

Seven-coordinated Organosilicon(IV) Complexes with Schiff Bases

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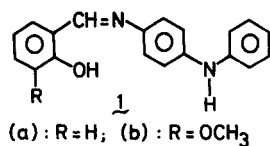
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Received 25 October 1984; revised 9 January 1985; accepted 30 January 1985

Organosilicon(IV) complexes with Schiff bases such as *N*-salicylidene-*p*-aminodiphenylamine and *o*-vanillidene-*p*-aminodiphenylamine have been prepared and characterized. The elemental analyses and IR and PMR data indicate that these are seven-coordinated complexes of silicon. These complexes behave as 1:1 electrolytes in DMF.

Six-coordinated complexes of organosilicon(IV) with *N*-salicylidene-aniline-4-sulphonamides were prepared and characterized by us in an earlier communication¹. Herein we report the preparation and characterization of seven-coordinated complexes of organosilicon(IV) with Schiff bases derived from *p*-aminodiphenylamine and salicylaldehyde and *o*-vanillin.

All the chemicals used were of reagent grade. The schiff bases, *N*-salicylidene-*p*-aminodiphenylamine (**1a**) and *o*-vanillidene-*p*-aminodiphenylamine (**1b**) were prepared by refluxing equimolar quantities of *p*-aminodiphenylamine and salicylaldehyde or *o*-vanillin in ethanol on a water-bath for 2 hr. The reaction mixture was cooled and the shining crystals of the schiff bases were collected and recrystallised from ethanol.



Complexes (I and II) with the ligands **1a** and **1b**, respectively were prepared by mixing the appropriate schiff base with dimethyldichlorosilane (DMDCS) in dry benzene in the molar ratio of 1 : 1. The mixture was stirred constantly and allowed to stand overnight. The complexes obtained were filtered, recrystallised from dry benzene and dried *in vacuo* over P₂O₅.

Complexes (I and II) are amorphous in nature, insoluble in common organic solvents but soluble in polar solvents such as DMF and DMSO. The elemental analyses (Table 1) confirms 1:2 (metal-

Table 1—Analytical and Physical Data of Complexes

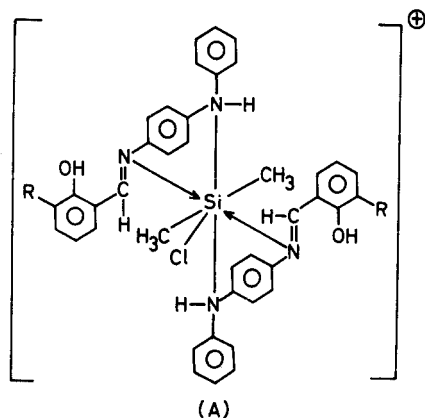
Mol. formula	Found (Calc), %			
	N	Cl	C	H
(C ₁₉ H ₁₅ ON ₂) ₂ - (CH ₃) ₂ SiCl ₂ (I)	7.94 (8.20)	10.07 (10.40)	68.08 (68.08)	5.38 (5.28)
(C ₂₀ H ₁₇ O ₂ N ₂) ₂ - (CH ₃) ₂ SiCl ₂ (II)	7.9 (7.33)	9.64 (9.28)	68.37 (65.88)	5.32 (5.48)

ligand) stoichiometry for the complexes. The molar conductivities of 10⁻³ M solutions of the complexes in DMF are 82.81 and 96.27 ohm⁻¹cm²mol⁻¹, indicating their 1:1 electrolytic behaviour in solution.

The characterization of the complexes (I and II) is based on the IR (in KBr matrix) and PMR (DMSO-*d*₆ solution; TMS internal standard) spectra of the complexes vis-a-vis those of the free ligands. In the IR spectra of ligands (**1a**, **b**), νN-H appeared as a medium intensity band in the region 3390-3400 cm⁻¹. This mode was shifted towards lower wavenumbers (3340-3350 cm⁻¹) in the spectra of the complexes suggesting coordination of the NH of *p*-aminodiphenylamine moiety to silicon atom². The bands in the region 2660-2650 cm⁻¹ in the free ligands assignable to H-bonded νOH remained unaffected in the spectra of the complexes, indicating non-participation of OH in coordination³⁻⁶. This was further supported by the appearance of phenolic νC-O in the ligands and the complexes around 1265 cm⁻¹. The νC=N of the free ligand appearing around 1590 cm⁻¹ underwent shift to higher wavenumbers in the complexes (~1625 cm⁻¹) suggesting coordination of azomethine nitrogen to silicon. Appearance of νC=N in the lower frequency region is due to extended conjugation involving aromatic ring⁷. In analogy with literature reports⁸ a shoulder at 1390-1410 cm⁻¹ has been assigned to the CH deformation of the Si-C-H linkage. Similarly, the bands at 850, 700 and 520-530 cm⁻¹ have been attributed to ν(Si-CH₃), ν(Si-N) and ν(Si-Cl) vibrations⁹⁻¹¹.

The PMR spectra of the ligands exhibited a sharp signal at δ 13.3 due to H-bonded (intramolecular) *o*-hydroxy proton. This signal remained unchanged in the complexes signifying the nonreactivity of *o*-hydroxy group during complexation. The aromatic protons in the ligands and the complexes appeared in the region of δ 6.9-8.0. The singlet due to NH proton at δ 5.0 in the ligands appeared as a doublet at δ 4.1 and

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4.20 in the complexes indicating that the two NH groups involved in complexation were non-equivalent. This was further supported by the splitting of the sharp signal at δ 3.89 in the ligand (**1b**) due to *m*-OCH₃ group protons into a doublet δ 3.6-3.8 in the corresponding complexes. From this, it can be concluded that in the

complexes the ligands must exist in *trans*-configuration. A sharp doublet in the complexes around δ 1.2 to 1.5 which was absent in the spectra of ligands has been assigned to methyl protons of DMDCS.

All the available data point to structure (A) for the complexes in which silicon is seven-coordinated.

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