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Amino Acid Schiff Base Complexes of Dimethyldichlorosilane

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Abstract

A few complexes of dimethyldichlorosilane with Schiff bases derived from the condensation of salicylaldehyde, benzaldehyde, pyridine-3-carboxyaldehyde and pyridine-4-carboxyaldehyde with glycine and α-alanine were prepared. The complexes were characterized by elemental analysis, conductivity measurements, infrared and proton magnetic resonance spectral data. Antibacterial activity data show that the silane complexes are better inhibitors than the corresponding free ligands.

Introduction

Salicylaldehyde amino acid Schiff-base complexes [1–5] have been used to model N-pyridoxylidene amino acids which are considered to be important intermediates in biological amination processes [6, 7]. The coordination of a metal ion to such Schiff base compounds stabilizes the azomethine linkage, under conditions that would otherwise promote bond cleavage.

Continuing our earlier research [8–15] on biologically active complexes, an attempt has now been made to synthesize amino acid Schiff base complexes of dimethyldichlorosilane. The complexes have been characterized by elemental analyses, conductivity measurements, infrared and nuclear magnetic resonance spectral data. Bacteriostatic activity has also been explored.

Experimental

Synthesis and Characterization

All the chemicals used in this work were of reagent grade. Glycine (Riedel, m.p. 262 °C) and alanine (BDH, m.p. 295 °C) were used without further purification. Dimethyldichlorosilane (DMDCS) was of Fluka grade.

The following ligands were prepared according to published procedures [16] and are shown in Scheme 1. The aromatic aldehyde and glycine or alanine were mixed in a 5:1 molar ratio in 250 ml of dry ethanol and then refluxed for six hours. The reaction mixture was concentrated and the precipitate filtered, washed with petroleum ether and then recrystallized from ethanol–petroleum ether. The reaction yield was typically 45%.

The ligands (**A–G**) and dimethyldichlorosilane were combined in a 1:1 molar ratio in 250 ml of dry benzene and mixed thoroughly. The complex precipitated and was allowed to digest overnight at room temperature prior to filtration. The precipitate was washed repeatedly with dry benzene, then dried under vacuum over P_2O_5.

Chlorine in the complexes was estimated as silver chloride, nitrogen using the Kjeldahl method, and a microanalytical technique was used to estimate carbon [17].

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) data were obtained using a Perkin–Elmer 180 spectrophotometer. Samples were prepared as KBr pellets. Nuclear magnetic resonance (NMR) spectra were recorded on a S-60-C NMR instrument. All NMR samples were dissolved in deuterated dimethylsulfoxide (d_6-DMSO), and tetramethylsilane (TMS) was used as the internal standard.

Antibacterial Tests

The antibacterial tests were carried out using the cup-plate method [18] in nutrient agar against four microorganisms: *E. Coli*, *B. Subtilis*, *S. Aureus* and *P. Vulgaris*. These bacterial strains were used because

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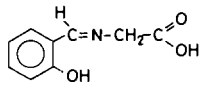
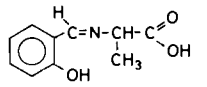
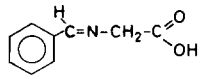
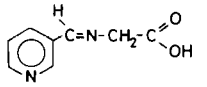
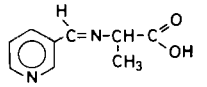
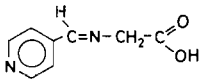
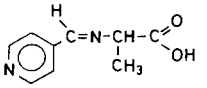
Ligand	Structure	Name	M.p. (°C)
A		N-Salicylidene glycine	210–211
B		N-Salicylidene α-alanine	185–187
C		N-benzylidene glycine	170–171
D		N-β-pyridylidene glycine	168–169
E		N-β-pyridylidene-α-alanine	172–174
F		N-ν-pyridylidene glycine	210–212
G		N-ν-pyridylidene-α-alanine	255–257

Scheme 1.

they are known commensals and pathogens of human beings. The procedure involved the following steps.

Preparation of Media for Microorganisms

The media were prepared by dissolving peptone (0.5%), yeast extract (0.15%), beef extract (0.15%), sodium chloride (0.35%), potassium dihydrogen phosphate (0.13%), and potassium monohydrogen phosphate (0.13%) in 100 ml of distilled water. The media were then autoclaved for 20 min. under a pressure of 15 lbs. The microorganisms were inoculated in the sterilized media and incubated at 37 °C for 24 h.

Preparation of Basal Media for Testing

Nutrient agar medium was prepared by dissolving bacteriological peptone (0.60%), yeast extract (0.30%) and beef extract (0.13%) in 100 ml of distilled water. This solution was filtered, a 2.1% solution of agar was added, and the solution was sterilized in an autoclave for 20 min. At a pressure of 15 lbs. 1 ml of 10% sterilized glucose solution was then added to the solution. All the glassware and Petri dishes were thoroughly sterilized prior to use.

Testing Procedure

The agar broth was melted using a hot water bath and then cooled to 45 °C. About 25 to 50 ml of basal media were poured into each of the Petri dishes and the solution was allowed to solidify. The bacterial culture was then sprayed over each plate. A 10 mm diameter cup was bored out in the centre of each agar plate and the punched part scooped out. 0.1 ml of test compound in DMF at a concentration of 200 μg/ml was added dropwise. The plates were then incubated for 24 h at 37 °C. The extent of inhibition was obtained by measuring the width in mm of the zone of inhibition formed, and the activity of the compounds was assessed by comparing to that of phenol as a standard.

Results and Discussion

Analytical Data

Table I lists the analytical data for the complexes (**I–VII**) which correspond to the ligands (**A–G**). Salicylidene amino acid complexes (**I–II**) are light yellow in color while those derived from pyridyl aldehydes (**IV–VII**) are dark yellow. All the complexes (**I–VII**) are insoluble in common organic solvents but soluble in DMF, DMSO, water and ethanol. Results of elemental analyses (Table I) agree well with a 1:2 (metal:ligand) stoichiometry. The molar conductivities are in the range, 30–61 ohm^{-1} cm^2 mol^{-1}, suggesting that the complexes are non-electrolytes in solution.

Infrared Spectra

In the spectra of ligands, a medium intensity band at 3400 cm^{-1} is assigned to the ν(N–H) stretch. This band disappears upon complexation. For the ligands,

TABLE I. Analytical and Physical Data for the Dimethyldichlorosilane Complexes.

Complex No.	Molecular Formula of Complex	% Cl		% N		% C		Molar Cond. (ohm^{-1} cm^2 mol^{-1})	M.p. (°C)
		Calc.	Found	Calc.	Found	Calc.	Found		
I	$C_{20}H_{24}N_2O_6SiCl_2$	14.58	15.02	5.75	5.28	49.28	49.45	58.05	310 (dec)
II	$C_{22}H_{28}N_2O_6SiCl_2$	13.79	13.98	5.44	5.06	51.26	50.87	55.00	286
III	$C_{20}H_{24}N_2O_4SiCl_2$	16.63	17.13	6.57	6.07	56.20	56.72	60.85	270–272
IV	$C_{18}H_{22}N_2O_4SiCl_2$	16.03	16.76	9.48	9.24	48.76	49.62	50.45	295
V	$C_{20}H_{26}N_3O_4SiCl_2$	15.11	15.76	8.94	8.77	51.06	52.62	53.00	258
VI	$C_{18}H_{22}N_3O_4SiCl_2$	16.03	17.02	9.49	9.13	48.76	48.98	49.86	280
VII	$C_{20}H_{26}N_3O_4SiCl_2$	15.11	15.48	8.94	8.64	51.06	51.93	30.05	274

bands in the region, 1605–1635 cm^{-1} are assigned to a combination of ν(C=C) and ν(C=N) vibrations [19]. In the spectra of the complexes, the bands shift to the range of 1630–1655 cm^{-1} which indicates that silicon must have coordinated with the nitrogen of the azomethine group [20]. In both ligands and complexes, the bands around 1585 cm^{-1} and 1380 cm^{-1} are attributed to asymmetric and symmetric $\nu(COO^-)$ vibrational modes. This implies that the carboxylate group has not taken part in chelation. For the N-salicylidene glycine and N-salicylidene α-alanine ligands, the band at 1275 cm^{-1} has been assigned to ν(C–O) phenolic stretch. This band does not change position or disappear on complexation which indicates that the hydroxide is not involved in the coordination to silicon. Bands in the range 580–600 cm^{-1} and 610–630 cm^{-1} have been assigned to ν(Si–Cl) and ν(Si–C) respectively [21, 22].

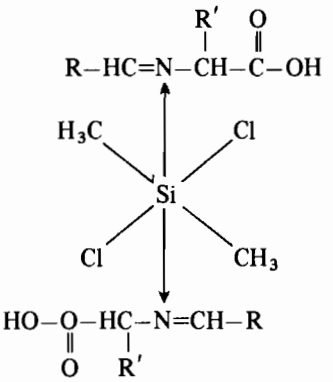
Nuclear Magnetic Resonance Spectra

The ^{1}H NMR spectrum of N-salicylidene glycine is characterized by four signals at 10.69, 8.57, 7.11 and 3.2 ppm which are assigned to the proton associated with the *ortho* hydroxy group of salicylaldehyde, the azomethine proton, phenyl protons and the CH_2 protons of the glycine residue. The spectrum of N-salicylidene-α-alanine is similar to that of N-salicylidene glycine but possesses an extra signal at 2.3 ppm which is assigned to the protons of the methyl group in alanine.

In the spectra of complexes (**I** and **II**) the resonance signal due to the proton of the azomethine group is shifted to higher field while the hydroxy proton signal remains unchanged. The data suggests that the azomethine group is coordinating to silicon while the hydroxyl group does not participate in the ligand binding. A new multiplet appears in the complexes in the region 1.0 to 1.5 ppm and is attributed to the methyl protons of dimethyldichlorosilane.

In the spectra of pyridylidene amino acid Schiff bases (**D–G**), we observe signals at 8.98, 8.64, 8.18, 7.57, 8.51 and 3.3 ppm. Of these the first four signals are due to pyridine ring protons; the signal at 8.51 ppm is due to the proton of the azomethine group, and the signal at 3.3 ppm is attributed to the CH_2 protons of the glycyl moiety. In the α-alanine Schiff bases (**E** and **G**), we observe an additional proton signal at 2.4 ppm which has been assigned to the methyl protons of the α-alanine group. In the spectra of complexes (**IV–VII**), the only shift observed is that due to the proton of azomethine group. Hence the metal ion has coordinated to the azomethine nitrogen.

On the basis of the analytical and spectral data, the tentative structure shown in Scheme 2 may be proposed for the complexes under study.



Scheme 2. R=C_6H_5, *o*-C_6H_4OH, 3-C_5H_4N or 4-C_5H_4N. R′ = H or CH_3.

Antibacterial Test Results

The antibacterial activity of the ligands and complexes is summarized in Table II. The data for the standard (phenol) are also recorded. The results show that all compounds exhibit antibacterial activity and in many cases, the silicon complexes are more potent in their inhibition properties than the free ligands. This can be explained in terms of the greater lipid solubility and cellular penetration of the complexes [23].

TABLE II. Antibacterial Activity of Ligands and their Complexes.

Ligand/Complex	Zone of Inhibition in mm - Organism			
	E. Coli	*B. Subtilis*	*S. Aureus*	*P. Vulgaris*
A	16	16	19	21
I	24	20	21	23
B	15	20	17	20
II	20	21	22	25
C	18	20	15	19
III	20	20	23	24
D	26	24	–	20
IV	22	26	24	28
E	26	19	23	19
V	24	28	24	26
F	18	25	21	26
VI	29	25	28	27
G	24	26	23	22
VII	24	28	28	27
Phenol (Standard)	25	18	15	20

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