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Titanium(IV) Derivatives of N-[*o*-Hydroxy Substituted (or H) Benzyl] Glycines

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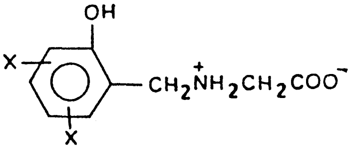
Several titanium(IV) derivatives of N-[*o*-hydroxy substituted (or H) benzyl] glycines have been prepared by the interaction of titanium tetraisopropoxide with the latter in 1 : 1, 1 : 2, 1 : 3 and 1 : 4 molar ratios in benzene medium. The compounds thus prepared were generally obtained as coloured solids, out of which those containing isopropoxy group(s) were found to be hygroscopic. All these compounds were characterized by azeotrope and elemental analyses, as well as by spectral measurements.

INTRODUCTION

In a systematic programme of work on preparation of organometallic/metallo-organic derivatives of N-[*o*-hydroxy substituted (or H) benzyl] glycines(I), several monobutyltin and monophenyltin derivatives of I have been reported earlier from these laboratories[1–3]. The work described here relates to the preparation of titanium(IV) derivatives of I, *viz.*, (*i*) N-(2-hydroxy benzyl) glycine (H_3hbg), (*ii*) N-(2-hydroxy-3-methyl benzyl) glycine (H_3hmbg-3) (*iii*) N-(2-hydroxy-6-methyl benzyl) glycine (H_3hmbg-6) and (*iv*) N-(2-hydroxy-5-methyl benzyl) glycine (H_3hmbg-5) by alcoholysis reaction[1–3] involving the interaction of titanium tetraisopropoxide with I in 1 : 1, 1 : 2, 1 : 3 and 1 : 4 molar ratios in benzene medium. The various compounds thus prepared were obtained as coloured solids and amongst them those containing isopropoxy group(s) were hygroscopic. All these compounds were characterized by azeotrope and elemental analysis, as well as by IR and PMR spectral measurements.



(Where X = $-H$ or $-CH_3$)
(I)

EXPERIMENTAL

Benzene (BDH, AR), isopropanol (BDH, Glaxo AnalaR) and solvent ether (E. Marck) were dried by standard procedures[4]. Titanium tetraisopropoxide (Merck-Schuchardt) was used as such, while N-[*o*-hydroxy substituted (or H) benzyl]-glycines were prepared employing already reported methods[1]. Titanium(IV) was estimated by a known method[5], whenever required.

The details of the glass apparatus used have been given before[1,2]. Stringent precautions were taken to exclude moisture throughout the experiments as earlier[1,2]. The melting points were recorded on a CAT no. 8103 digital m.p. apparatus. The IR spectra were taken in KBr pellets and recorded on a Perkin-Elmer Model-983 spectrometer, while the PMR spectra were taken in DMSO-d_6 solution and recorded on a Varian EM-390, 90 MHz spectrometer.

Reaction between $Ti(OPr^i)_4$ and H_3hmbg-5; 1 : 1 Molar ratio

A mixture $Ti(OPr^i)_4$ (0.9212 g, 3.2407 mmole) and H_3hmbg-5 (0.6324 g, 3.2394 mmole) suspended in dry benzene (60 mL) taken in a round-bottomed flask was refluxed on a wax bath at 95–100°C, using a fractionating column. After *ca.* 10 h of reflux, isopropanol liberated was fractionated out azeotropically and estimated by an oxidimetric method[6, 7] upon the completion of the reaction, the excess of solvent from the reaction mixture was removed in *vacuo*, when the product, $Ti(OPr^i)$(hmbg-5) isolated as a brownish orange solid, which was washed with dry benzene (3–4 times) followed by dry ether (2–3 times) and finally dried under suction. The compound was found to be soluble in carbon tetrachloride, dimethylsulphoxide and dimethylformamide, sparingly soluble in benzene and toluene, but insoluble in other common organic solvents.

It may be mentioned here that since $(Ti(OPr^i)_4$ is soluble in benzene, while H_3hmbg-5 is insoluble, the latter was taken in slightly less than the required stoichiometric amount in order to avoid contamination of impurities likely to occur by the unreacted H_3hmbg-5. The amount of isopropanol liberated was, therefore, calculated according to the amount of H_3hmbg-5 taken.

Similar procedures of preparation and purification were adopted in case of other derivatives. The relevant analytical details, characteristic IR frequencies and the PMR data are recorded in Table 1–3, respectively.

RESULTS AND DISCUSSION

It may be recalled here that N-[*o*-hydroxy substituted (or H) benzyl] glycines exist in zwitter ionic form (Structure-I). The various reactions between titanium tetraisopropoxide and H_3hmbg-5 may be illustrated as:

$$Ti(OPr^i)_4 + H_3\text{hmbg-5} \longrightarrow Ti(OPr^i)(\text{hmbg-5}) + 3Pr^iOH$$

$$Ti(OPr^i)_4 + 2H_3\text{hmbg-5} \longrightarrow Ti(H\text{hmbg-5})_2 + 4Pr^iOH$$

$$Ti(OPr^i)_4 + 3H_3\text{hmbg-5} \longrightarrow Ti(OPr^i)(H_2\text{hmbg-5})_3 + 3Pr^iOH$$

$$Ti(OPr^i)_4 + 4H_3\text{hmbg-5} \longrightarrow Ti(H_2\text{hmbg-5})_4 + 4Pr^iOH$$

Identical reactions followed in case of H_3hbg, H_3hmbg-3 and H_3hmbg-6.

Spectral studies[8–12]

Infrared spectra: The IR spectrum of $Ti(OPr^i)$(hmbg-5) displays a medium broad band in the region 3100–3000 cm^{-1} which may be assigned to aromatic ν(C—H). The band corresponding to the phenolic (—OH) group, as observed in H_3hmbg-5, is found to be absent here suggesting the bonding of the phenolate oxygen to titanium. The disappearance of band due to the $>\overset{+}{N}H_2$ group together with the absence of absorption corresponding to the >NH group shows possible bonding of nitrogen to titanium. Further, a shift of 40 cm^{-1} in ν(C—N) again

TABLE-1
ANALYTICAL DETALIS OF N-[*o*-HYDROXY SUBSTITUTED (OR H) BENZYL] GLYCINES AND THEIR TITANIUM(IV) DERIVATIVES

Compound (molar ratio)/(colur)	Reflux time (h)	m.p. (°C)	Elemental analysis % found (calcd.)			
			C	H	N	Ti
H_3hbg	—	50	59.60	6.09	7.68	—
(off white)			(59.66)	(6.12)	(7.73)	
H_3hmbg-3	—	190	61.46	6.68	7.08	—
(off white)			(61.52)	(6.71)	(7.18)	
H_3hmbg-6	—	88	61.48	6.67	7.10	—
(off white)			(61.52)	(6.71)	(7.18)	
H_3hmbg-5	—	148	61.47	6.67	7.12	—
(off white)			(61.52)	(6.71)	(7.18)	
Ti(OPr^i)(hbg)	10	>300	50.31	5.25	4.89	16.78
(1 : 1) (light yellow)			(50.54)	(5.27)	(4.91)	(16.81)
Ti(Hhbg)$_2$	10	>300	53.04	4.41	6.88	11.78
(1 : 2) (light yellow)			(53.22)	(4.43)	(6.90)	(11.80)
Ti(OPr^i)(H$_2$hbg)$_3$	10	>300	55.60	5.68	6.48	7.38
(1 : 3) (light yellow)			(55.65)	(5.72)	(6.49)	(7.40)
Ti(H$_2$hbg)$_4$	10	>300	56.04	5.19	7.28	6.23
(1 : 4) (yellow)			(56.26)	(5.21)	(7.30)	(6.24)
Ti(OPr^i)(hmbg-3)	11	210	52.08	5.68	4.66	16.02
(1 : 1) (brownish yellow)			(52.19)	(5.69)	(4.68)	(16.03)
Ti(Hhmbg-3)$_2$	10	205	55.29	5.05	6.41	11.00
(1 : 2) (brownish yellow)			(55.31)	(5.07)	(6.45)	(11.04)
Ti(OPr^i)(H$_2$hmbg-3)$_3$	12	200	57.41	6.23	6.06	6.92
(1 ; 3) (brownish yellow)			(57.48)	(6.24)	(6.09)	(6.95)
Ti(H$_2$hmbg-3)$_4$	10	210	58.20	5.80	6.77	5.79
(1 : 4) (brownish yellow)			(58.26)	(5.82)	(6.79)	(5.81)
Ti(OPr^i)(hmbg-6)	11	>300	52.03	5.68	4.66	16.00
(1 : 1) (yellow)			(52.19)	(5.69)	(4.68)	(16.03)
Ti(Hhmbg-6)$_2$	10	>300	55.08	5.06	6.43	10.99
(1 : 2) (lemon yellow)			(55.31)	(5.07)	(6.45)	(11.04)
Ti(OPr^i)(H$_2$hmbg-6)$_3$	12	>300	57.41	6.20	6.07	6.89
(1 : 3) (yellow)			(57.48)	(6.24)	(6.09)	(6.95)
Ti(H$_2$hmbg-6)$_4$	12	>300	58.18	5.79	6.77	5.79
(1 : 4) (yellow)			(58.26)	(5.82)	(6.79)	(5.81)
Ti(OPr^i)(hmbg-5)	10	>300	52.08	5.67	4.68	15.98
(1 : 1) (brownish orange)			(52.19)	(5.69)	(4.68)	(16.03)
Ti(Hhmbg-5)$_2$	11	>300	55.28	5.05	6.40	10.94
(1 : 1) (bright yellow)			(55.31)	(5.07)	(6.45)	(11.04)
Ti(OPr^i)(H$_2$hmbg-5)$_3$	12	230	57.25	6.21	6.08	6.94
(1 : 3) (chrome yellow)			(57.48)	(6.24)	(6.09)	(6.95)
Ti(H$_2$hmbg-5)$_4$	10	200	58.18	5.81	6.78	5.79
(1 : 4) (lemon yellow)			(58.26)	(5.82)	(6.79)	(5.81)

Abbreviations: OPr^i = OC_3H_7, H_3hbg = $OHC_6H_4CH_2\overset{+}{N}H_2CH_2COO^-$ and H_3hmbg-3 (or -6 or -5) = $OHC_6H_3(CH_3)CH_2\overset{+}{N}H_2CH_2COO^-$.

TABLE-2

CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) OF N-[*o*-HYDROXY SUBSTITUTED (OR H) BENZYL] GLYCINES AND THEIR TITANIUM(IV) DERIVATIVES

Compound (molar ratio)	ν(OH) and aromatic ν(C—H)	ν(N—H) and aromatic ν(C—H)	ν(C—H) of —CH_2— and —CH_3 groups	ν(NH) of $>\overset{+}{N}H_2$	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(Ti—O)	ν(Ti—N)
H_3hbg	3450–3000 (vb)	—	2940 (w) 2850 (w)	2600 (wb)	1630 (vsb)	1400 (s)	—	1230 (m)	—	—
H_3hmbg-3	3600–3000 (vb)	—	2950 (vb) 2855 (wb)	2390 (wb)	1635 (vsb)	1405 (m)	—	1230 (s)	—	—
H_3hmbg-6	3500–3000 (vb)	—	2910 (mb) 2860 (wb)	2375 (wb)	1640 (vsb)	1405 (m)	—	1225 (m)	—	—
H_3hmbg-5	3500–3000 (vb)	—	2910 (mb) 2870 (w)	2380 (w)	1635 (vsb)	1400 (s)	—	1220 (m)	—	—
Ti(OPr^i)(hbg) (1 : 1)	—	3100–3000$^+$ (b)	2960 (m)	—	1620 (vsb)	1385 (mb)	235	1245 (mb)	580 (w)	470 (m)
Ti(Hhbg)$_2$ (1 : 2)	—	3200–3000 (b)	2980 (m) 2940 (w)	—	1625 (vsb)	1390 (vsb)	235	1255 (s)	570 (w)	490 (m)
Ti(OPr^i)(H_2hbg)$_3$ (1 : 3)	3450–3300* (b)	3200–3000 (mb)	2925 (m)	—	1620 (vsb)	1390 (mb)	230	1260 (vs)	580 (w)	480 (w)
Ti(H_2hbg)$_4$ (1 : 4)	3400–3300* (b)	3200–3000 (mb)	2960 (w)	—	1630 (vsb)	1385 (mb)	245	1255 (s)	570 (w)	460 (m)
Ti(OPr^i)(hmbg-3) (1 : 1)	—	3100–3000$^+$ (vsb)	2960 (m) 2930 (vw)	—	1630 (vsb)	1385 (vsb)	245	1266 (mb)	680 (w)	480 (m)
Ti(Hhmbg-3)$_2$ (1 : 2)	—	3200–3000 (b)	2960 (w) 2940 (vw)	—	1630 (vsb)	1385 (mb)	245	1270 (m)	560 (m)	440 (s)

Compound (molar ratio)	ν(OH) and aromatic ν(C—H)	ν(N—H) and aromatic ν(C—H)	ν(C—H) of —CH_2— and —CH_3 groups	ν(NH) of $>\overset{+}{N}H_2$	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(Ti—O)	ν(Ti—N)
Ti(OPr^i)(H_2hmbg-3)$_3$ (1 : 3)	3400–3300* (vb)	3200–3000 (mb)	2940 (vw)	—	1625 (vsb)	1380 (mb)	245	1260 (m)	580 (w)	450 (m)
Ti(H_2hmbg-3)$_4$ (1 : 4)	3400–3300* (vb)	3180–3000 (mb)	2960 (w) 2840 (m)	—	1635 (vsb)	1390 (mb)	245	1260 (m)	590 (m)	440 (s)
Ti(OPr^i)(hmbg-6) (1 : 1)	—	3120–3000† (vb)	2960 (m) 2920 (w)	—	1630 (vsb)	1385 (mb)	245	1255 (vs)	610 (vw)	450 (m)
Ti(Hhmbg-6)$_2$ (1 : 2)	—	3250–3000 (vb)	2960 (w) 2940 (w)	—	1630 (vsb)	1395 (mb)	235	1250 (s)	585 (m)	440 (w)
Ti(OPr^i)(H_2hmbg-6)$_3$ (1 : 3)	3400–3000* (vb)	3200–3000 (mb)	2955 (w)	—	1625 (vsb)	1390 (mb)	235	1255 (w)	560 (w)	440 (vw)
Ti(H_2hmbg-6)$_4$ (1 : 4)	3425–3300* (b)	3150–3000 (mb)	2980 (w) 2940 (m)	—	1625 (vsb)	1390 (mb)	235	1270 (s)	580 (w)	460 (m)
Ti(OPr^i)(hmbg-5) (1 : 1)	—	3100–3000† (mb)	2960 (m) 2910 (w)	—	1625 (vsb)	1390 (mb)	235	1260 (vs)	550 (w)	440 (m)
Ti(Hhmbg-5)$_2$ (1 : 2)	—	3250–3000 (b)	2900 (m) 2845 (m)	—	1630 (vsb)	1380 (mb)	250	1260 (s)	540 (m)	450 (w)
Ti(OPr^i)(H_2hmbg-5)$_3$ (1 : 3)	3450–3300* (mb)	3150–3000 (mb)	2940 (vw) 2840 (w)	—	1630 (vsb)	1390 (mb)	240	1255 (vs)	550 (m)	440 (m)
Ti(Hhmbg-5)$_4$ (1 : 4)	3425–3300* (b)	3200–3000 (mb)	2900 (s)	—	1625 (vsb)	1380 (vsb)	245	1260 (vs)	570 (m)	470 (m)

*ν(OH) alone, †ν(C—H) alone.

Abbreviations: s = strong, vs = very strong, b = broad, vsb = very strong broad, m = medium, mb= medium broad, w = weak, wb = weak broad, vw = very weak.

TABLE-3
PROTON MAGNETIC RESONANCE (PMR) SPECTRAL DATA (δ VALUES) OF N-[*o*-HYDROXY SUBSTITUTED (OR H) BENZYL]-GLYCINES AND THEIR TITANIUM(IV) DERIVATIVES

Compound	Aromatic ring	Phenolic (OH)	$>\overset{+}{N}H_2$	>NH	—CH_2—		—CH_3 attached with benzene ring	*Gem* dimethyl of isopropoxy groups
					Benzene ring	Glycine part		
H_3hbg	6.70–7.30 (q)	4.50–5.90 (h)	3.60 (s)	—	3.25 (s)	2.45 (s)	—	—
H_3hmbg-3	6.50–7.10 (t)	4.50–5.70 (h)	3.55 (s)	—	3.15 (s)	2.50 (s)	2.15 (s)	—
H_3hmbg-6	6.40–7.10 (t)	4.40–5.60 (h)	3.65 (s)	—	3.20 (s)	2.45 (s)	2.15 (s)	—
H_3hmbg-5	6.50–7.00 (t)	4.50–5.50 (h)	3.70 (s)	—	3.25 (s)	2.45 (s)	2.15 (s)	—
$Ti(OPr^i)(hmbg$-5) (1 : 1)	6.40–7.55 (m)	—	—	—	3.20 (s)	2.50 (s)	2.15 (s)	1.00–1.50 (d)
$Ti(Hhmbg$-6$)_2$ (1 : 2)	6.50–7.25 (t)	—	—	3.90 (s)	3.10 (s)	2.45 (s)	2.00 (s)	—
$Ti(OPr^i)(H_2hmbg$-3$)_3$ (1 : 3)	6.65–7.40 (m)	4.90–5.60 (h)	—	3.80 (s)	3.15 (s)	2.50 (s)	2.15 (s)	1.02 (d)
$Ti(H_2hbg)_4$ (1 : 4)	6.50–7.50 (t)	4.75 (h)	—	3.85 (s)	3.20 (s)	2.60 (s)	—	—

Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, h = hump.

indicates bonding of nitrogen to titanium. The absence of any characteristic band corresponding to the C═O group in the region 1750–1650 cm^{-1} rules out the possibility of a normal ester type of linkage between the carboxylate oxygen and titanium. A shift of 10 cm^{-1} in $\nu_{sym}(COO)$, as compared to H_3hmbg-5, suggests the bonding of carboxylate oxygen to titanium. The separation value, $\Delta\nu(COO)$ $[\nu_{asym}(COO)-\nu_{sym}(COO)]$ of 235 cm^{-1} as observed here suggests the absence of bridged or coordinated carboxylate group. The weak absorption at 550 cm^{-1} occurs due to ν(Ti—O), while the medium absorption at 440 cm^{-1} may be assigned to ν(Ti—N).

On the basis of the foregoing considerations, it appears that the titanium atom in $Ti(OPr^i)$(hmbg-5) shows tetravalency, as a result of bonding with one of the oxygens from the carboxylate group, the nitrogen obtained by the deprotonation of the $>\overset{+}{N}H_2$ group and the oxygen from the phenolic group, along with an isopropoxy group (Structure-II).

Proton magnetic resonance (PMR) spectra: The PMR spectrum of the derivative, $Ti(OPr^i)$(hmbg-5) displays a multiplet between δ6.40–7.55 corresponding to the aromatic ring protons. The hump observed between δ4.50–5.50 in H_3hmbg-5 is found to be absent here indicating the deprotonation of the phenolic group, as a result of bonding of the phenolate oxygen to titanium. The singlet at δ3.70 due to the $>\overset{+}{N}H_2$ protons, as observed in H_3hmbg-5, is found to disappear here without the appearance of any new peak suggesting bonding of nitrogen to titanium. The singlets at δ3.20 and δ2.50 may be assigned to the protons associated with the $—CH_2—$ group attached with the benzene ring and the glycine part of H_3hmbg-5, respectively. A singlet at δ2.15 corresponds to the $—CH_3$ group protons attached with the benzene ring, whereas a doublet in the region δ1.00–1.50 may be attributed to the *gem*-dimethyl protons of the isopropoxy group. Thus, the inferences drawn here are well in conformity to those inferred from the IR measurements earlier.

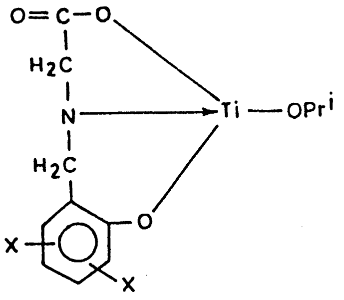
The IR and PMR data in resepct of the other derivatives were interpreted similarly and the main findings relating to their structures are as under:

The derivatives, $Ti(OPr^i)$(hbg), $Ti(OPr^i)$(hmbg-3) and $Ti(OPr^i)$(hmbg-6) also contain a tetravalent titanium atom in each case displaying similar modes of bonding as those observed in $Ti(OPr^i)$(hmbg-5) (Structure-II).

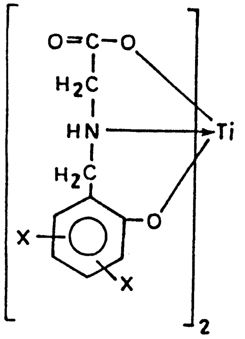
The titanium atom in $Ti(Hhbg)_2$, $Ti(Hhmbg\text{-}3)_2$, $Ti(Hhmbg\text{-}6)_2$ and $Ti(Hhmbg\text{-}5)_2$ displays hexa-coordination in each case as a consequence of boding with one of the oxygens from each of the two carboxylate groups, the nitrogen from each of the two imino groups and the oxygen from each of the two phenolic groups available from two mole of I (Structure-III).

The derivatives, $Ti(OPr^i)(H_2hbg)_3$, $Ti(OPr^i)(H_2hmbg\text{-}3)_3$, $Ti(OPr^i)(H_2hmbg\text{-}6)_3$ and $Ti(OPr^i)(H_2hmbg\text{-}5)_3$ contain a hepta-coordinated titanium atom in each case by way of bonding with one of the oxygens from each of the three carboxylate groups and the nitrogen from each of the three imino groups available from three mole of I, along with an isopropoxy group (Structure-IV).

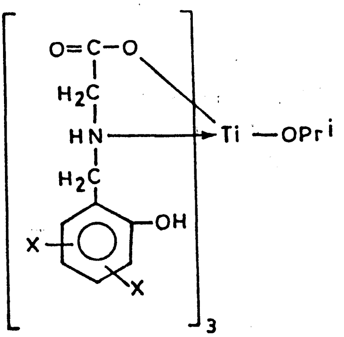
The titanium atom in the derivatives $Ti(H_2hbg)_4$, $Ti(H_2hmbg\text{-}3)_4$, $Ti(H_2hmbg\text{-}6)_4$ and $Ti(H_2hmbg\text{-}5)_4$ exhibits octa-coordination in each case as a result of bonding with one of the oxygens from each of the four carboxylate groups and the nitrogen from each of the four imino-groups available from four moles of I (Structure-V).



(Where $X = -H$ or $-CH_3$)
(II)



(Where $X = -H$ or $-CH_3$
(III)



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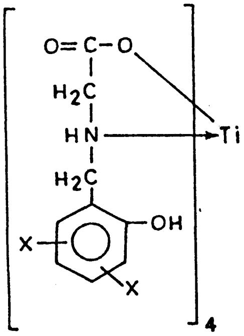
(IV)



(Where $X = -H$ or $-CH_3$)
(V)

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