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Tin(IV) Complexes of Schiff Bases Derived from Pentane-2,4-dione or 2-Hydroxy-1-naphthaldehyde

By

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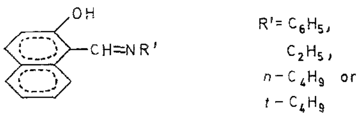
The 1 : 2 molar reactions of tin(IV) chloride with the Schiff bases, $CH_3C(OH):CHC(CH_3):NR$ and $2\,HOC_{10}H_6CH:NR'$ (where $R = C_2H_5$, n-C_3H_7 or n-C_4H_9 and $R' = C_6H_5$, C_2H_5, n-C_4H_9 or t-C_4H_9) have resulted in the synthesis of $SnCl_4 \cdot (SBH)_2$ type derivatives (where *SB*H represents the Schiff base molecule). These have been characterized by elemental analysis, conductivity measurements and IR spectral studies.

In recent years reactions of tin(IV) chloride with different types of Schiff bases have been reported[1–5]. *Kogan* et al.[6] have described reaction of tin(IV) chloride with pentane-2,4-dione imines. The present investigation forms part of our studies on tin(IV) complexes with a variety of Schiff bases and in this paper several new tin(IV) derivatives of Schiff bases obtained by the condensation of pentane-2,4-dione with ethylamine, n-propylamine and n-butylamine and 2-hydroxy-1-naphthaldehyde with aniline, ethylamine, n-butylamine and *tert.*-butylamine are reported. These azomethines may be structurally represented as follows:



Experimental

The reactions were carried out under strictly anhydrous conditions. Benzene (BDH) was first refluxed over sodium wire for several hours and then distilled azeotropically with ethanol. $SnCl_4$ (*Riedel*) was kept over

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Table 1. *Physical Properties and Analyses of the Schiff Bases*

S. No.	Schiff base	State and m. p. (°C)	b. p. (°C/mm)	Analyses (%) C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)
1	Pentane-2,4-dione-ethylimine ($C_7H_{13}NO$)	Yellow liquid	62/0.4	66.75 (66.83)	10.12 (10.23)	10.87 (11.02)
2	Pentane-2,4-dione-*n*-propylimine ($C_8H_{15}NO$)	Yellow liquid	85/3.0	67.92 (68.10)	10.51 (10.64)	9.85 (9.93)
3	Pentane-2,4-dione-*n*-butylimine ($C_9H_{17}NO$)	Yellow liquid	80/0.5	69.60 (69.68)	10.85 (10.96)	8.89 (9.02)
4	2-hyroxy-1-naphthylmethyleneaniline ($C_{17}H_{13}NO$)	Yellow solid 98—99	172/0.2	82.40 (82.56)	5.33 (5.30)	5.76 (5.66)
5	2-hydroxy-1-naphthylmethyleneethylamine ($C_{13}H_{13}NO$)	Yellow solid 123—124	136/0.2	78.54 (78.36)	6.72 (6.58)	7.25 (7.03)
6	2-hydroxy-1-naphthylmethylene-*n*-butylamine ($C_{15}H_{17}NO$)	Yellow solid 68—69	142/0.2	79.52 (79.30)	7.72 (7.54)	6.32 (6.16)
7	2-hydroxy-1-naphthylmethylene-*tert.*-butylamine ($C_{15}H_{17}NO$)*	Yellow solid 101—102	137/0.2	79.56 (79.30)	7.66 (7.54)	6.36 (6.16)

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* Has been used to distinguish between the compounds of same formula.

Table 2. *Synthesis and Characteristics of* tin(IV) *Schiff Base Complexes*

S. No.	$SnCl_4$, g	Schiff base, g	Compound, yield (g), nature	Analyses (%) Sn Found (Calcd.)	Cl Found (Calcd.)	N Found (Calcd.)	Molar conductance (ohm^{-1} cm^2 mol^{-1})
1	1.68	$C_7H_{13}NO$ 1.65	$SnCl_4(C_7H_{13}NO)_2$ (3.30), yellowish white solid.	23.49 (23.08)	28.13 (27.60)	5.84 (5.44)	8.60
2	1.42	$C_8H_{15}NO$ 1.54	$SnCl_4(C_8H_{15}NO)_2$ (2.89), pale yellow semi solid.	22.12 (21.89)	26.20 (26.17)	5.30 (5.16)	8.41
3	2.54	$C_9H_{17}NO$ 2.98	$SnCl_4(C_9H_{17}NO)_2$ (5.52), yellow solid.	20.13 (20.81)	25.11 (24.89)	4.81 (4.90)	8.50
4	2.79	$C_{17}H_{13}NO$ 5.30	$SnCl_4(C_{17}H_{13}NO)_2$ (7.99), yellow solid.	15.21 (15.72)	18.67 (18.81)	1.71 (1.85)	8.81
5	0.93	$C_{13}H_{13}NO$ 1.42	$SnCl_4(C_{13}H_{13}NO)_2$ (2.26), green solid.	18.39 (18.03)	21.90 (21.57)	3.93 (4.25)	6.49
6	1.18	$C_{15}H_{17}NO$ 2.05	$SnCl_4(C_{15}H_{17}NO)_2$ (3.2), yellow solid.	16.31 (16.62)	20.34 (19.87)	4.00 (3.91)	6.11
7	1.34	$C_{15}H_{17}NO$ * 2.34	$SnCl_4(C_{15}H_{17}NO)_2$ * (3.60), yellow solid.	16.98 (16.62)	20.56 (19.87)	4.23 (3.91)	6.43

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* Has been used to distinguish between the compounds of same formula.

copper turnings and redistilled before use. Dimethylformamide (BDH) was purified as described earlier[4]. The middle fraction boiling at 55 ± 1 °C/35 mm was collected and stored in blackened and stoppered pyrex flasks. The specific conductivity of the solvent was found to be 0.5–1.5×10^{-7} ohm^{-1} cm^{-1} at 25 ± 1 °C.

Preparation of Schiff bases

Schiff bases of pentane-2,4-dione were prepared by mixing the reactants i.e. pentane-2,4-dione and alkylamines in equimolar ratio in presence of benzene and refluxing for several hours, followed by the removal of water—benzene azeotrope. These were distilled before use.

Schiff bases of 2-hydroxy-1-naphthaldehyde were obtained by taking equimolar amounts of 2-hydroxy-1-naphthaldehyde and amines in presence of ethanol. The exothermic reactions resulted in formation of yellow crystalline products, which were recrystallized from the solvent. The analyses and physical properties of the Schiff bases are recorded in table 1.

Synthesis of tin(IV) Schiff base complexes

Reactions of tin(IV) chloride with the Schiff bases in 1 : 2 molar ratio have been carried out. $SnCl_4$ was dissolved in benzene and the calculated amount of the Schiff base was then slowly added with constant shaking. In those cases, where the Schiff base was insoluble in cold benzene, it was first dissolved by refluxing and then the solution was cooled. An exothermic reaction took place and the solid compound separated out immediately. After decanting off the solvent, the resulting solids were repeatedly washed with benzene. The solvent was then removed in vacuo and the products were finally dried at 40–60 °C/0.5 mm for 3–4 hours. The resulting derivatives are insoluble in most of the common organic solvents but soluble in *DMF*. Their analyses, physical properties and molar conductance are given in table 2.

Analytical methods and physical measurements

Tin was estimated gravimetrically as tin oxide. Chlorine was determined as AgCl and N by the *Kjeldahl's* method.

The conductance measurements were made with a Tesla RLC bridge using a cell having cell constant 0.74 cm^{-1}.

The infrared spectra of the Schiff bases and their complexes in nujol mulls were recorded on a Perkin Elmer 337 Grating IR spectrophotometer in the range, 4,000–400 cm^{-1}.

Results and Discussion

The non-electrolytic nature of these complexes is indicated by the low molar conductance values as determined in *DMF* at $10^{-3}M$ concentration and 25 ± 1 °C and these fall in the range 6.11–8.81 ohm^{-1} cm^2 mol^{-1} (Table 2). The complexes are sparingly soluble in benzene and hence their molecular weights could not be determined ebullioscopically.

In these reactions, $SnCl_4(SBH)_2$ type of complexes could only be isolated. Even 1 : 1 and other molar ratio reactions were found to yield this type of derivatives.

Table 3. *Infrared Absorption Frequencies (in* cm^{-1}*) of the Schiff Bases and their* tin(IV) *Complexes*

Schiff base	ν C=N	ν O—H	ν N—H	Tin(IV) complex	ν C=N	ν O—H	ν N—H
$C_7H_{13}NO$	1605	3475 mb	3275 mb	$SnCl_4(C_7H_{13}NO)_2$	1612	3250 mb	3200 m
$C_8H_{15}NO$	1608	3400 mb	3160 mb	$SnCl_4(C_8H_{15}NO)_2$	1615	3350 mb	3200 m
$C_9H_{17}NO$	1605	3406 mb	3160 mb	$SnCl_4(C_9H_{17}NO)_2$	1615	3350 mb	3200 m
$C_{17}H_{13}NO$	1615	—	—	$SnCl_4(C_{17}H_{13}NO)_2$	1635	3400 mb	—
$C_{13}H_{13}NO$	1615	—	—	$SnCl_4(C_{13}H_{13}NO)_2$	1645	3400 mb	—
$C_{15}H_{17}NO$	1615	—	—	$SnCl_4(C_{15}H_{17}NO)_2$	1635	3350 mb	—
$C_{15}H_{17}NO$ *	1615	—	—	$SnCl_4(C_{15}H_{17}NO)_2$ *	1645	3400 mb	—

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* Has been used to distinguish between the compounds of same formula.

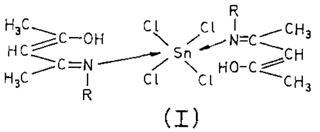
Coordination of the azomethine nitrogen to the tin atom is probably indicated by the shift of ν C=N frequency towards higher side[7]. In the IR spectra of Schiff bases, a strong band due to ν C=N appears at ≈ 1,605 cm^{-1} in pentane-2,4-dione imines and ≈ 1,615 cm^{-1} in 2-hydroxy-1-naphthaldehyde imines, whereas in the tin complexes this band is observed at ≈ 1615 cm^{-1} and ≈ 1,640 cm^{-1} resp. (Table 3).

Pentane-2,4-dione imines can exist as keto as well as enol tautomers and the appearance of bands at ≈ 3,400 cm^{-1} and ≈ 3,200 cm^{-1} may be ascribed to the hydrogen bonded O—H and N—H resp. These bands also appear in the case of their tin(IV) complexes indicating the presence of O—H and N—H groups in these derivatives.

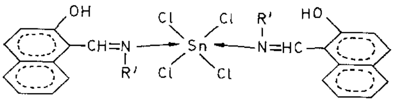
In the case of Schiff bases of 2-hydroxy-1-naphthaldehyde, no such absorption bands are observed as due to strong hydrogen bonding, the O—H stretching frequency is appreciably lowered and probably overlaps with ν C—H vibrations. However, ~~in the tin(IV)~~ complexes medium intensity bands appear at ≈ 3400 cm^{-1} showing the presence of the OH group. The noncoordinating nature of the phenolic OH group has also been reported in the complexes of tin(IV) chloride with salicylaldehyde and 2-hydroxy-1-naphthaldehyde and only 1 : 2 complexes could be isolated[8].

If only the nitrogen of the azomethine group may coordinate then in the 1 : 1 complex the metal atom will be pentacoordinated. However, nonformation of 1 : 1 complexes probably indicates the unstable nature of the pentacoordination state for the tin atom as reported earlier also[7–9].

In view of the nonelectrolytic nature and hexacovalency of tin(IV) in these newly synthesized 1 : 2 complexes of pentane-2,4-dione imines (I) and 2-hydroxy-1-naphthaldehyde (II) the following probable structures may be indicated:



(I)



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