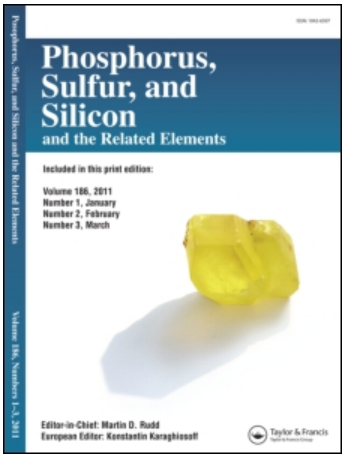

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF 2-(N-SALICYLIDENE)-5-CHLOROBENZOPHENONE DERIVATIVES OF ORGANOSILICON(IV)

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF 2-(N-SALICYLIDENE)-5-CHLOROBENZOPHENONE DERIVATIVES OF ORGANOSILICON(IV)

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A few tri-, di- and monorganosilicon(IV) derivatives of Schiff base, 2-(N-salicylidene)-5-chlorobenzophenone have been synthesised by the reactions of the corresponding tri-, di- and monorganosilicon(IV) chlorides with sodium salt of 2-(N-salicylidene)-5-chlorobenzophenone (prepared *in situ*) in different molar ratios. These newly synthesised derivatives have been characterised by elemental analyses, molecular weights, conductivity measurements and spectral (IR and PMR) studies and their coordination behaviour has been systematically discussed.

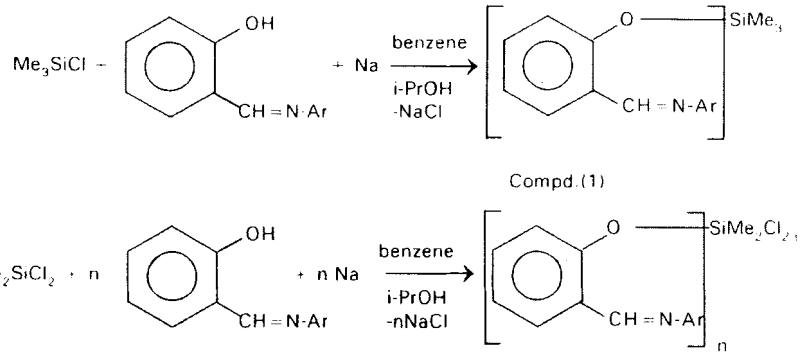
Organosilicon complexes of oxygen, nitrogen and sulfur donor ligands have been reported,[1–3] and are widely used in medicinal and pharmaceutical chemistry.[4–6] Certain organosilicon compounds have been extensively used in Chemical vapour deposition and deoxygenation reactions in organic transformations.[7] Our continuing interest in the synthesis of biologically active complexes have led us to prepare and study the structural as well as other aspects of organosilicon(IV) complexes of 2-(N-salicylidene)-5-chlorobenzophenone, an important metabolite precursor for the synthesis of drugs.[8]

Keywords: 2-(N-salicylidene)-5-chlorobenzophenone; coordination behaviour; organosilicon(IV) complexes; molecular weight; conductivity measurement; spectral studies

RESULTS AND DISCUSSION

Tri-, di- and monorganosilicon(IV) derivatives 2-(N-salicylidene)-5-chlorobenzophenone have been synthesised by the reaction of corresponding tri-, di- and monorganosilicon(IV) chlorides with the sodium salt of the ligand (prepared *in*

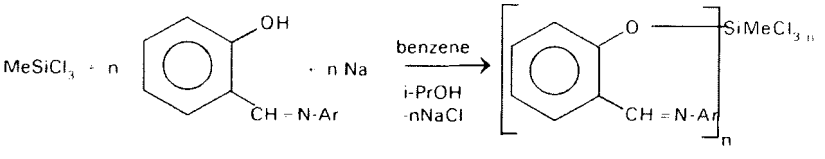
*Corresponding author.



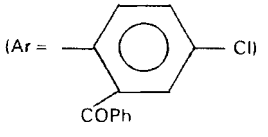
situ by the reaction of sodium isopropoxide with the ligand) in different stoichiometric ratios.

Where, n = 1, Compd. (2); n = 2, Compd. (3).

All these new complexes have been prepared by refluxing the reactants in dry benzene. Intermolecular nucleophilic substitution with elimination of chloride ion leads to the formation of products. All these derivatives are light yellow crystalline solids, which are further purified by crystallization from benzene-pet.ether (40–60°) mixture. All these compounds are soluble in common and coordinating organic solvents like $CHCl_3$, CCl_4, DMF and DMSO etc. These derivatives are highly susceptible even to trace amounts of moisture. Molar conductance values reveal the non-electrolytic nature of the complexes.[9] Molecular weight determination in chloroform solution shows monomeric nature of these complexes.



Where, n = 1, Compd.(4); n = 2, Compd.(5); n = 3, Compd.(6).



IR Spectral Data

The infrared spectra of these organosilicon(IV) complexes have been recorded in the form of KBr pellets in the range 4000–400 cm^{-1}. Tentative assignments have been made on the basis of earlier publications.[10,11]

The spectrum of the ligand shows bands in the region 3380–3260, 1680 and 1620 cm^{-1} which have been assigned to ν(O-H), ν(C=O), ν(C=N), respectively.[12] The disappearance of ν(O-H) in the complexes indicate deprotonation of phenolic O-H and consequent coordination of phenolic oxygen atom to silicon, which is further substantiated by the appearance of bands in the region 1105–1090 cm^{-1}, that may be due to Si-O-C stretching vibrations.[13,14] The bands observed at 1610 cm^{-1} due to C=N and at 1680 cm^{-1} due to C=O in the ligand, do not show any discernible shift in the spectra of complexes suggesting non-participation of the C=N and keto group in coordination (Table No. 1).

NMR Spectral Data

The ^1H NMR spectra of these complexes have been recorded in $CDCl_3$ and DMSO-d_6 using TMS as an internal standard.

The PMR spectrum of ligand is characterised by appearance of a signal at δ 12.40 ppm for phenolic -OH group, at δ 10.60 ppm for azomethine group and a multiplet at δ 6.84–7.86 ppm attributable to protons of phenyl moiety. The resonance at δ 12.40 ppm is absent in the spectra of the complexes suggesting deprotonation of phenolic -OH and its subsequent involvement in coordination. The resonance due to azomethine protons appear in the region at δ 10.6 to 11.6 ppm with negligible shift ($\pm$0.15 ppm) in comparison to the free ligand position, suggesting monodentate nature of the ligand. The resonance due to phenyl moiety remains uneffected in the complexes and the resonance due to methyl protons are observed in the region δ 0.50–0.75 ppm (Table No. 1)

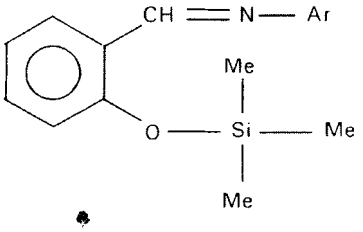
Thus based on the above spectral studies, monodentate mode of coordination for ligand and tetra-coordinated structures may be tentatively proposed for triorganosilicon(IV) (a), diorganosilicon(IV) (b) and monorganosilicon(IV) (c) derivatives of 2-(N-salicylidene)-5-chlorobenzophenone.

EXPERIMENTAL

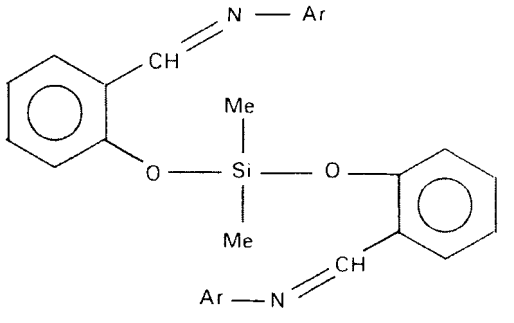
Moisture have been carefully excluded throughout the experimental manipulations. Solvents (benzene, isopropanol, ethanol etc.) are dried by standard methods.[15] Analytical grade chemicals are used for all experiments. All the melting

TABLE No. 1 Physical and spectral data of complexes

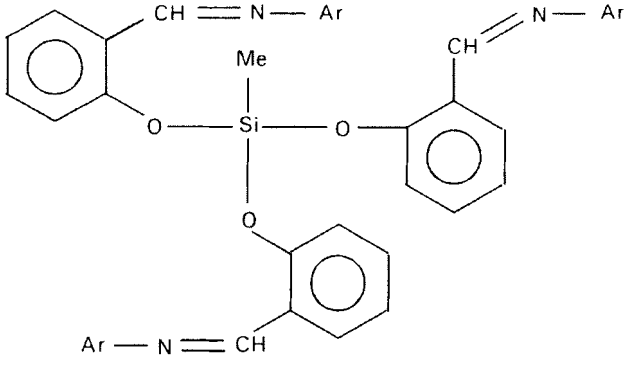
Sl. No.	*Compound/ Mol.Wt. Calcd/(found)*	*Physical state*	*M.P. (O°c)*	*I.R.(cm^{-1})*			*PMR (δ ppm)*
				ν(C=O)	*ν(C=N)*	*ν(Si-O-C)*	
1.	$C_{31}H_{22}NO_2SiCl$ 407.5(417)	Light Yellow Crystalline Solid	120–122	1680	1605	1105	0.51(S,9H,CH_3) 10.60(S,1H,CH=N). 6.42–7.76(m,12H, arom.)
2.	$C_{22}H_{19}NO_2SiCl_2$ 428(436)	Light Yellow Crystalline Solid	133–135	1685	1600	1100	0.63(S,6H,CH_3) 11.45(S,1H,CH=N) 6.42–7.25(m,12H, arom.)
3.	$C_{42}H_{32}N_2O_4SiCl_2$ 727(742)	Yellow Crystalline Solid	117–119	1690	1590	1090	0.56(S,6H,CH_3) 11.20(S,2H,CH=N) 6.34–7.82(m,12H, arom.)
4.	$C_{21}H_{16}NO_2SiCl_3$ 448.50(456)	Yellow Crystalline Solid	121–123	1685	1595	1095	0.75(S,3H,CH_3) 11.36(S,1H,CH=N) 6.65–7.80(m,12H, arom.)
5.	$C_{41}H_{29}N_3O_4SiCl_3$ 747.5(753)	Light Yellow Crystalline Solid	132–134	1680	1605	1100	0.71(S,3H,CH_3) 11.54(S,2H,NH) 6.20–7.86(m,24H, arom.)
6.	$C_{61}H_{42}N_3O_6SiCl_3$ 1046.5(1057)	Light Yellow Crystalline Solid	146–148	1685	1600	1105	0.62(S,3H,CH_3) 11.26(S,3H,NH) 6.54–7.96(m,36H, arom.)



(a)



(b)



(c)

points are uncorrected. The IR and NMR spectra are recorded on a Perkin-Elmer model 577 in the range 4000–400 cm^{-1} and JEOL JNM FX-90 Q spectrophotometers, respectively. Chemical shifts are recorded in ppm (δ) relative to TMS as an internal standard. Microanalyses are performed by Coleman Carbon, Hydrogen and Nitrogen analysers for C, H & N, respectively. Sulfur, chlorine and silicon have been estimated gravimetrically as described elsewhere[15] and are in good agreement with the calculated values (Table No.2).

TABLE No. 2 Synthetic and analytical data of complexes

Sl. No.	*Reactants in g. (m mole)*			*Molar ratio*	*Yield in g. (%)*	*Analyses % Found/(clacd.)*				
	Organo silicon chloride	*Ligand*	*Sodium metal*			*C*	*H*	*N*	*Si*	*Cl*
1.	Me_3SiCl 0.72 (6.64)	2.23 (6.64)	0.15 (6.64)	1:1:1	2.02 (74)	67.73 (67.64)	5.35 (5.39)	3.32 (3.43)	6.85 (6.87)	8.26 (8.71)
2.	Me_2SiCl_2 0.94 (7.28)	2.44 (7.28)	0.16 (7.28)	1:1:1	2.56 (81)	61.62 (61.68)	4.40 (4.43)	3.21 (3.27)	6.49 (6.54)	16.49 (16.58)
3.	Me_2SiCl_2 0.82 (6.35)	4.26 (12.70)	0.29 (12.70)	1:2:2	4.15 (89)	69.23 (69.32)	4.38 (4.40)	3.79 (3.85)	3.82 (3.85)	9.61 (9.76)
4.	$MeSiCl_3$ 0.63 (4.22)	1.41 (4.22)	0.09 (4.22)	1:1:1	1.42 (75)	56.15 (56.18)	3.54 (3.56)	3.10 (3.12)	6.22 (6.24)	23.45 (23.74)
5.	$MeSiCl_3$ 0.71 (4.76)	3.19 (9.50)	0.21 (9.50)	1:2:2	3.16 (88)	65.77 (65.80)	5.46 (5.48)	3.42 (3.74)	3.65 (3.74)	14.19 (14.24)
6.	$MeSiCl_3$ 0.72 (4.83)	4.86 (14.49)	0.33 (14.49)	1:3:3	4.16 (82)	69.85 (69.94)	3.99 (4.01)	4.00 (4.01)	2.60 (2.67)	10.15 (10.17)

Synthesis of 2-(N-salicylidene)-5-chlorobenzophenone

To the boiling solution of salicylaldehyde (6.10 g, 0.05 mmole) in benzene (100 ml), are added 2-amino-5-chlorobenzophenone (11.58 g, 0.05 mmole) in a round bottom flask. The contents are stirred and heated for one hour. After cooling, 2-(N-salicylidene)-5-chlorobenzophenone readily crystallised, which is filtered off and dried under reduced pressure. It is recrystallised from benzene to give yellow coloured crystals, 13.55 g (87%), m.p. 160°c.

Reaction between trimethylsilicon(IV) chloride and sodium salt of 2-(N-salicylidene)-5-chlorobenzophenone

0.15 g (6.64 mmole) of sodium metal and 15 ml of isopropanol are taken in a round bottom flask (fitted with a dried and cooled water condenser and guard tube) and refluxed for about half an hour till a clear solution of sodium isopropoxide was obtained. After cooling, 2.23 g (6.64 mmole) of 2-(N-salicylidene)-5-chlorobenzophenone is added and the mixture is further refluxed for two hours again. 0.72 g (6.64 mmole) of trimethylsilicon chloride was added and the mixture was further refluxed for two hours to ensure the completion of reaction. The desired product (74%) is isolated by evaporation of volatiles from the filtrate

after filtering off the precipitated sodium chloride. The product was further purified by crystallisation using a benzene-petroleum ether (40°–60°) mixture.

All other organosilicon(IV) derivatives of 2-(N-salicylidene) -5-chlorobenzophenone have been synthesized analogously. The pertinent data for this compound and other derivatives are listed in Table No.2.

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