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Schiff-base Complexes of Dimethyldichlorosilane

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Several Schiff-bases obtained by the condensation of monoamine or diamine with substituted benzaldehyde were synthesized and then coordinated with dimethyldichlorosilane. The products of reaction were characterized by elemental analyses, conductivity measurements, and infrared and nuclear magnetic resonance spectroscopic data. A majority of the complexes exhibit a 1:1 (silicon: Schiff-base) stoichiometry and a few have 1:2 stoichiometry.

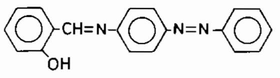
Introduction

In recent years, a variety of Schiff-base chelates have been coordinated to dimethyldichloro tin [1–5]. Very little work has been done on the corresponding Schiff-base complexes of dimethyldichlorosilane. In this study, Schiff-base complexes of dimethyldichlorosilane were synthesized and characterized by elemental analyses, conductivity measurements, infrared (IR) and nuclear magnetic resonance (NMR) spectral data.

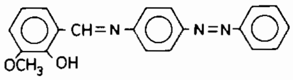
Experimental

All the chemicals used in this work were of reagent grade. The ligands were prepared by an adaption of a previously reported synthesis [6]. Monoamine Schiff-bases (A, B) were prepared by combining an equimolar ratio of p-amino-azobenzene with salicylaldehyde or vanillaldehyde, and then refluxing in alcohol on a water bath for two hours. The reaction mixture was then cooled, and the Schiff-base crystals were recrystallized from ethanol. Diamine Schiff-bases (C–J) were prepared by mixing 0.10 mol of diamine with 0.20 mol of either salicylaldehyde or vanillaldehyde in methanol, and then refluxing the reaction mixture on a water bath for 30 minutes. After cooling, the crystals of Schiff-base were separated and recrystallized from methanol.

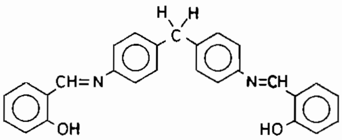
The following Schiff-bases were prepared:



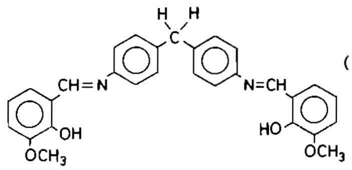
(A) salicylidene-p-amino-azobenzene



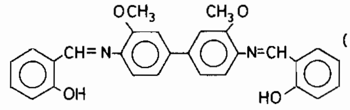
(B) o-vanillidene-p-amino-azobenzene



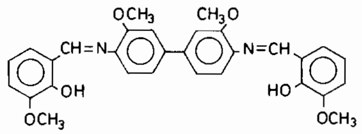
(C) di-salicylidene-p,p'-diamino diphenyl-methane



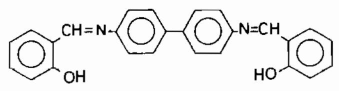
(D) di-o-vanillidene-p,p'-diamino diphenyl-methane



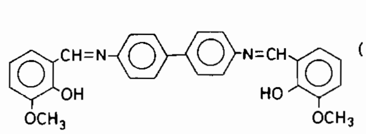
(E) di-salicylidene-o-dianisidine



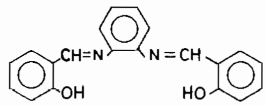
(F) di-o-vanillidene-o-dianisidine



(G) di-salicylidene-benzidene



(H) di-o-vanillidene-benzidene



(I) di-salicylidene-o-phenylenediamine

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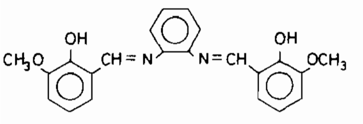

(J)

di-o-vanillidene-o-phenylenediamine

The complexes were prepared by mixing various Schiff-bases (0.01 mol) with dimethyldichlorosilane (0.01 mol) in dry benzene. The resulting mixtures were allowed to settle overnight; they were then filtered, washed repeatedly with dry benzene using a Soxhlet extractor and finally dried under vacuum over P_2O_5.

Elemental analyses were carried out by a procedure discussed elsewhere [7]. Silicon was determined as its oxide by a direct ignition method. Chlorine was determined as the silver chloride precipitate. The method of Kjeldahl was used to determine the nitrogen content of the complexes. Carbon and hydrogen were determined by a microanalytical method.

Conductivities were measured in dimethylformamide (DMF) using an Elico-CM-82 conductivity bridge with a cell having a cell constant of 0.829 cm^{-1}. All conductivity measurements were performed at room temperature using 10^{-3} *M* solutions of complex.

The infrared (IR) spectral results from 4000 to 200 cm^{-1} were obtained using a Perkin-Elmer 180 spectrophotometer. Samples were prepared as KBr pellets. Nuclear magnetic resonance (NMR) spectra were recorded using a S-60C NMR instrument. All NMR samples were dissolved in deuterated dimethylsulfoxide (d_6-DMSO), and tetramethylsilane (TMS) was used as the internal standard.

Results and Discussion

Analytical Data

All the complexes are colored and amorphous in nature and they are insoluble in common organic solvents, but soluble in DMF and DMSO. The elemental analyses (see Table I) for complexes I and II agree well with 2:1 (Schiff-base: silicon) stoichiometry; a 1:1 stoichiometry is observed for complexes III to X. The molar conductivities are in the range of 82–104 ohm^{-1} cm^2 mol^{-1} suggesting 1:1 electrolyte behavior [8]. Apparently in DMF, the solvent displaces one of the chloro ligands to form the 1:1 electrolyte $[X_2(CH_3)_2SiCl(DMF)](Cl)$ where X = ligands A or B or the 1:1 electrolyte $[Y(CH_3)_2SiCl(DMF)]$ where Y = ligands C–J.

Infrared Spectra

Tables of important infrared frequencies and their assignments are available upon request from the

TABLE I. Analytical and Physical Data of Dimethyldichlorosilane Complexes with Schiff Bases Derived From Monoamines and Diamines.

Ligand	Complex number	Empirical formula of the complex	%N	%Cl	%C	%H	Molar cond. (ohm^{-1} cm^2 mol^{-1})
A	I	$(C_{19}H_{15}ON_3)_2(CH_3)_2SiCl_2$	11.57* (11.48)	9.81 (9.69)	65.90 (65.68)	4.55 (4.92)	93.01
B	II	$(C_{20}H_{17}O_2N_3)_2(CH_3)_2SiCl_2$	10.71 (10.61)	9.05 (8.96)	63.75 (63.74)	4.76 (5.05)	96.26
C	III	$(C_{27}H_{22}N_2O_2)(CH_3)_2SiCl_2$	5.26 (5.23)	13.37 (13.25)	65.32 (65.07)	4.90 (5.23)	89.16
D	IV	$(C_{29}H_{26}N_2O_4)(CH_3)_2SiCl_2$	4.75 (4.70)	12.01 (11.91)	62.70 (62.54)	5.00 (5.38)	91.68
E	V	$(C_{28}H_{24}N_2O_4)(CH_3)_2SiCl_2$	4.85 (4.82)	12.20 (12.20)	63.25 (61.98)	5.01 (5.16)	83.23
F	VI	$(C_{30}H_{28}N_2O_6)(CH_3)_2SiCl_2$	4.31 (4.37)	11.00 (11.06)	56.35 (59.92)	5.03 (5.30)	94.06
G	VII	$(C_{26}H_{20}N_2O_2)(CH_3)_2SiCl_2$	5.40 (5.37)	13.65 (13.60)	64.78 (64.51)	4.70 (4.99)	101.22
H	VIII	$(C_{28}H_{24}N_2O_4)(CH_3)_2SiCl_2$	4.91 (4.82)	12.25 (12.20)	62.00 (61.98)	4.90 (5.16)	103.97
I	IX	$(C_{20}H_{16}N_2O_2)(CH_3)_2SiCl_2$	6.31 (6.29)	16.12 (15.93)	59.62 (59.35)	4.50 (4.94)	82.24
J	X	$(C_{22}H_{20}N_2O_4)(CH_3)_2SiCl_2$	5.60 (5.54)	14.17 (14.03)	57.30 (57.05)	4.81 (5.15)	91.57

*Figures in parentheses are calculated values.

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In all the ligands, A to J, the absorption band around 1600 cm^{-1} is assigned to an azomethine group. The low frequency of the azomethine group is attributed to its conjugation with an aromatic ring [9] and its hydrogen bonding [10, 11] to an o-hydroxy group of an adjacent salicyl or vanillyl moiety. It should be noted that this band is not due purely to ν(C–N), but is a combination band which includes both ν(C–N) and ν(C–C). In the complexes, I–X, the frequency characteristic of the C=N group is shifted to around 1630 cm^{-1} suggesting coordination through the azomethine nitrogen [12]. In the ligands A and B, it is difficult to assign frequencies for the N=N stretch because of the overlapping caused by C=C vibrations. However in view of the assignments made earlier by Rao, a broad band of medium intensity around 1605 cm^{-1} is assigned to a combination of ν(C=C) and ν(N=N) [13]. In complexes I and II this band is observed at 1600 cm^{-1} which indicates that it is not affected by the complexation.

In agreement with the work reported by Nasiak and Post [14], a shoulder in the region 1410–1390 cm^{-1} in the complexes is assigned to the C–H deformation stretch of the Si–C–H linkage. A strong band around 850 cm^{-1} which is not present in the ligands is attributed to ν(Si–CH$_3$) of dimethyl-dichlorosilane [15]. Of the two bands observed at 760 cm^{-1} and 710 cm^{-1}, the former is assigned to ν(Si–N) stretch [16–18]. A sharp band observed around 525 cm^{-1} is assigned to a ν(Si–Cl) stretch [19].

In both ligands and complexes a band observed at 2650 cm^{-1} (due to the intramolecular hydrogen bonding of the orthohydroxy group) which remains unchanged indicates that complexation has no effect on this group [20, 21]. This is also confirmed by the position of the phenolic C–O band in the ligands and complexes which is unchanged at 1280 cm^{-1}. Thus, the ortho-hydroxy groups in the ligands have not participated in coordination and the complexes formed are adducts.

Nuclear Magnetic Resonance Spectra

NMR chemical shifts for the Schiff bases and the complexes are depicted in Tables II and III respectively.

In the ligands, the signal observed at 13.3 ppm is attributed to the orthohydroxy proton engaged in intramolecular hydrogen bonding. The second signal observed around 8.36 to 8.90 ppm is assigned to the azomethine proton. The signals due to the phenyl

TABLE II. Proton Magnetic Resonance Chemical Shifts* of Schiff Base Ligands and Their Assignments.

A	B	C	D	E	F	G	H	I	J	Assignments
13.20	13.15	13.17	13.22	13.26	13.29	13.30	13.20	13.19	12.96	Hydroxy proton
8.39	8.36	8.46	8.39	8.75	8.89	8.46	8.40	8.43	8.37	Azomethine protons
6.8 to 7.8	7.0 to 8.0	6.8 to 7.8	7.0 to 8.0	7.2 to 8.10	6.8 to 7.8	6.9 to 7.9	7.1 to 8.0	6.9 to 7.89	6.8 to 7.7	Phenyl protons
–	–	4.12	4.20	–	–	–	–	–	–	Methylene protons of p,p'-diaminodiphenyl methane
–	3.89	–	3.86	–	3.88	–	3.79	–	4.01	Methoxy protons

*In ppm (δ) relative to TMS.

TABLE III. Proton Magnetic Resonance Chemical Shifts* of Dimethyldichlorosilane Schiff-Base Complexes.

I	II	III	IV	V	VI	VII	VIII	IX	X	Assignments
13.25	13.15	13.20	13.20	13.25	13.20	13.30	13.20	13.20	13.00	Hydroxy protons
9.56	9.60	9.70	9.75	9.67	9.60	9.72	9.64	9.83	9.77	Azomethine protons
7.0 to 8.0	6.8 to 7.8	6.8 to 7.8	7.0 to 8.0	7.1 to 8.1	6.8 to 7.8	7.0 to 8.0	7.2 to 8.0	7.0 to 8.0	6.8 to 7.8	Phenyl protons
–	3.70	–	3.85	–	3.86	–	3.80	–	4.00	Methoxy protons
–	–	4.15	4.20	–	–	–	–	–	–	Methylene protons of p,p -diaminodiphenyl methane
1.23 to 1.41	1.22 to 1.45	1.31 to 1.46	1.21 to 1.46	1.30 to 1.41	1.20 to 1.37	1.19 to 1.40	1.24 to 1.44	1.20 to 1.48	1.29 to 1.42	Methyl protons

*In ppm (δ) relative to TMS.

protons are observed in the region 6.80 to 8.10 ppm. In the ligands C and D the signals in the region 4.12 to 4.20 ppm are attributed to the methylene protons of the p,p′-diamino-diphenylmethane moiety. All vanillidene Schiff-base chelates exhibit proton resonance signals around 3.79 to 4.01 ppm which are ascribed to the protons of the methoxy group. The signals due to the methoxy groups of orthodianisidine also occur in the same region.

In the complexes, the signal around 13.25 ppm due to the orthohydroxy proton remains unchanged indicating nonparticipation of this group in coordination. The shift of the peak due to the azomethine proton from about 8.50 to 9.80 ppm indicates coordination through the azomethine nitrogen to the silicon atom.

The complex mutliplet due to the phenyl protons remains virtually unchanged. The signals due to OCH_3 and methylene protons do not show much variation after complexation. A sharp doublet in the complexes in the region 1.19 to 1.48 ppm, which is not seen in the ligands, is assigned to the methyl protons of dimethyldichlorosilane.

Conclusions

A few complexes of dimethyldichlorosilane with several Schiff-bases have been synthesized. Elemental analyses indicate that Schiff-bases with one azomethine moiety (Schiff-bases A and B) form 2:1 (Schiff-base: silicon) complexes, whereas Schiff-bases possessing two azomethine groups (Schiff-bases C to J) form 1:1 complexes. Conductivity data suggest 1:1 electrolyte behavior.

The IR data seem to preclude any reaction between the OH and SiCl since ν(C–O) and ν(O–H) do not appear to shift on complexation. The NMR data also indicate that the o-hydroxy group is not involved in bonding.

On the basis of the above information, all the complexes are formulated to be hexacoordinate with the Schiff-base coordinating to dimethyldichlorosilane via an azomethine linkage.

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