pro kg Lösung in dem Gebiet, wo $c_D > c_A$ ist. Die nach (8) erwartete Linearität reicht von hohen Donatorkonzentrationen bis zu 61,0 Mol-% P_4. Aus Abb. 4 kann die Assoziationskonstante als negative Geradensteigung abgelesen werden zu $K_g = (0{,}031 \pm 0{,}002)$ kg/Mol. Extrapolation von Δ/c_D gegen Null ergibt relativ zu reinem PBr_3 eine Verschiebung des Komplexes von $\Delta_0 = +(42 \pm 2)$ ppm. Die Fehlerangaben beziehen sich auf die Ablesegenauigkeit von K_g und Δ_0 aus der $\Delta/c_D - \Delta$-Geraden. Die Assoziationskonstante in Molenbruch-einheiten errechnet sich nach Gl. (9) zu $K_m = 0{,}25 \pm 0{,}02$. Dieser Wert in Gl. (6) eingesetzt, ergibt innerhalb der Fehlergrenzen mit PBr_3 als Standard für die chemische Verschiebung des Komplexes den aus Abb. 4 ermittelten Wert.

Titanium(IV) Complexes of Bifunctional Tridentate or Tetradentate Schiff Bases

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Reactions of titanium isopropoxide with bifunctional tridentate Schiff bases, such as salicylidene-*o*-aminophenol, acetylacetone-*o*-aminophenol and benzoylacetone-*o*-aminophenol and bifunctional tetradentate Schiff bases, such as bis-acetylacetone ethylenediimine, bis-benzoylacetone ethylenediimine, bis-salicylaldehyde ethylenediamine and glyoxal-*o*-aminohpenol have been investigated in different stoichiometrc ratios. The resulting products $Ti(OPr^i)_2(SB)$, $Ti(SB)_2$, $Ti(OPr^i)_2(S'B')$, $Ti(OPr^i)_2(S''B'')$ and $Ti(OPr^i)(S''B'')(S''B''H)$ (where SBH_2 = bifunctional tridentate Schiff base, $S'B'H_2$ = bis-acetylacetone or bis-benzoylacetone ethylenediimine and $S''B''H_2$ = bis-salicylaldehyde ethylenediamine or glyoxal-*o*-aminophenol) have been isolated in almost quantitative yields. The molecular weights of the products soluble in benzene have been determined ebullioscopically and plausible structure indicated. The thermogravimetric analysis of the salicylidine-*o*-aminophenol derivatives has also been carried out.

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Titanium(IV) derivatives of different types of Schiff bases appear to be quite interesting. In earlier publications[1] from these laboratories, the synthesis of some new titanium(IV) derivatives of bifunctional tridentate Schiff bases and their important properties were reported. In the present study, some new compounds of titanium(IV) with bifunctional tridentate or tetradentate Schiff bases have been synthesized with a view to make comparative studies of the resulting derivatives. Very recently, BRADLEY et al.[2] have also reported some novel Ti(IV)-Schiff base compounds and confirmed the structure of one of these derivatives with the help of X-ray crystallography.

In general, the reactions of titanium isopropoxide with bifunctional tridentate Schiff bases in 1 : 1 and 1 : 2 molar ratios may be represented as given below:

$$Ti(OPr^i)_4 + SBH_2 \rightarrow Ti(OPr^i)_2(SB) + 2\,Pr^iOH\uparrow.$$

$$Ti(OPr^i)_4 + 2\,SBH_2 \rightarrow Ti(SB)_2 + 4\,Pr^iOH\uparrow.$$

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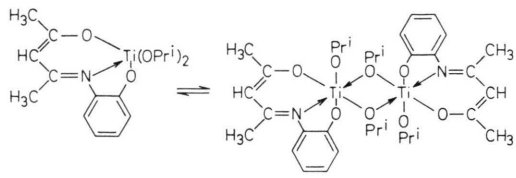
[1] P. PRASHAR and J. P. TANDON, J. Less-Common Metals **13**, 541 [1967]

[2] D. C. BRADLEY, M. B. HURSTHOUSE, and I. F. RENDALL, Chemical Communication **13**, 672 [1969].

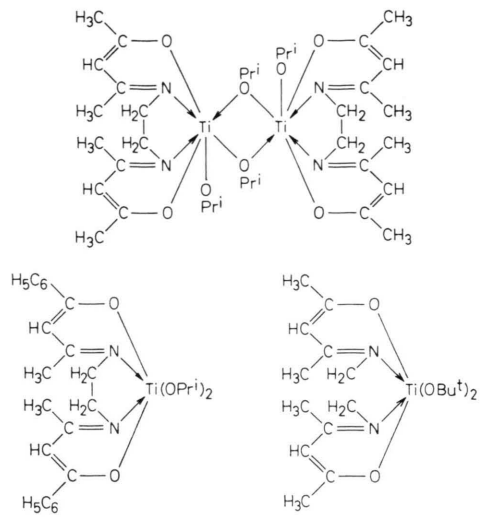
Heat was evolved and immediately a red coloured compound started separating when the Schiff base was added to the benzene solution of titanium isopropoxide. The resulting derivatives were found to be almost insoluble or sparingly soluble in benzene. However, diisopropoxy titanium(IV) acetylacetone-*o*-aminophenol compound was found to be quite soluble in benzene and showed a molarity of 1.5. Probably, an equilibrium exists between the monomer and dimer species as shown below:



The reactions of titanium isopropoxide with bis-acetylacetone ethylenediimine or bis-benzoylacetone ethylenediimine in 1 : 1 molar ratio may be shown as follows:

$$Ti(OPr^i)_4 + S'B'H_2 \rightarrow Ti(OPr^i)_2(S'B') + 2\,Pr^iOH\uparrow.$$

The reactions were also carried out in 1 : 2 molar ratio and the resulting product dried under vacuum. The analysis corresponded to the formula, $Ti(OPr^i)_2(S'B')(S'B'H_2)$. On being washed with ether a yellow filtrate of the Schiff base itself was obtained and the analysis of the resulting compound corresponded to $Ti(OPr^i)_2(S'B')$. It, therefore, shows that even with excess of the Schiff base, diisopropoxy titanium(IV)-Schiff base compound is the final product. The molecular weights of the diisopropoxy titanium(IV) bis-acetylacetone ethylenediimine and diisopropoxy titanium(IV) bis-benzoylacetone ethylenediimine corresponded to the monomeric and dimeric state respectively. Probably, the monomeric nature in the latter case is due to the presence of bulkier phenyl group. This could further be confirmed by reacting the benzene solution of diisopropyoxy titanium(IV) bis-acetylacetone ethylenediimine with excess of tertiary butanol. The resulting compound, tertiary dibutoxy titanium(IV) bis-acetylacetone ethylenediimine was found to be a monomer. This also indicates that in the diisopropoxy titanium(IV) bis-acetylacetone ethylenediimine, the dimerization takes place through the bridging isopropoxy groups[1]. Their probable structure may be indicated as follows:



The reactions of titanium isopropoxide with bis-salicylaldehyde ethylenediamine and glyoxal-*o*-aminophenol were also carried out in molar ratios of 1 : 1 and 1 : 2. The resulting derivatives were of the type, $Ti(OPr^i)_2(S''B'')$ and $Ti(OPr^i)(S''B'')(S''B''H)$. With a view to prepare compounds of the type $Ti(S''B'')_2$, 1 : 2 molar reactions were also carried out in presence of excess of Schiff base or *p*-toluene sulphonic acid as catalyst, but were found to be unsuccessful.

The TGA curve (fig. 1, curve A) of the Schiff base salicylidene-*o*-aminophenol does not show any effect upto a temperature of 160 °C. Thereafter a heavy loss in the weight was recorded, which is probably due to the sublimation of the Schiff base itself.

Diisopropoxy titanium(IV) salicylidene-*o*-aminophenol was found to be stable upto 400 °C and thereafter a rapid decomposition was observed upto 460 °C. Finally, it gets converted into TiO_2 at 690 °C (fig. 1, curve B).

The TGA curve (fig. 1, curve C) of titanium (IV) bis-salicylidene-*o*-aminophenol is almost similar to that of diisopropoxy titanium(IV) salicylidene-*o*-aminophenol. However, the complete conversion into TiO_2 takes place at 980 °C.

Experimental Section

Titanium isopropoxide was prepared by the ammonia method[3]. It was distilled out (101 °C/8 mm) and then analysed:

Calc. for $Ti(OPr^i)4$: Ti 16.85 OPr^i 83.15,
Found: Ti 16.71 OPr^i 82.15.

Schiff base		Analysis C [%]	H [%]	N [%]	Physical characteristics
Salicylidene-*o*-aminophenol	(a)	73.00	5.20	6.54	Orange solid, m.p. 188—189 °C,
($C_{13}H_{11}NO_2$)	(b)	73.21	5.20	6.57	sublimed at 188—190 °C/1.5—2.0 mm
Acetylacetone-*o*-aminophenol	(a)	68.83	6.81	7.25	Yellow needles, m.p. 189—191 °C
($C_{11}H_{13}NO_2$)	(b)	69.10	6.85	7.32	
Benzoylacetone-*o*-aminophenol	(a)	76.00	5.89	5.46	Yellow solid, m.p., 163—165 °C
($C_{16}H_{15}NO_2$)	(b)	75.84	5.97	5.53	
Bis-acetylacetone ethylene-diimine	(a)	64.03	8.91	12.39	Straw coloured solid, m.p.,
($C_{12}H_{20}N_2O_2$)	(b)	64.27	8.98	12.48	118—119 °C.
Bis-benzoylacetone ethylene-diimine	(a)	75.97	6.92	7,97	Colourless solid, m.p., 180—181 °C.
($C_{22}H_{24}N_2O_2$)	(b)	75.82	6.94	8.04	
Bis-salicylaldehyde ethylene-diamine	(a)	71.32	6.03	10.31	Yellow solid, m.p., 140—142 °C
($C_{16}H_{16}N_2O_2$)	(b)	71.60	6.01	10.43	
Glyoxal-*o*-aminophenol	(a)	69.69	5.07	11.57	Colourless solid, m.p. ,213—215 °C
($C_{14}H_{12}N_2O_2$)	(b)	69.98	5.03	11.66	

Table 1. Schiff bases and their analyses. (a) = analysis of the compound. (b) = calculated for the formula.

Isopropanol (B.D.H.) was dried over sodium and then fractionated over aluminium isopropoxide. Benzene (B.D.H.) was dried over sodium wire, followed by azeotropic fractionation in presence of ethanol. All the Schiff bases were prepared by direct condensation of aldehydes or ketones with apropriate amines in absolute alcohol and recrystallized from the same solvent, except salicylidene-*o*-aminophenol, which was sublimed. Their physical properties and analyses are recorded in Table 1.

Thermogravimetric analysis was carried out on a Stanton (Massflow type) Automatic Recording Thermogravimetric Balance. The weighed quantity of the sample was heated under a controlled rate of heating (4 °C/min).

Titanium was determined by the dioxide method and nitrogen by the Kjeldahl method. Isopropanol was determined by oxidation with normal dichromate in 12.5% sulphuric acid [4].

Titanium isopropoxide [g]	Schiff base [g]	Molar ratio	Condition and time [h]	Product and state [g]	Amount of isopropanol in the azeotrope [g]	Analysis Ti [%]	N [%]	Remarks
1.46	Salicylidene-*o*-aminophenol ($C_{13}H_{11}NO_2$), 1.11	1:1	Refluxed 3	$Ti(OPr^i)_2(C_{13}H_9NO_2)$ Red solid (1.85)	(a) 0.60 (b) 0.62	12.52 12.69	3.67 3.71	On heating no change up to 270 °C
1.39	Salicylidene-*o*-aminophenol ($C_{13}H_{11}NO_2$), 2.10	1:2	Refluxed 5	$Ti(C_{13}H_9NO_2)_2$ Red solid (2.13)	(a) 1.14 (b) 1.17	10.20 10.18	5.88 5.96	On heating no change up to 270 °C
1.67	Acetylacetone-*o*-aminophenol ($C_{11}H_{13}NO_2$), 1.12	1:1	Refluxed 1½	$Ti(OPr^i)_2(C_{11}H_{11}NO_2)$ Red sticky solid (2.02)	(a) 0.70 (b) 0.71	13.37 13.48	3.89 3.94	Molarity: 1.5
1.36	Acetylacetone-*o*-aminophenol ($C_{11}H_{13}NO_2$), 1.83	1:2	Refluxed 5	$Ti(C_{11}H_{11}NO_2)_2$ Red solid (2.00)	(a) 1.13 (b) 1.15	11.12 11.23	6.53 6.56	On heating no change up to 240 °C and then decomposed
1.28	Benzoylacetone-*o*-aminophenol ($C_{16}H_{15}NO_2$), 1.16	1:1	Refluxed 3½	$Ti(OPr^i)_2(C_{16}H_{13}NO_2)$ Red solid (1.79)	(a) 0,54 (b) 0.54	11.40 11.48	3.32 3.35	On heating no change up to 270 °C
0.79	Benzoylacetone-*o*-aminophenol ($C_{16}H_{15}NO_2$), 1.42	1:2	Refluxed 6½	$Ti(C_{16}H_{13}NO_2)_2$ Red solid (1.52)	(a) 0.65 (b) 0.66	8.67 8.69	5.06 5.08	On heating no change up to 270 °C

Table 2. Reactions of titanium isopropoxide with the bifunctional tridentate Schiff bases in benzene. (a) = analysis of the compound. (b) = calculated for the formula.

[3] D. C. Bradley, R. C. Mehrotra, and W. Wardlaw, J. Chem. Soc. [London] **1952**, 2027.

[4] D. C. Bradley and W. Wardlaw, J. Chem. Soc. [London] **1950**, 3450.

Reactions

The reactions of titanium isopropoxide with the Schiff bases in different molar ratios were carried out in the medium of anhydrous benzene. The isopropanol liberated in these reactions was collected azeotropically and estimated. The products were rendered free of solvent under reduced pressure and then finally dried. Some of these derivatives were recrystallized either from benzene or isopropanol. The experimental details of the synthesis of the different derivatives are recorded in Tables 2 and 3.

Reaction of diisopropoxy titanium(IV) bis-acetylacetone ethylenediimine and excess of tertiary butanol in benzene

A benzene solution of diisopropoxy titanium(IV) bis-acetylacetone ethylenediimine (1.98 g) and excess of tert. butanol (8 g) were refluxed for 10 h in a fractionating column, and the isopropanol-benzene azeotrope was removed slowly. The resulting product was made free from solvent and dried under reduced pressure (0.1 mm) for 3 hours. A brown solid (2.05 g) soluble in benzene resulted. It was then analysed, Found: Isopropanol in azeotrope, 0.59 g (2 moles require 0.60 g).

Calc. for $Ti(Bu^t)_2(C_{12}H_{18}N_2O_2)$:

Ti 11.51 N 6.73. Molecular Wt. 416.2,

Found:

Ti 11.49 N 6.70. Molecular Wt. 435.6.

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Titanium isopropoxide [g]	Schiff base [g]	Molar ratio	Condition and time [h]	Product and state [g]	Amount of isopropanol in the azeotrope [g]	Analysis Ti [%]	Analysis N [%]	Remarks
1.03	Bis-acetylacetone ethylenediimine ($C_{12}H_{20}N_2O_2$), 0.82	1:1	Refluxed 5	$Ti(OPr^i)_2(C_{12}HN_2O_2)$ Brown solid (1.40)	(a) 0.43 (b) 0.44	12.33 12.34	7.30 7.22	Softened at 68 °C and melted at 75 °C It then soon decomposed. Molarity: 1.9.
1.03	Bis-acetylacetone ethylendiimine ($C_{12}H_{20}N_2O_2$), 1.63	1:2	Refluxed 5	$Ti(OPr^i)_2(C_{12}HN_2O_2)$ -($C_{12}H_{20}N_2O_2$) Brown solid (2.13)	(a) 0.43 (b) 0.44	8.09 7.83	9.32 9.15	Washed with ether, dried in vacuuo and analysed, found: Ti 12.32%; N 7.34%.
1.05	Bis-benzoylacetone ethylenediimine ($C_{22}H_{24}N_2O_2$), 1.30	1:1	Refluxed 5	$Ti(OPr^i)_2(C_{22}H_{22}N_2O_2)$ Brown solid (1.90)	(a) 0.44 (b) 0.44	9.25 9.35	5.38 5.46	Softened at 90 °C and then decomposed on further heating. Molarity: 0.9.
0.57	Bis-benzoylacetone ethylenediimine ($C_{22}H_{24}N_2O_2$), 1.39	1:2	Refluxed 5	$Ti(OPr^i)_2(C_{22}H_{22}N_2O_2)$ ($C_{22}H_{24}N_2O_2$) Brown solid (1.70)	(a) 0.24 (b) 0.24	5.58 5.57	6.47 6.51	Washed with ether, dried in vacuuo and analysed. Found: Ti 9.24%; N 5.40%.
0.95	Bis-salicylaldehyde ethylenediimine ($C_{16}H_{16}N_2O_2$), 0.89	1:1	Refluxed 4	$Ti(OPr^i)_2(C_{16}H_{14}N_2O_2)$ Reddish black solid (1.44)	(a) 0.42 (b) 0.43	10.92 11.08	6.41 6.47	Softened at 120 °C and then decomposed at 155 °C.
1.06	Bis-salicylaldehyde ethylenediamine ($C_{16}H_{16}N_2O_2$), 2.00	1:2	Refluxed 6	$Ti(OPr^i)(C_{16}H_{14}N_2O_2)$ -($C_{16}H_{15}N_2O_2$) Reddish black solid (2.32)	(a) 0.66 (b) 0.67	7.40 7.47	8.76 8.76	Softened at 130 °C and then decomposed on further heating.
0.66	Glyoxal-*o*-aminophenol ($C_{14}H_{12}N_2O_2$), 0.56	1:1	Refluxed 5	$Ti(OPr^i)_2(C_{14}H_{10}N_2O_2)$ Purple solid (0.94)	(a) 0.28 (b) 0.28	11.80 11.85	6.90 6.93	On heating no change up to 270 °C.
1.05	Glyoxal-*o*-aminophenol ($C_{14}H_{12}N_2O_2$), 1.78	1:2	Refluxed 7	$Ti(OPr^i)(C_{14}H_{10}N_2O_2)$ - ($C_{14}H_{11}N_2O_2$) Purple solid (2.15)	(a) 0.88 (b) 0.89	8.25 8.20	9.75 9.59	On heating no change up to 270 °C.

Table 3. Reactions of titanium isopropoxide with the bifunctional tetradentate Schiff bases. (a) = analysis of the compound. (b) = calculated for the formula.