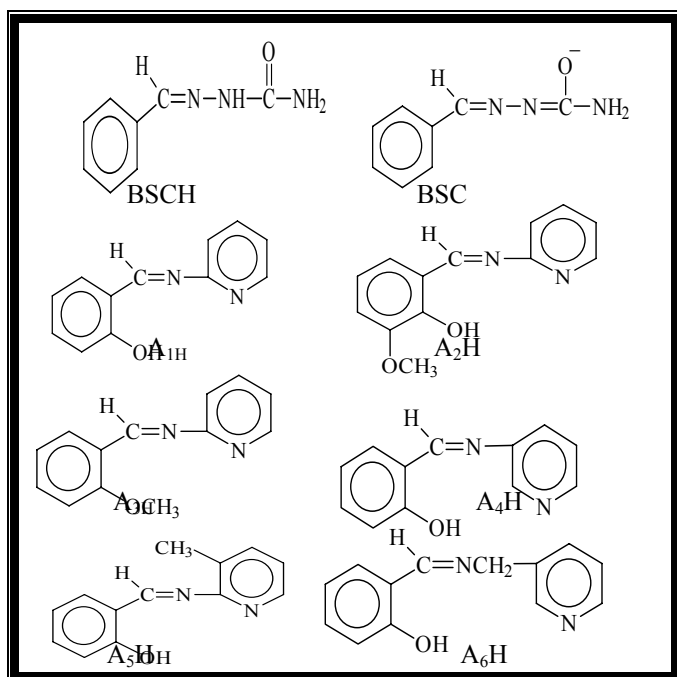


Figure 1: Structures of the ligands

EXPERIMENTAL

I-MATERIALS:

The following reagents have been used as supplied: salicylaldehyde, substituted salicylaldehyde, aminopyridine, substituted aminopyridine, benzaldehyde, semicarbazide hydrochloride have been supplied by Hopkin and Williams LTD and Fluka AG-Switzerland.

II-ANALYTICAL AND PHYSICAL MEASUREMENTS:

Elemental analysis for the resulted complexes have been carried out on a CHN Analyzer type 1106(Carlo-Erba) at Chemistry 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 room temperature. Infrared spectra have been recorded on Pye-Unicam 1100 spectrophotometer in the 400-4000 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.

III- PREPARATION OF THE LIGANDS :

Benzaldehyde semicarbazone has been prepared according to the literature method [10] by refluxing equimolar quantities of semicarbazide hydrochloride, benzaldehyde and sodium acetate solution for about one hour. The semicarbazone thus formed has been filtered off from its cold solution, washed with cold water and recrystallised from ethanol (m.p.=200 °C).

Schiff-base ligands have been prepared according to the literature methods [6,7] by refluxing equimolar quantities of 2- or 3-aminopyridine and the appropriate aldehyde for about one hour. The Schiff-bases thus formed have been filtered off from their cold solutions, washed with distilled water and crystallized from hot methanol (m.p. of L₁H=67-67.8, L₂H=96-98, L₃H=136-140, L₄H=68, L₅H=87-89, L₆H=50-54 °C).

IV-PREPARATION OF SILICON COMPLEXES :

A-Neutral medium-

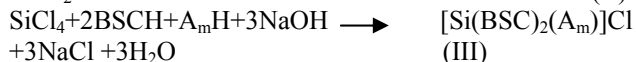
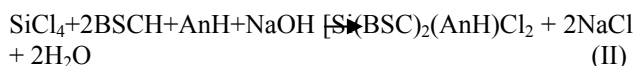
Complexes of the type $[\text{Si}(\text{BSCH})_2(\text{AH})]\text{Cl}_4$ have been prepared by the reaction of silicon(IV) chloride with ethanolic solutions of benzaldehyde semicarbazone and Schiff-bases ligands in 1:2:1 molar ratio using (7.5-10 ml). The mixtures have been refluxed for 3 hr., evaporated to about half their volumes and cooled. The resulting products have been filtered off, washed with cold ethanol and dried .

B-Basic medium-

Complexes of the type $[\text{Si}(\text{BSC})_2(\text{A}_n\text{H})]\text{Cl}_2$ or $[\text{Si}(\text{BSC})_2(\text{A})]\text{Cl}$ have been prepared by the reaction of silicon(IV) chloride with benzaldehyde semicarbazone and Schiff-bases in 1:2:1 molar ratio. Ethanolic sodium hydroxide solution has been added to the mixtures until pH ~9.0-9.3. The products have been filtered off, washed with cold ethanol and dried .

RESULT AND DISCUSSION

The reaction of silicon(IV) chloride with benzaldehyde semicarbazone and Schiff-bases in 1:2:1 molar ratio in both neutral and basic medium may be represented by the following reactions :



(where $\text{AH}=\text{A}_1\text{H} - \text{A}_6\text{H}$, $\text{A}_n\text{H}=\text{A}_2\text{H}$ or A_3H , $\text{A}_m\text{H}=\text{A}_1\text{H}$, A_4H , A_5H , A_6H)

The resulted complexes are solids, soluble in ethanol, dimethylformamide and dimethylsulphoxide. The elemental composition of the complexes are clearly assigned to 1:2:1 molar ratio of silicon(IV) chloride: benzaldehyde semicarbazone: Schiff-base in neutral and basic medium, respectively (Table 1). The values of the molar conductivities approach those expected for 1:4, 1:2 and 1:1 electrolytes[22] for complexes of type I, II and III, respectively .

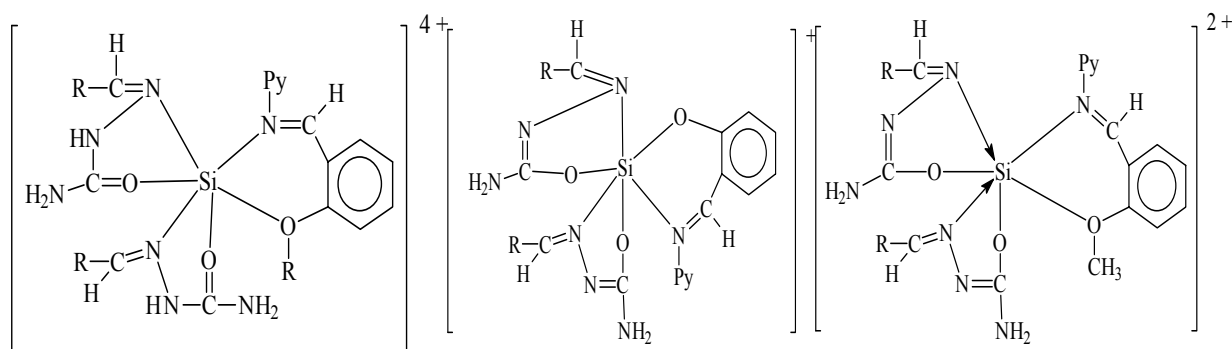


Figure 2 Proposed structures of the complexes

No.	Compounds	Colours	M. P. °C	\wedge_M	% Analysis (Calc. /Obs.)		
					C	H	N
1	[Si(BSCH) ₂ (A ₁ H)]Cl ₄	Yellow	Not melt	150	48.42	4.06	16.13
					47.96	3.95	16.07
2	[Si(BSCH) ₂ (A ₂ H)]Cl ₄	Brown	172	139	44.93	3.77	12.47
					44.69	3.65	12.30
3	[Si(BSCH) ₂ (A ₃ H)]Cl ₄	Brown	283 d	165	49.16	4.26	15.81
					48.69	4.08	15.62
4	[Si(BSCH) ₂ (A ₄ H)]Cl ₄	Pale yellow	Not melt	145	48.42	4.06	16.13
					47.96	3.95	16.07
5	[Si(BSCH) ₂ (A ₅ H)]Cl ₄	Pale green	223-225	148	49.16	4.26	15.81
					48.69	4.09	15.55
6	[Si(BSCH) ₂ (A ₆ H)]Cl ₄	Brown	Not melt	160	49.16	4.26	15.81
					48.69	4.08	15.62
7	[Si(BSC) ₂ (A ₁)Cl	White	Not melt	46	57.47	4.30	19.15
					56.97	4.22	19.04
8	[Si(BSC) ₂ (A ₂)]Cl ₂	Brown	Not melt	65	51.64	3.92	14.33
					51.32	4.03	14.21
9	[Si(BSC) ₂ (A ₃)]Cl ₂	White	Not melt	78	54.80	4.44	17.65
					54.62	4.33	17.55
10	[Si(BSC) ₂ (A ₄)]Cl	White	Not melt	37	57.47	4.30	19.15
					56.97	4.22	19.04
11	[Si(BSC) ₂ (A ₅)]Cl	White	Not melt	38	58.13	4.54	18.70
					57.68	4.42	18.55
12	[Si(BSC) ₂ (A ₆)]Cl	White	Not melt	49	58.13	4.54	18.70
					57.88	4.41	18.58

Table 1: Analytical data & physical properties of the complexes
 \wedge_M = Molar conductivities in $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, d= decomposition point .

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Comp.*	ν C=N (semi)	δ NH (semi)	ν C=O (semi)	ν NH ₂ (semi)	ν C-O (semi)	ν C=N (Py)	ν C=N (S.B)	ν C-O & OH	ν Si- O	ν Si- N
BSCH & A ₁ H	1580	3500	1675	1450	-	1576	1630	1280, 3100	-	-
1	1540	3500	1650	1450	-	1575	1590	1300, 2700	755 655	520 580
7	1540	3500	-	1450	1350	1575	1595	1300	750 675	530 580
BSCH & A ₂ H	1580	3500	1675	1450	-	1576	1630	1250, 3100	-	-
2	1540	3500	1650	1450	-	1575	1590	1300, 2700	730 680	520 580
8	1540	3500	-	1450	1350	1575	1595	1300	730 675	530 570
BSCH & A ₃ H	1580	3500	1675	1450	-	1576	1630	-	-	-
3	1540	3500	1650	1450	-	1575	1595	-	740 690	525 570
9	1540	3500	-	1450	1350	1575	1590	-	740 685	530 575
BSCH & A ₄ H	1580	3500	1675	1450	-	1587	1645	1280, 3100	-	-
4	1540	3500	1650	1450	-	1585	1600	1300, 2700	735 620	535 580
10	1540	3500	-	1450	1350	1585	1600	1300	735 635	530 580
BSCH & A ₅ H	1580	3500	1675	1450	-	1576	1630	1280, 3100	-	-
5	1540	3500	1650	1450	-	1575	1590	1300, 2700	735 660	530 575
11	1540	3500	-	1450	1350	1575	1590	1300	735 660	530 575
BSCH & A ₆ H	1580	3500	1675	1450	-	1587	1632	1280, 3100	-	-
6	1540	3500	1650	1450	-	1585	1600	1300, 2700	740 640	525 575
12	1540	3500	-	1450	1350	1585	1600	1300	745 650	525 580

Table 2: IR spectra of the ligands & their complexes (frequencies expressed in cm⁻¹)

* Correspond to compounds in table -1

The position of the ligand in the range 3300-3500 cm^{-1} remained unaltered in the complexes indicating that there was no coordination through the NH group[9].

The infrared spectra of Schiff-bases showed a strong band in the region 1630-1645 cm^{-1} as due to C=N stretching vibration [4]. This band shifted towards a lower frequency (Table 2), which demonstrated that the imine nitrogen was coordinated to the metal ion[4]. The next band in the region 1576-1587 cm^{-1} as due to C=N group remained unaltered upon coordination[4]. Moreover the shift in the C-O (phenolic, methoxy) vibration band on complexation supported the coordination of phenolic and methoxy groups to the metal ion[3,6].

The spectra of all silicon complexes showed new bands around 520-580, 630-655 cm^{-1} due to $\nu_{\text{Si-N}}$ and $\nu_{\text{Si-O}}$, respectively. The presence of these bands supported the coordination of the ligands under investigation with the metal ion[7,23].

The electronic spectra of the ligands and their complexes in ethanolic solutions (10^{-4}M) have been recorded. The maximum at about 228-233, 262-280 and 320-355 nm which were due to the electronic transitions $\pi-\pi^*$ in the aryl ring, $\pi-\pi^*$ and $n-\pi^*$ in C=N group respectively[7]. 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, 24].

CONCLUSION

This work in fact is a continuation of our studies including mixed ligand complexes. In this work some observations have been achieved that lead to establish the following points:

- 1- Benzaldehyde semicarbazone acts as bidentate chelating ligand, joint to silicon(IV) ion through nitrogen and oxygen atoms.
- 2- Schiff-bases act as bidentate chelating ligands, joint to the metal ion through nitrogen and oxygen atoms.
- 3- Silicon(IV) ion is probably hexacoordinated having octahedral geometry (Fig. 2).
- 4- Mononuclear complexes have been proposed[21,22] for all the resulted complexes

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