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### Si(IV) Complexes with Schiff Bases

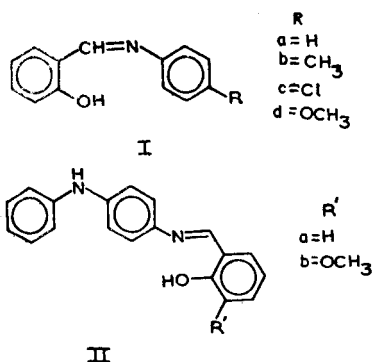
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Schiff bases derived from salicylaldehyde and aniline, *p*-toluidine, *p*-chloroaniline and *p*-anisidine react with silicon(IV) chloride in dry benzene medium to form the adducts of the type  $(SB)_4SiCl_4$ , whereas the Schiff bases derived from salicylaldehyde and *o*-vanillin with *p*-aminodiphenylamine form the adducts of the type  $(SB')_2SiCl_4$ . These hygroscopic, coloured adducts behave as non-electrolytes in acetonitrile. The infrared spectral study reveals that coordination has taken place through the azomethine nitrogen. It appears that silicon exhibits coordination number eight in  $(SB)_4SiCl_4$  type of complexes and six in  $(SB')_2SiCl_4$ .

THE vast amount of literature added to the growth of understanding the nature of silicon-nitrogen bonds in the complexes of silicon(IV) is mainly due to Wannagat and coworkers<sup>1</sup>. Recently, Paul and coworkers<sup>2</sup> have reported a few Si(IV) complexes with nitrogen donor ligands. However, the limited literature known on silicon(IV) Schiff base complexes<sup>3</sup> has prompted us to undertake a systematic study of silicon(IV) complexes with Schiff bases of types (I) and (II) derived from salicylaldehyde and aniline (Ia), *p*-toluidine (Ib), *p*-chloroaniline (Ic) and *p*-anisidine (Id) and *p*-aminodiphenylamine (IIa) and *o*-vanillin and *p*-aminodiphenylamine (IIb).



The Schiff bases were prepared from reagent grade chemicals according to the method reported elsewhere<sup>4</sup> and dried *in vacuo* over phosphorous pentoxide before use.

All the manipulations were done in a partially evacuated dry-box under oxygen-free nitrogen.

The complexes were prepared as follows: A solution of silicon tetrachloride super dry benzene<sup>5</sup> was treated with a slight excess of Schiff base dissolved in the same solvent and left for several hours with occasional shaking at room temperature. Sufficient time was allowed for the precipitate to settle. The complex was filtered, washed free from the reagent with benzene and dried *in vacuo* over fused calcium chloride.

The data in Table 1 show that silicon tetrachloride forms adducts with all the Schiff bases employed. The Schiff bases Ia-d form adducts of 1:4 stoichiometry whereas IIa and IIb form adducts of 1:2 stoichiometry. All these adducts are dark coloured, hygroscopic substances, soluble in acetonitrile, DMF and DMSO. These undergo hydrolysis readily in water.

The molar conductance values in purified acetonitrile<sup>5</sup> (concentration  $10^{-3}M$ ) fall in the range 31-62  $\text{ohm}^{-1} \text{cm}^2/\text{mole}$ , indicating non-electrolyte nature of the complexes in acetonitrile. Molar conductance of 1:1 electrolyte in acetonitrile<sup>6</sup> falls in the range 190-195  $\text{ohm}^{-1} \text{cm}^2/\text{mole}$ . The low conductance observed may be due to the partial solvolysis of the complexes in acetonitrile.

Some adducts with *o*-hydroxyazomethines are documented in the literature, especially with Sn(IV), Ti(IV) and Si(IV). In view of these evidences it may be considered that presently synthesized complexes are also adducts, and not substitution complexes involving *o*-hydroxy group of the Schiff bases in which case a molecule of hydrogen chloride liberated would have attached with azomethine nitrogen to give 1:1 electrolytes. Further support to this conjecture is provided by the IR data in nujol.

The broad weak bands in the Schiff bases in the region 2800-2600  $\text{cm}^{-1}$  are retained in the corresponding complexes. The coordination through nitrogen should either weaken the strength of H-bonding or allow the formation of H-bonding with the  $\pi$ -system of the azomethine group. The bond due to phenolic C—O in the region 1289-1272  $\text{cm}^{-1}$  in the Schiff bases does not show any shift towards the higher frequency region in the complexes. These observations suggest that the *o*-hydroxy group of the Schiff bases Ia-d and IIa, b, is not involved in the bond formation.

TABLE 1 — PHYSICAL PROPERTIES AND ANALYSIS OF SILICON(IV) SCHIFF BASE COMPLEXES  
 [Silicon estimated as  $SiO_2$ ]

Sl No.	Empirical formula	Si(%)		N(%)		Cl(%)		Colour
		Found	Calc.	Found	Calc.	Found	Calc.	
1	$(C_{13}H_{11}NO)_4SiCl_4$	2.91	2.92	5.24	5.85	14.80	14.82	Orange
2	$(C_{14}H_{13}NO)_4SiCl_4$	2.88	2.76	5.56	5.52	14.00	14.01	do
3	$(C_{13}H_{10}NOCl)_4SiCl_4$	2.56	2.56	5.29	5.12	12.89	12.98	Yellowish green
4	$(C_{14}H_{13}NO_2)_4SiCl_4$	2.77	2.60	5.38	5.19	12.64	12.17	do
5	$(C_{19}H_{16}N_2O)_2SiCl_4$	3.66	3.70	7.48	7.41	18.86	19.04	Brownish black
6	$(C_{20}H_{18}N_2O_2)_2SiCl_4$	3.72	3.47	6.86	6.95	17.50	17.62	do

\*For correspondence.

The strong bands appearing in the region 1616-1600  $\text{cm}^{-1}$  in the Schiff bases and attributable to  $\nu\text{C}=\text{N}$  appear in the region 1653-1639  $\text{cm}^{-1}$  in the adducts 1-4 (Table 1), indicating that the coordination has taken place through the azomethine nitrogen.

The assignment of this band in the adducts 5 and 6 (Table 1) is rather cumbersome. In these Schiff bases IIa and IIb, one can expect a band due to  $\delta\text{NH}$ . As it is a band of weak intensity, it is rather difficult to locate this band amidst the high intensity  $\text{C}=\text{N}$  and aromatic  $\text{C}=\text{C}$  vibrations. In these bases a high intensity band is observed at 1598  $\text{cm}^{-1}$  and is assigned to the mixture of  $\text{C}=\text{N}$  and first high intensity band of aromatic  $\text{C}=\text{C}$  vibration. In the complexes 5 and 6, we notice clear resolution of this band; one appearing in the region 1626-1616  $\text{cm}^{-1}$  and the other in the region 1590-1587  $\text{cm}^{-1}$ . The high frequency band in the complexes is attributed to  $\nu\text{C}=\text{N}$ .

The band around 3400  $\text{cm}^{-1}$  in the bases IIa and IIb is assigned to  $\nu\text{NH}$ . This band in the complexes 5 and 6 does not show any split or shift indicating that NH is not involved in coordination.

The non-electrolytic behaviour of the complexes in acetonitrile, the spectral observations and the possibility of coordination numbers six and eight in silicon(IV)<sup>7,8</sup> make us believe that silicon may assume coordination number eight in the complexes 1-4 and coordination number six in the complexes 5 and 6.

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#### Chelated Antimony Compounds\*

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**Monochelated antimony(V) tetrachlorides have been prepared from antimony pentachloride and organic bidentate chelating ligands salicylaldehyde, 8-hydroxy-**

**quinoline, N-benzoyl-N-phenylhydroxylamine, dehydroacetic acid and acetoacetanilide. Bis-chelated triphenylantimony(V) compounds have been obtained from triphenylantimony(V) dibromide and sodio-derivative of bidentate ligands. Tris(salicylaldehydato)-antimony(III) has also been prepared. The spectral and other properties of the new compounds have been studied.**

**P**REPARATION and structures of several organo antimony compounds have been described in literature<sup>1-6</sup>. Results obtained from the reaction between stannic chloride or organotin chlorides with organic chelating ligands<sup>7</sup> prompted us to prepare similar antimony compounds.

Preparations were carried out using absolutely dry solvents under moisture-free conditions; filtrations were done using a positive pressure of dry nitrogen gas.

*Tris(salicylaldehydato)antimony(III)* — Antimony trichloride (2.28 g; 0.01 mole) was dissolved in benzene (50 ml) and reacted with sodio-derivative of salicylaldehyde (0.04 mole; prepared via sodium methoxide) by refluxing for 2 hr. The reaction mixture was concentrated, sodium chloride and the excess sodio-salicylaldehyde filtered off, and remaining benzene removed under reduced pressure. The product was washed with hexane and solvent removed under reduced pressure. The yellow product, m.p. 180°, weighed 4.36 g (90% yield) [Found: Sb, 25.10; C, 52.01; H, 3.12. Calc. for  $\text{C}_{21}\text{H}_{15}\text{O}_6\text{Sb}$ : Sb, 25.11; C, 51.96; H, 3.09%]. Molecular weight: (1) by ebullioscopy in benzene, 490 and (2) by differential vapour pressure method, 482; calc. 485.

*8-Hydroxyquinolino)antimony tetrachloride* — Antimony pentachloride (2.99 g; 0.01 mole) and 8-hydroxyquinoline (1.45 g; 0.01 mole) were mixed in carbon tetrachloride (50 ml) and refluxed for 2 hr to remove all HCl. The solvent was removed under reduced pressure, the product washed with hexane and dried *in vacuo*. The orange hygroscopic solid, insoluble in benzene, m.p. 170°, weighed 3.3 g (80% yield) [Found: Sb, 29.75; Cl, 34.67; C, 26.66; H, 1.26. Calc. for  $\text{C}_9\text{H}_6\text{ONSbCl}_4$ : Sb, 29.80; Cl, 34.74; C, 26.47; H, 1.20%].

*(Triphenyl)antimony dibromide* — It was obtained as a white crystalline powder by the action of bromine on (triphenyl)antimony in glacial acetic acid; it was recrystallized from benzene as needles, m.p. 216° (ref. 8) [Found: Sb, 23.93; C, 42.42; H, 3.01; Br, 31.07. Calc. for  $\text{C}_{18}\text{H}_{15}\text{SbBr}_2$ : Sb, 23.75; C, 42.14; H, 2.93; Br, 31.18%].

*Bis(8-hydroxyquinolino)(triphenyl)antimony* — (Triphenyl)antimony dibromide (5.12 g; 0.01 mole) was dissolved in benzene (50 ml) and reacted with the sodio-derivative of 8-hydroxyquinoline (0.03 mole) by refluxing for 2 hr, and the product isolated as in the case of salicylaldehydato complex. The yellow powder, soluble in benzene, m.p. 175°, weighed 5.75 g (90% of theory) [Found: Sb, 19.10; C, 67.62; H, 4.01. Calc. for  $\text{C}_{36}\text{H}_{27}\text{O}_2\text{N}_2\text{Sb}$ : Sb, 18.99; C, 67.42; H, 4.21%].

Other compounds were prepared similarly (Table 1).

In the presence of a solvent, antimony halides form unstable addition compounds with salicyl-

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