

Fig. 4—Differential capacitance curves for $7.5 \times 10^{-4} M$ Cd(II) in $1N H_2SO_4$ and varying concentration of thiophene ([Thiophene] = (a) $0.5 \times 10^{-2} M$; (b), 1.0 (c) 2.0 (d), 3.0 (e) $4.0 \times 10^{-2} M$)

TABLE 2—APPARENT STANDARD RATE CONSTANT (K_s AT $25^\circ C$, OF THE EXCHANGE Cd(II)/ Cd(Hg) IN $1N H_2SO_4$ AT DIFFERENT THIOPHENE CONCENTRATIONS

[Cd(II) = 7.5×10^{-4} g ion /litre]					
10^4 [Thiophene]	F	C_m	R_m	$\frac{R_r-1}{\omega_r}$	$K_s \times 10^3$
zero	1000	3.610	52	32	8.29
	3000	1.722	58	33	8.04
Zero + 2% ethanol	1000	3.203	68	40	6.69
	3000	1.130	58	42.5	6.31
0.5	1000	3.012	68	59	4.58
	3000	1.520	47	60.5	4.46
1.0	1000	2.804	95	61	4.35
	3000	1.503	70	64	4.15
2.0	1000	2.504	105	72	3.77
	3000	1.310	73	73.5	3.69
3.0	1000	2.300	110	80	3.42
	3000	1.090	77	82	3.34
4.0	1000	1.95	118	93	2.88
	3000	1.04	85	98	2.73

analysing vectorially the results of impedance measurements. This method is a simple one and has been used before to give reliable results⁹. The K_s values calculated for the exchange Cd(II)/Cd(Hg) in $1N H_2SO_4$ and $1N H_2SO_4 + 2\%$ alcohol and with different concentrations of thiophene are included in Table 2. In Table 2 are also given the various quantities involved in the calculation.

The results presented in Table 2 show that in $1N H_2SO_4$, the K_s values for the reduction of Cd(II) over the frequency range 1000-3000 Hz are highly satisfactory and the use of the simple model of faradaic impedance is quite justifiable under these conditions. The average K_s amounts to 8.16×10^{-2} cm/sec. This value agrees with those reported

earlier using different techniques in either neutral or acid sulphate media¹⁰⁻¹².

In $1N H_2SO_4 + 2\%$ alcohol as a base solution, the average K_s value amounts to 6.5×10^{-2} cm/sec. In the presence of thiophene, K_s values decrease with increasing thiophene concentration. This may be interpreted in terms of increase in the surface coverage by thiophene with increase in its concentration.

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Preparation & Characterization of a Few Coordination Compounds of Titanium(IV) with Schiff Bases

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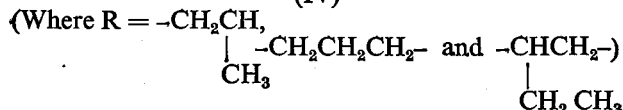
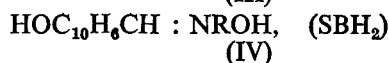
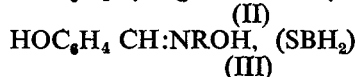
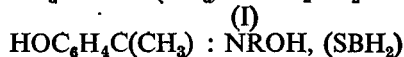
Titanium(IV) complexes of dibasic tridentate schiff bases formed by the condensation of 2,4-pentanedione, 2-hydroxyacetophenone, salicylaldehyde or 2-hydroxy-1-naphthaldehyde with 2-hydroxyethyl-, 2-hydroxy-1-propyl-, 3-hydroxy-1-propyl- and 1-hydroxy-2-butyl-amines have been prepared. The reactions between titanium isopropoxide, 4-(2-hydroxyethyl) amino-3-pentene-2-one (H_2acac) and the schiff bases (SBH_2) in 1:1:1 molar ratio result in the formation of several new derivatives of the type $Ti(acac)(SB)$ in quantitative yields. The mixed complexes are monomeric in boiling chloroform. The coordination of oxygen (phenolic and alcoholic) and azomethine nitrogen of the schiff base to the metal atom is confirmed on the basis of infrared and proton magnetic resonance spectral studies.

REACTIONS of titanium alkoxides with nitrogen containing ligands have been studied¹⁻⁵. However, the reactions of mixed ketamines and aldimines with titanium isopropoxide have not been investi-

TABLE I — ANALYTICAL DATA OF MIXED COMPLEXES OF TITANIUM

Mol. formula of mixed complex	Found (%) (Calc.)			
	Ti	C	H	N
MIXED COMPLEXES OF SCHIFF BASES(I) AND (II)				
Ti(C ₇ H ₁₁ O ₂ N) (C ₁₁ H ₁₅ O ₂ N)	12.60(12.61)	56.71(56.80)	6.25(6.31)	7.32(7.36)
Ti(C ₇ H ₁₁ O ₂ N) (C ₁₁ H ₁₅ O ₂ N)	12.50(12.61)	56.69(56.80)	6.35(6.31)	7.40(7.36)
Ti(C ₇ H ₁₁ O ₂ N) (C ₁₁ H ₁₅ O ₂ N)	12.21(12.16)	58.01(57.82)	6.71(6.59)	7.21(7.10)
MIXED COMPLEXES OF SCHIFF BASES (I) AND (III)				
Ti(C ₇ H ₁₁ O ₂ N) (C ₁₀ H ₁₁ O ₂ N)	12.98(13.09)	54.90(55.68)	5.55(5.61)	7.63(7.64)
Ti(C ₇ H ₁₁ O ₂ N) (C ₁₀ H ₁₁ O ₂ N)	12.95(13.09)	55.42(55.68)	6.62(5.61)	7.59(7.64)
Ti(C ₇ H ₁₁ O ₂ N) (C ₁₁ H ₁₅ O ₂ N)	12.58(12.61)	56.23(56.80)	6.34(6.31)	7.32(7.36)
MIXED COMPLEXES WITH SCHIFF BASES(I) AND (IV)				
Ti(C ₇ H ₁₁ O ₂ N) (C ₁₁ H ₁₅ O ₂ N)	11.43(11.52)	60.41(60.52)	5.79(5.76)	6.75(6.72)
Ti(C ₇ H ₁₁ O ₂ N) (C ₁₁ H ₁₅ O ₂ N)	11.55(11.52)	60.32(60.52)	5.82(5.76)	6.70(6.72)
Ti(C ₇ H ₁₁ O ₂ N) (C ₁₁ H ₁₅ O ₂ N)	11.20(11.14)	61.30(61.34)	6.01(6.04)	6.43(6.50)

gated earlier. It was, therefore, of interest to synthesize such coordination compounds of titanium with schiff bases (I-IV). I was derived from 2,4-pentanedione and 2-hydroxyethylamine; II from 2-hydroxyacetophenone and 2-hydroxy-1-propyl-, 3-hydroxy-1-propyl-and-1-hydroxybutyl-amines; III from salicylaldehydes and the above three amines; and IV from 2-hydroxy-1-naphthaldehyde and the above amines.



To titanium isopropoxide in dry benzene was added calculated amounts of H₂acac and SBH₂. The contents were refluxed and the isopropanol liberated collected azeotropically with benzene. The progress of the reaction was ascertained by estimating the amount of isopropanol in the azeotrope. After removing the solvent over pump, the products were dried at 40-50°/0.5 mm for 2-3 hr. The compounds obtained are listed in Table 1.

All the derivatives Ti(acac)(SB) are coloured solids, soluble in chloroform, DMF and DMSO and are nonelectrolytes in DMF. These have been found to be monomeric in boiling chloroform.

The coordination of central titanium atom to oxygen and probably to nitrogen of the ligand moiety can be substantiated by the absence of IR absorptions in the region 3350-3100 cm⁻¹ where broad bands are observed in the spectra of schiff bases. Further, bands of medium intensity in the titanium complexes in the region 650-600 cm⁻¹ may be assigned to ν

(Ti-O) vibrations⁷. A strong band ~1620 cm⁻¹ in all the schiff bases due to ν C=N shifts (Δν = 10cm⁻¹) to lower wave number in the spectra of the complexes, indicating coordination of azomethine nitrogen to central titanium atom. Bands of medium to strong intensity in the titanium complexes in the region 550±20 cm⁻¹ may be assigned to ν (Ti-N)⁸.

Further, the bonding of oxygen and nitrogen atoms of the ligand moiety to titanium atom is supported by the PMR spectra of N-(2-hydroxyethyl) amino-3-pentene-2-one (H₂acac), N-(2-hydroxy-1-propyl) salicylaldimine (H₂A), N-(3-hydroxy-1-propyl) salicylaldimine (H₂B) and N-(1-hydroxy-2-butyl) salicylaldimine (H₂C) as well as their titanium complexes.

In the case of schiff bases H₂A, H₂B and CH₂, the signals in the regions δ 8.70-9.45 and 2.40-3.39 may be assigned to the phenolic OH and alcoholic OH respectively. Schiff base, H₂acac shows a signal at δ 11.15 attributable to the hydrogen bonded NH. The disappearance of these signals in the spectra of the corresponding titanium complex supports coordination through oxygen and nitrogen atoms. The signals for the azomethine protons at δ 7.98, 8.05 and 8.55 in these schiff bases shift downfield in the titanium complexes (at δ 8.3, 8.52 and 9.0) showing their deshielding and which is possibly due to the donation of lone pair of electrons by azomethine nitrogen to titanium atom resulting in the formation of metal-nitrogen coordinate linkage.

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Aldimine & Ketamine Derivatives of Titanium(IV)

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Reactions of titanium isopropoxide with aldimines and ketamines in equimolar ratios have been carried out. The products have been obtained in almost quantitative yields and characterized on the basis of elemental analyses, molecular weight determinations, exchange reactions, conductance measurements and IR, PMR and UV spectral data.

IN continuation of our earlier work^{1,2} on the reactions of titanium(IV) isopropoxide with a few bibasic tri- and tetra-dentate schiff bases, we describe in this note the preparation and characterization of the products obtained by the reaction of titanium isopropoxide (1:1 molar ratio) with schiff bases containing ONNO donor system. The ligands were obtained by the condensation of salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2,4-pentanedione or 2-hydroxyacetophenone with 1,2-propylenediamine or 1,3-propylenediamine.

Synthesis of titanium derivatives—To titanium isopropoxide (0.70-0.95 g) in anhydrous benzene (40 ml) was added the calculated amount of the schiff base (0.58-1.27 g) and the mixture refluxed over a fractionating column and the isopropanol liberated in the reaction collected azeotropically with benzene. The progress of the reaction was ascertained by the estimation of isopropanol periodically in the azeotrope. On its completion (8-10 hr), the solvent was removed and the products were dried under reduced pressure after repeated washing with ether/*n*-hexane (yield 80%). The analysis and physical properties are recorded in Table 1.

Interchange reactions of bis(isopropoxy)titanium(IV)-schiff base derivatives with 2-methylpentane-2,4-diol—2-Methylpentane-2,4-diol was mixed in 1:1 molar ratio with the benzene solution of bis(isopropoxy)titanium(IV)-schiff base derivative. The contents were refluxed under a fractionating column and the azeotrope collected slowly till the distillate attained a constant temperature (80°). The resulting products were dried *in vacuo* (Table 1).

Ti(OPrⁱ)₂(SB) type of products were obtained by the reactions of titanium isopropoxide and the schiff bases (SBH₂) in 1:1 molar ratio. However, the reaction when carried out in 1:2 molar ratio gave Ti(OPrⁱ)(SB) (SBH) type of derivatives, instead of the expected Ti(SB)₂.

All the newly synthesized derivatives are coloured solids or semi-solids and soluble in DMF. Due to the presence of two isopropoxy groups, these are susceptible to hydrolysis in air. The molecular weight determinations show them to be monomeric in nature.

Further, Ti(OPrⁱ)₂(SB) reacted with bibasic tridentate schiff base (S'B'H₂) having ONO donor system in 1:1 molar ratio, to give products of the type Ti(S'B')(SB). These were also found to be monomeric in nature.

The two isopropoxy groups in Ti(OPrⁱ)₂(SB) undergo replacement reactions with 2-methylpentane-2,4-diol. The resulting mixed derivatives are also monomeric in nature, quite soluble in DMF and behave as nonelectrolytes. However, as compared to the bis(isopropoxy)titanium(IV)-schiff base derivatives, these are quite resistant to hydrolysis and melt/decompose at higher temperatures.

The molar conductances of these derivatives in DMF show them to be nonelectrolytes.

The infrared spectra of the titanium(IV) derivatives and of the ligands indicate coordination of the ligands through azomethine nitrogen³ and phenolic oxygen^{4,5} as revealed by shift in $\nu_{C=N}$ and ν_{C-O} from

TABLE 1 — PHYSICAL PROPERTIES AND ANALYSES OF Ti(OPrⁱ)₂(SB) AND Ti(C₆H₁₂O₂)(SB) TYPE OF COMPLEXES

Compound and nature	Found (%) (Calc.)			
	Ti	C	H	N
<i>Compounds of schiff bases derived from 1,2-propylenediamine</i>				
Ti(OPr ⁱ) ₂ (C ₁₇ H ₁₆ N ₂ O ₂)	10.73	61.88	6.70	6.20
Orange foamy, m.p. 282°	(10.75)	(61.90)	(6.72)	(6.28)
Ti(C ₆ H ₁₂ O ₂)(C ₁₇ H ₁₆ N ₂ O ₂)	10.82	62.11	6.28	6.34
Orange m.p. 185°	(10.80)	(62.16)	(6.30)	(6.31)
Ti(OPr ⁱ) ₂ (C ₂₅ H ₂₀ N ₂ O ₂)	8.77	68.01	6.18	5.19
Dirty yellow, m.p. 320°	(8.78)	(68.13)	(6.23)	(5.13)
Ti(C ₆ H ₁₂ O ₂)(C ₂₅ H ₂₀ N ₂ O ₂)	8.80	68.50	5.90	5.21
Yellow foamy, m.p. 128°	(8.82)	(68.37)	(5.88)	(5.15)
Ti(OPr ⁱ) ₂ (C ₁₃ H ₂₀ N ₂ O ₂)	11.96	57.00	8.50	6.90
Reddish brown semi-solid	(11.93)	(56.71)	(8.46)	(6.96)
Ti(C ₆ H ₁₂ O ₂)(C ₁₃ H ₂₀ N ₂ O ₂)	11.93	56.80	8.01	7.08
Yellow, m.p. 104°	(11.99)	(56.99)	(7.99)	(7.00)
Ti(OPr ⁱ) ₂ (C ₁₉ H ₂₀ N ₂ O ₂)	10.15	63.25	7.15	5.95
Light yellow, m.p. 293-4°d	(10.12)	(63.28)	(7.17)	(5.90)
Ti(C ₆ H ₁₂ O ₂)(C ₁₉ H ₂₀ N ₂ O ₂)	10.10	63.37	6.95	5.97
Yellow, m.p. 305°d	(10.16)	(63.57)	(6.78)	(5.93)
<i>Compounds of schiff bases derived from 1,3-propylenediamine</i>				
Ti(OPr ⁱ) ₂ (C ₁₇ H ₁₆ N ₂ O ₂)	10.71	61.80	6.66	6.20
Orange foamy, m.p. 207°	(10.75)	(61.90)	(6.72)	(6.28)
Ti(C ₆ H ₁₂ O ₂)(C ₁₇ H ₁₆ N ₂ O ₂)	10.85	62.00	6.39	6.39
Reddish yellow, m.p. 202°	(10.80)	(62.16)	(6.30)	(6.31)
Ti(OPr ⁱ) ₂ (C ₂₅ H ₂₀ N ₂ O ₂)	8.73	68.00	6.35	5.20
Yellow, m.p. 158°	(8.78)	(68.13)	(6.23)	(5.13)
Ti(C ₆ H ₁₂ O ₂)(C ₂₅ H ₂₀ N ₂ O ₂)	8.79	68.40	5.78	5.20
Yellow, m.p. 169°	(8.82)	(68.37)	(5.88)	(5.15)
Ti(OPr ⁱ) ₂ (C ₁₃ H ₂₀ N ₂ O ₂)	11.92	56.67	8.45	6.88
Brown, m.p. 242° (d)	(11.92)	(56.71)	(8.46)	(6.96)
Ti(C ₆ H ₁₂ O ₂)(C ₁₃ H ₂₀ N ₂ O ₂)	11.94	57.10	7.70	7.10
Yellow, m.p. 303°	(11.99)	(56.99)	(7.99)	(7.00)
Ti(OPr ⁱ) ₂ (C ₁₉ H ₂₀ N ₂ O ₂)	10.08	63.05	7.12	5.86
Yellow foamy, m.p. 116°	(10.12)	(63.28)	(7.17)	(5.90)
Ti(C ₆ H ₁₂ O ₂)(C ₁₉ H ₂₀ N ₂ O ₂)	10.19	63.55	6.76	5.96
Yellow, m.p. 284°	(10.16)	(63.56)	(6.78)	(5.93)