

Complexes of Group (IV) Metals with 5,5'-Methylene-bis(salicylaldehyde) & Its Schiff Base with Hydrazine

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5,5'-Methylene-bis(salicylaldehyde) (I) and its schiff base(II) with hydrazine hydrate have been synthesized. Group (IV) metal complexes with(I) and (II) have been prepared and characterized on the basis of elemental analysis, IR spectroscopy, conductance measurement and molecular weight determination. Molar conductivities of their millimolar solutions in DMSO indicate the complexes to be non-ionic. On the basis of IR spectral studies, an octahedral structure has been proposed for the complexes of (I) and (II).

Substantial work has been done by Shah¹⁻⁵ and coworkers on polychelates derived from schiff bases of 5,5'-methylene-bis(salicylaldehyde) and various amines. However, no attempt seems to have been made to study the group(IV) metal chelates with this bis-bidentate monomeric ligand and its schiff bases with amines. In this paper we report the synthesis and characterization of Si(IV), Ge(IV), Sn(IV), Ti(IV) and Zr(IV) chloride complexes of 5, 5'-methylene-bis(salicylaldehyde)(I) and its schiff base(II) with hydrazine.

Materials and Methods

Formaldehyde, SiCl₄, SnCl₄, TiCl₄, ZrCl₄(BDH), GeCl₄ (Koch Light), salicylaldehyde (E.Merck), trioxane and hydrazine hydrate (fluka) were used as received. The IR spectra (250-4000 cm⁻¹) were recorded on a Beckman spectrophotometer in KBr and nujol mull. The conductivity measurements were made on an Elico conductivity bridge type CM-82T. The molecular weights were determined by viscosity method using an Ostwald viscometer.

Synthesis of 5,5'-methylene-bis(salicylaldehyde) and its metal chelates

5,5'-Methylene-bis(salicylaldehyde) was prepared by the method of Marvel *et al.*⁶ The complexes were prepared by stirring at room temperature 20 ml of MCl₄ solution (0.01 M) for 5 hr with 40 ml (0.01 M) solution of the ligand in chloroform. The mixture was left overnight. The colourless complexes which precipitated were washed with chloroform and dried *in vacuo*. All the manipulations were done in a dry box.

Synthesis of the schiff base

5,5'-Methylene-bis(salicylaldehyde) (0.02 mol) taken in 20 ml of acetone was added to hydrazine hydrate

(0.01 mol) in methanol (50 ml). The resulting mixture was refluxed for 3 hr on a water-bath when a dark brown compound was obtained. The solid was filtered washed with ether and dried *in vacuo*. The compound remains stable even on exposure to air and moisture.

Preparation of the complexes of the schiff base

Metal tetrachloride (0.01 mol) dissolved in 20 ml of CCl₄ was added to a solution (20 ml) of the schiff base (0.01 mol) in acetone. A solid was obtained after stirring the mixture for about 5 hr. The complexes were washed with ether and dried *in vacuo*. They had 1:1 (MCl₄: schiff base) ratio as confirmed by a quantitative estimation of chlorine.

Results and Discussion

The analytical results for the ligand and the complexes are in agreement with proposed compositions (Tables 1,2). The chelates appear to be

Table 1—Analytical and Melting Point Data of 5,5'-Methylenebis(salicylaldehyde) Complexes of Group(IV) Metal Chlorides

Compound	m.p. (°C)	Found (Calc.)			
		C%,	H%,	Cl%,	Molec. wt
C ₁₅ H ₁₂ O ₄	141	70.28 (70.31)	4.69 (4.72)	—	248.00 (256.22)
(C ₁₅ H ₁₁ O ₄) ₂ SiCl ₂	185	59.08 (59.11)	3.61 (3.63)	11.60 (11.64)	609.69 (609.57)
(C ₁₅ H ₁₁ O ₄) ₂ GeCl ₂	183	55.04 (55.09)	3.35 (3.39)	10.80 (10.85)	654.06 (654.11)
(C ₁₅ H ₁₁ O ₄) ₂ SnCl ₂	180	51.42 (51.46)	3.12 (3.16)	10.10 (10.14)	700.08 (700.11)
(C ₁₅ H ₁₁ O ₄) ₂ TiCl ₂	178	57.22 (57.25)	3.46 (3.52)	11.24 (11.28)	629.29 (629.32)
(C ₁₅ H ₁₁ O ₄) ₂ ZrCl ₂	182	53.53 (53.56)	3.28 (3.29)	10.58 (10.55)	672.60 (672.64)

Table 2—Analytical and Melting Point Data of Schiff Base Complexes of Group (IV) Metal Chlorides

Schiff base/Complex	m.p. (°C)	Found (Calc.)				
		C%	H%	N%	Cl%	Molec.wt.
(C ₃₀ H ₂₄ O ₆ N ₂)	150	73.73 (73.76)	4.93 (4.95)	5.70 (5.73)	—	485.00 (488.44)
(C ₃₀ H ₂₄ O ₆ N ₂)SiCl ₄	d.320	52.53 (52.57)	3.64 (3.67)	4.22 (4.25)	21.51 (21.53)	655.22 (658.33)
(C ₃₀ H ₂₄ O ₆ N ₂)GeCl ₄	d.240	51.23 (51.26)	3.40 (3.44)	3.97 (3.98)	20.13 (20.17)	700.00 (702.83)
(C ₃₀ H ₂₄ O ₆ N ₂)SnCl ₄	d.220	48.08 (48.10)	3.21 (3.23)	3.71 (3.74)	18.91 (18.93)	746.25 (748.93)
(C ₃₀ H ₂₄ O ₆ N ₂)TiCl ₄	d.300	53.09 (53.13)	3.52 (3.56)	4.10 (4.13)	20.89 (20.91)	676.12 (678.14)
(C ₃₀ H ₂₄ O ₆ N ₂)ZrCl ₄	d.260	49.91 (49.94)	3.32 (3.35)	3.85 (3.88)	19.63 (19.65)	719.48 (721.46)

thermally stable. The molar conductance values of the complexes in DMSO are below the expected range of a uni-univalent electrolyte (1.53-9.0 ohm⁻¹cm²mol⁻¹).

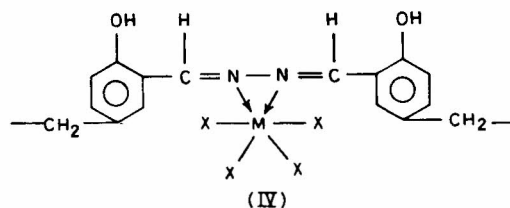
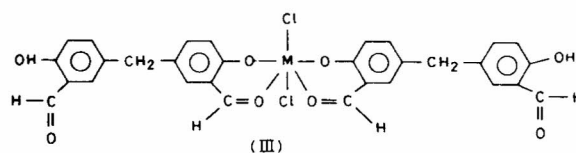
The IR spectrum of 5, 5'-methylene-bis(-salicylaldehyde)(I) shows a very weak band at 3360 cm⁻¹ due to phenolic OH which disappears on complexation indicating coordination through phenolic oxygen after deprotonation of OH. The stretching frequency of the aldehydic (C=O) group normally appears⁷ in the range 1740-1720 cm⁻¹. It is known that the $\nu(\text{C}=\text{O})$ is lowered while $\nu(\text{C}-\text{O})$ is enhanced after complexation⁸⁻¹¹. In the present case the $\nu(\text{C}=\text{O})$ frequency is negatively shifted (1685 cm⁻¹) from its position at 1720 cm⁻¹ in the free ligand. It is thus concluded that both the phenolic as well as aldehydic oxygens are simultaneously coordinated to the metal rendering it octahedral (structure III).

Complexes of (I) are formed by the replacement of hydrogen from phenolic group as HCl which has been ascertained by the quantitative test of chlorine in the complexes.

Some new absorption bands observed in the complexes in the ranges 400-965 cm⁻¹ and 320-424 cm⁻¹ have been attributed to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{C})$ modes. The (M-O) stretching frequencies appear at 920, 900, 420, 965 and 920 cm⁻¹ in Si, Ge, Sn, Ti and Zr, complexes respectively. These observations are in consonance with those reported for (M-O) stretching frequencies for complexes of group (IV) elements^{8,10,12,13}.

The schiff base derived from(I) and hydrazine hydrate shows a medium absorption band at 3360 cm⁻¹ assigned to phenolic OH which persists even after complexation ruling out the possibility of replacement of phenolic hydrogen by metal atom. A strong band at 1315 cm⁻¹ in the schiff base may be assigned to δOH (phenolic). The $\nu(\text{C}=\text{N})$ frequency at 1630 cm⁻¹ in the ligand is lowered by about 12 cm⁻¹

indicating the coordination solely through nitrogen atoms^{14,15}. This lowering in $\nu(\text{C}=\text{N})$ on complexation may be ascribed to a decrease in bond order of carbon-nitrogen double bond. The far IR region of the spectra is very significant as it includes the M-N and M-X stretches. The M-X absorption bands are stronger and appear at lower wave numbers as compared to (M-N) absorption bands. This supports the contention that the schiff base is coordinating with the metal through nitrogen atoms only. An octahedral structure(IV) may, therefore, be proposed for the complexes.



M = Si(IV), Ge(IV), Sn(IV), Ti(IV) and Zr(IV).

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