

## NEW COMPLEXES OF SILICON

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### الخلاصة

يتفاعل كل من قواعد شيف (L) (المحضرة من الساليسالديهايد المعوض وغير المعوض و 2-أمينو بيريدين و 2-أمينو-3-مثيل بيريدين) والبايرول-2-حامض كاربوكسيل (PCA) مع رباعي كلوريد السليكون ( $\text{SiCl}_4$ ) بنسبة 1:2:1 على التوالي لاعطاء معقدات ذات الصيغة العامة  $[\text{Si}(\text{L}-\text{H})(\text{X}-\text{H})_2]\text{Cl}$  في الوسط المتعادل والصيغة  $[\text{SiLX}_2]\text{Cl}_4$  في الوسط القاعدي (حيث أن L: قواعد شيف و PCA:X) والتي تم تشخيصها بالطرق الفيزيائية والطيفية.

وجد أن قواعد شيف تتناسق مع السليكون كليكاندات ثنائية السن عن طريق ذرة نتروجين الايمين وذرة اوكسجين الهيدروكسيل المعوضة في الموقع 2-من حلقة البنزين، ويتناسق PCA مع السليكون أيضاً كليكاند ثنائي السن عن طريق ذرة نتروجين الباييرول ومجموعة الكاربوكسيل المعوضة في الموقع 2-من نفس الحلقة لاعطاء معقدات يكون فيها السليكون سداسي التناسق. أظهرت محاليل المعقدات أنها موصلة للكهربائية في الكحول الايثيلي مشيرة بذلك إلى امتلاكها التركيب  $[\text{Si}(\text{L}-\text{H})(\text{X}-\text{H})_2]\text{Cl}$  في الوسط المتعادل والتركيب  $[\text{SiLX}_2]\text{Cl}$  في الوسط القاعدي، وقد تم توضيح ومناقشة النتائج التي تم الحصول عليها.

### ABSTRACT

Schiff-base ligands (L), prepared from substituted and non-substituted salicylaldehyde and 2-aminopyridine or 2-amino-3-methyl pyridine, and pyrrol-2-carboxylic acid (PCA or X), have been reacted with tetrachlorosilicon in 1:2:1 molar ratio respectively to give complexes of the general formula  $[\text{Si}(\text{L}-\text{H})(\text{X}-\text{H})_2]\text{Cl}$  in neutral medium and  $[\text{SiLX}_2]\text{Cl}_4$  in basic medium. The complexes obtained were characterized physicochemically and spectroscopically.

The Schiff-base seems to coordinate with silicon atom in a bidentate fashion via the most reactive bonding sites; the central imine (azomethine)-nitrogen and phenolic oxygen atom. (PCA) coordinate with silicon also as a bidentate ligand via pyrrol nitrogen atom and carboxylic oxygen atoms to give complexes with silicon of hexa-coordination number. All the complexes produced showed conductive species, in ethanol indicating the ionic structure  $[\text{SiLX}_2]\text{Cl}_4$  in neutral medium and  $[\text{SiLX}_2]\text{Cl}$  in basic medium.

### INTRODUCTION

The last years has been renewed interest in the coordination compounds formed by treating various organic ligands with silicon (1-4). This is mainly due to the interest in the structure and the reactivity of these materials towards different ligands. Few studies have been made of the complexing by pyrrol ligands with silicon (5-10). The chelates silicon forms with these ligands are of interest as compounds in which the silicon attains its highest coordination number of six. As continuation of our study in this field (11), the present study concern the preparation and the structural study concerning the bonding between the functional groups of the ligands and the silicon ion.

### EXPERIMENTAL

#### General

IR spectra were recorded on Pye-Unicam SP2000 spectrophotometer in the range  $200\text{-}4000\text{cm}^{-1}$  using KBr disk techniques. Elemental analyses, of the complexes were carried out on a CHN analyser 1106 (Carlo Erba).

Electronic spectra were recorded on a Shimadzu UV/Vis spectrophotometer UV-160 for  $10^{-3}\text{M}$  solutions of the complexes in ethanol at  $25^\circ\text{C}$ , using a 1cm quartz cell.

Conductivity measurements were made on  $10^{-3}\text{M}$  solutions of the complexes in ethanol and DMF at ambient temperature  $25^\circ\text{C}$  using a conductivity meter, model 4070 (Jenway).

#### Preparation of Compounds:

##### Starting materials:

$\text{SiCl}_4$  was commercial products (Fluka) and used as supplied. Pyrrol-2-carboxylic acid (Fluka) was dried on vacuum at room temperature. The Schiff-bases ( $\text{L}_{a-c}$ ) were prepared in our laboratories (12), by refluxing equimolar quantities of 2-aminopyridine or 2-amino-3-methylpyridine and the appropriate salicylaldehyde for 1h. The Schiff-base thus formed was filtered off from its cold solution and recrystallized from hot methanol.

### Preparation of Complexes

All the complexes were carried out with the molar ratio 1:1:2 of  $\text{SiCl}_4$ :Schiff-base:PCA respectively.

#### a. Complexes formed in neutral medium:

(1mmol) of Schiff-base and (2mmol) of PCA were dissolved in absolute methanol then (1mmol) of  $\text{SiCl}_4$  was added, the clear reaction mixture was refluxed for one hour, the precipitated product was filtered off, washed with methanol and recrystallised from hot methanol.

#### b. Complexes formed in basic medium:

Schiff-base and PCA were dissolved in absolute methanol then  $\text{SiCl}_4$  was added (in the same no. of mmol as in a), to this clear reaction mixture, a methanol solution of NaOH was added until complete and fast precipitation of coloured product was observed at pH=8. The mixture was refluxed for one hour, the solid product was filtered, washed with methanol and recrystallised from hot methanol.

## RESULTS AND DISCUSSION

The physical properties of new silicon (IV) complexes are listed in Table 1. Their elemental compositions are clearly assigned to 1:1:2 molar ratio of  $\text{SiCl}_4$ :Schiff-base:PCA in both neutral and basic media. The molar conductance measurement in  $10^{-3}\text{M}$  EtOH solution showed 1:4 conductances in neutral medium and 1:1 conductive species in basic medium, indicating the electrolytic nature for all complexes.

A careful looking to Scheme 1, one can deduce that it is possible for the silicon to coordinate regioselectively with Schiff-bases ( $L_{a-c}$ ) via both nitrogen atoms (the azamethine nitrogen and the pyridine one) to give four member chelate ring or most possibly via the azamethine nitrogen and the oxygen atom of the phenolic group, to give six member chelate ring, which is the favourable structure from steric point of view. However these observation were demonstrated by the routine IR spectral measurements, which related that complexation had taken place via  $\text{N} \rightarrow \text{Si}$  and  $\text{O} \rightarrow \text{Si}$  linkage and this is clear from  $\nu(\text{Si-N})$  and  $\nu(\text{Si-O})$ , which appeared as a new bands in the region  $(515-545) \text{ cm}^{-1}$  (4) and  $(715-745) \text{ cm}^{-1}$  (4, 11) (Table 1) respectively. The coordinated nitrogen being of the imine rather than of the pyridine one and this is clear from the increase in the  $\nu(\text{C}=\text{N}_{\text{im}})$  value on going from the free ligand to its complex, whereas the  $\nu(\text{C}=\text{N}_{\text{py}})$  value remains almost constant, that is a good indication for N-imine bonding (13, 14, 16). Further more, the IR spectra of the complexes showed new band at  $(635-655) \text{ cm}^{-1}$  which attributed to  $\nu(\text{Si-Cl})$  (2).

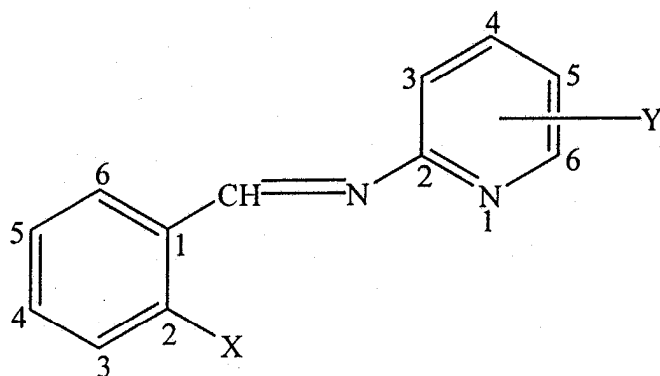
Free ligand PCA show band in the region (3380-3300)  $\text{cm}^{-1}$  which is attributed to the intermolecular hydrogen bonded NH stretch (10), this band is shifted to lower region on complexation, indicating to the formation of bonding between the pyrrolic nitrogen and the silicon (6, 10) in all complexes, moreover the bands of  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{sy}}(\text{COO}^-)$  for free ligand which appeared at (1685)  $\text{cm}^{-1}$  and (1335)  $\text{cm}^{-1}$  respectively observed at (1580-1595)  $\text{cm}^{-1}$  and (1400-1435)  $\text{cm}^{-1}$  in complexes (10, 17) with differences of (90-105)  $\text{cm}^{-1}$  and (65-100)  $\text{cm}^{-1}$  respectively, this indicates that the carboxylate group act as monodentate group (10) (Scheme 2) in all complexes. Infrared absorption spectra for both phenolic OH (of Schiff-bases ( $L_{\text{a-c}}$ )) (3135-3456)  $\text{cm}^{-1}$  and carboxylic OH (of PCA (2820)  $\text{cm}^{-1}$ ) are shifted in complexes [1-3] (complexes of neutral medium) (Scheme 2) to lower values indicating coordination through these two groups without deprotonation (6, 16, 18), while disappear in basic medium due deprotonation in complexes [4-6] (complexes of basic medium).

UV-Vis spectral data for all complexes (Table 1) showed absorption bands attributed to Schiff-base and PCA in its complexes (4, 16), these absorption bands appeared in the region 245-256nm, 260-300nm and 308-335nm which are attributed to  $\pi \longrightarrow \pi^*$  electronic transition in the aryl ring of the Schiff-base,  $\pi \longrightarrow \pi^*$  electronic transition in both C=N group of Schiff-base and pyrrol-ring, and to  $n \longrightarrow \pi^*$  electronic transition in the C=N group too, respectively (4, 16).

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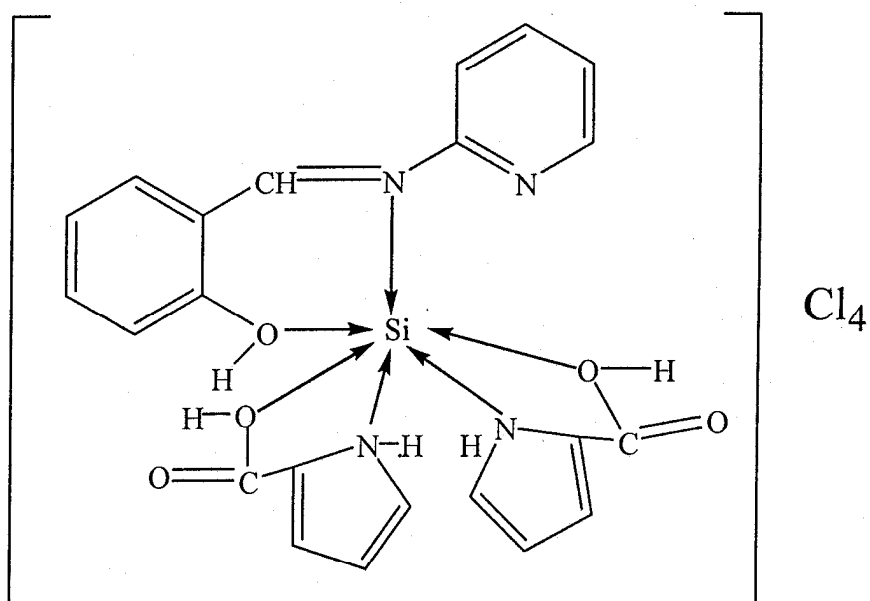
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**L**

- |                |                            |   |                     |
|----------------|----------------------------|---|---------------------|
| L <sub>a</sub> | X=2-OH                     | , | Y=H                 |
| L <sub>b</sub> | X=2-OH, 3-OCH <sub>3</sub> | , | Y=H                 |
| L <sub>c</sub> | X=2-OH                     | , | Y=3-CH <sub>3</sub> |

**Scheme 1: Schiff bases used in the coordination with SiCl<sub>4</sub>**



**Scheme 2: Model of silicon complexes in the neutral medium**

Table 1. Physical properties, analyses and spectra data of the complexes

Compl. No.	Comp.*	Colour	M.P. C°	Analysis found (Calc.)%			Selected IR bands (cm <sup>-1</sup> )							UV-Vis		Λ conductivity ohm <sup>-1</sup> .cm <sup>2</sup> .mol <sup>-1</sup>		
				C	H	N	ν(C=N <sub>im</sub> )	ν(C=N <sub>ip</sub> )	ν <sub>as</sub> (COO <sup>-</sup> )	ν <sub>s</sub> (COO <sup>-</sup> )	ν(Si-O)	ν(Si-N)	ν(Si-Cl)	λ <sub>max</sub> (nm)	EtOH			
	PCA																	
1	L <sub>a</sub>	Yellow																
	SiCl <sub>4</sub> L <sub>a</sub> .PCA	Dark pink	>300	44.55 (44.76)	3.34 (3.41)	9.35 (9.49)	1623 s. 1640 s.	1569 m. 1575 m.	1590 m.	1435 m.	725 s.	525 m	640 m	256	308	149		
2	L <sub>b</sub>	Yellow-orange																
	SiCl <sub>4</sub> L <sub>b</sub> .PCA	Pink	>300	44.22 (44.53)	3.44 (3.57)	8.95 (9.03)	1619 m. 1638 m	1575 m. 1570 m.	1585 m.	1400 s.	740 s.	545 s.	655 m	245	320	164		
3	L <sub>c</sub>	Yellow																
	SiCl <sub>4</sub> L <sub>c</sub> .PCA	Red	>300	45.22 (45.71)	3.71 (3.66)	9.08 (9.27)	1620 s. 1635 s.	1578 m. 1580 m.	1595 s.	1410 s.	715 s.	540 m	635 m	260	300	153		
4	SiCl <sub>4</sub> L <sub>a</sub> .PCA	Brown	239	50.44 (50.87)	4.00 (3.88)	10.64 (10.78)	1650 s.	1565 m.	1580 s.	1420 m.	725 s.	525 s.	640 m	249	310	34		
	SiCl <sub>4</sub> L <sub>b</sub> .PCA	Brown	287	49.96 (50.27)	3.97 (4.03)	10.04 (10.19)	1645 m.	1570 s.	1590 m.	1410 m.	735 m.	545 m	650 s	255	335	37		
6	SiCl <sub>4</sub> L <sub>c</sub> .PCA	Brown	296	51.33 (51.78)	51.78 (41.56)	10.22 (10.50)	1640 m.	1575 m.	1585 m.	1420 s.	745 m.	515 s.	640 m	260	318	50		

\* For Schiff-bases (L<sub>a-c</sub>) structures see Scheme 1.

\*\* For IR data s. strong; m, medium; w. weak