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

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

INTRODUCTION

The work described here relates to the preparation of tin(IV) derivatives of N-[*o*-hydroxy substituted (or H) benzyl] glycine (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 tin tetraisopropoxide with I in 1 : 1 and 1 : 2 molar ratios in benzene medium. The various compounds thus prepared were obtained as coloured solids which were found to be hygroscopic due to the presence of isopropoxy groups. All these compounds were characterized by azeotrope and elemental analysis, as well as by IR and PMR measurements.

EXPERIMENTAL

Benzene (BDH, AR), isopropanol (BDH, Glaxo AnalaR) and solvent ether (E. Merck) were dried by standard procedures[4]. Tin tetraisopropoxide was prepared by sodium method[5], while N-[*o*-hydroxy substituted (or H) benzyl] glycines were prepared by already reported method[1]. Tin(IV) was estimated by a known method[6], 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 melting point 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 $Sn(OPr^i)_4$ and H_3hmbg-6, 1 : 1 molar ratio

A mixture of $Sn(OPr^i)_4$ (1.5974 g; 4.4990 mmole) and H_3hmbg-6 (0.8781 g; 4.4980 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.* 15 h of reflux, isopropanol liberated was fractionated out azeotropically and estimated[7, 8]. On completion of the reaction the excess of solvent from the reaction mixture was removed *in vacuo*, when the product, $Sn(OPr^i)_2$(Hhmbg-6) isolated as a dull white solid. It was then washed with dry benzene (3–4 times) followed by ether (2–3 times) and finally dried under sunction. The compound was found to be soluble in dimethylsulphoxide but insoluble in other common organic solvents.

It may be mentioned here that since $Sn(OPr^i)_4$ is soluble in benzene, while H_3hmbg-6 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-6. The amount of isopropanol liberated was, therefore, calculated according to the amount of H_3hmbg-6 taken.

Similar procedures of preparation and purification were adopted in case of other derivatives. The relevant analytical details, characteristic IR frequencies and PMR data (in several representative cases) are recorded in Tables 1–3, respectively.

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

Compound (molar ratio)/(colour)	Reflux time (h)	m.p. (°C)	Elemental analysis %, found (calcd.)			
			C	H	N	Sn
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)	
$Sn(OPr^i)_2$(Hhbg)	18	>300	43.26	5.50	3.31	28.48
(1 : 1) (dull white)			(43.30)	(5.53)	(3.37)	(28.55)
$Sn(OPr^i)_2(H_2hbg)_2$	15	>300	48.11	5.69	4.68	19.80
(1 : 2) (cream)			(48.27)	(5.70)	(4.69)	(19.89)
$Sn(OPr^i)_2$(Hhmbg-3)	17	230	44.53	5.80	3.25	27.57
(1 : 1) (dull white)			(44.68)	(5.82)	(3.26)	(27.62)
$Sn(OPr^i)_2(H_2hmbg\text{-}3)_2$	17	230	49.89	6.07	4.46	18.93
(1 : 2) (dull white)			(49.94)	(6.08)	(4.48)	(18.99)
$Sn(OPr^i)_2$(Hhmbg-6)	15	230	44.61	5.80	3.25	27.58
(1 : 1) (dull white)			(44.68)	(5.82)	(3.26)	(27.62)
$Sn(OPr^i)_2(H_2hmbg\text{-}6)_2$	18	230	49.81	6.08	4.47	18.88
(1 : 2) (dull white)			(49.94)	(6.08)	(4.48)	(18.99)
$Sn(OPr^i)_2$(Hhmbg-5)	18	220	44.61	5.81	3.26	27.58
(1 : 1) (dull white)			(44.68)	(5.82)	(3.26)	(27.62)
$Sn(OPr^i)_2(H_2hmbg\text{-}5)_2$	18	180	49.82	6.08	4.47	18.95
(1 : 2) (cream)			(49.94)	(6.08)	(4.48)	(18.99)

Abbreviations: $Pr^iOH{=}OC_3H_7$, $H_3hbg = OHC_6H_4CH_2\overset{+}{N}H_2CH_2\overline{COO}$ and H_3hmbg-3 (or -6 or -5)= $OHC_6H_3(CH_3)CH_2\overset{+}{N}H_2CH_2\overline{COO}$.

TABLE-2

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

Compound	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	$>\overset{+}{N}H_2$	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(Sn—O)	ν(Sn—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)	—	—
$Sn(OPr^i)_2$(Hhbg)	—	3140–3000 (vb)	2980 (w)	—	1640 (vsb)	1390 (mb)	250	1260 (s)	540 (m) 480 (m)	420 (m)
$Sn(OPr^i)_2(H_2hbg)_2$	3450–3300* (vb)	3200–3000 (mb)	2980 (m)	—	1640 (vsb)	1395 (mb)	245	1270 (s)	510 (m) 480 (m)	420 (m)
$Sn(OPr^i)_2$(Hhmbg-3)	—	3200–3000 (vb)	2960 (w)	—	1640 (vsb)	1390 (mb)	250	1260 (s)	500 (m) 475 (w)	435 (m)
$Sn(OPr^i)_2(H_2hmbg\text{-}3)_2$	3400–3300* (vb)	3150–3000 (mb)	2980 (m)	—	1645 (vsb)	1390 (mb)	255	1260 (s)	500 (m) 475 (w)	440 (m)
$Sn(OPr^i)_2$(Hhmbg-6)	—	3200–3000 (b)	2980 (w)	—	1640 (vsb)	1395 (mb)	245	1255 (s)	530 (m) 480 (m)	440 (m)
$Sn(OPr^i)_2(H_2hmbg\text{-}6)_2$	3450–3300* (mb)	3200–3000 (mb)	2980 (w)	—	1640 (vsb)	1395 (mb)	245	1265 (vsb)	520 (m) 470 (m)	420 (m)
$Sn((OPr^i)_2$(Hhmbg-5)	—	3150–3000 (mb)	2980 (w)	—	1640 (vsb)	1395 (mb)	245	1260 (s)	520 (m) 450 (w)	440 (w)
$Sn(OPr^i)_2(H_2hmbg\text{-}5)_2$	3450–3320* (b)	3170–3000 (mb)	2980 (w)	—	1645 (vsb)	1390 (mb)	255	1260 (s)	520 (m) 470 (w)	440 (m)

*ν(OH) alone.

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

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

Compound	Aromatic ring	Phenolic (—OH)	$>\overset{+}{N}H_2$	>NH	—CH_2—		—CH_3 attached with benzene ring	*Gem* dimethyl of isopropoxy group(s)
					Benzene ring	Glycine part		
H_3hbg	6.50–7.30 (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)	—
$Sn(OPr^i)_2$(Hhmbg-6)	6.35–7.00 (m)	—	—	3.55 (s)	3.15 (s)	2.40 (s)	2.10 (s)	1.20 (d)
$Sn(OPr^i)_2(H_2hmbg\text{-}3)_2$	6.30–7.00 (m)	4.55–5.65 (h)	—	3.60 (s)	3.10 (s)	2.45 (s)	2.05 (s)	1.20 (d)

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

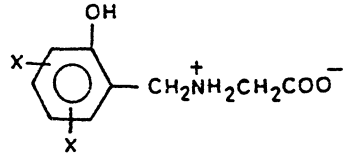
RESULTS AND DISCUSSION

It may be recalled here that N-[*o*-hydroxy substituted (or H) benzyl] glycines exist in zwitterionic form (Structure-I). The various reactions between tin tetraisopropoxide and H_3hmbg-6 may be illustrated as:

$$Sn(OPr^i)_4 + H_3hmbg\text{-}6 \longrightarrow Sn(OPr^i)_2(Hhmbg\text{-}6) + 2Pr^iOH$$

$$Sn(OPr^i)_4 + 2H_3hmbg\text{-}6 \longrightarrow Sn(OPr^i)_2(H_2hmbg\text{-}6)_2 + 2Pr^iOH$$

Identical reactions followed in case of H_3hbg, H_3hmbg-3 and H_3hmbg-5.



(Where X= -H or -CH_3)

(I)

Spectral studies[9–12]

Infrared spectra: The IR spectrum of $Sn(OPr^i)_2$(Hhmbg-6) displays a broad band in the region 3200–3000 cm^{-1} indicating possible overlapping of ν(N—H) and aromatic ν(C—H). The band corresponding to the phenolic (—OH) group, as observed in H_3hmbg-6, is found to be absent here suggesting the bonding of the phenolate oxygen to tin. The appearance of ν(N—H) in the lower region shows the coordination of nitrogen to tin. Further, a shift of 30 cm^{-1} as compared to H_3hmbg-6 in ν(C—N) again supports the bonding of nitrogen to tin. 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 tin. A shift of 10 cm^{-1} in ν_{sym}(COO), as compared to H_3hmbg-6 suggests the bonding of carboxylate oxygen to tin. The separation value, $\Delta\nu(COO)[\nu_{asym}(COO)-\nu_{sym}(COO)]$ of 245 cm^{-1}, as observed here, indicates the absence of bridged or coordinated carboxylate group. The medium bands at 530 cm^{-1} and 480 cm^{-1} occur due to ν(Sn—O), while a medium band at 440 cm^{-1} corresponds to ν(Sn—N).

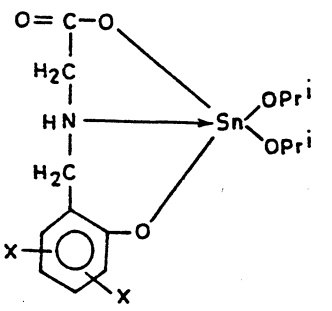
It is thus evident from the foregoing observations that the tin atom in $Sn(OPr^i)_2$(Hhmbg-6) shows *penta*-coordination, as a result of bonding with one of the oxygens from the carboxylate group, the nitrogen from the imino group, the oxygen from the phenolic group, along with two isopropoxy groups (Structure-II).

Proton magnetic resonance spectra: The PMR spectrum of $Sn(OPr^i)_2$ (Hhmbg-6) displays a multiplet between δ 6.35–7.00 corresponding to the aromatic ring protons. A hump between δ 4.40–5.60 in H_3hmbg-6 is found to be absent here indicating the deprotonation of the phenolic group as a result of bonding of the phenolate oxygen to tin. Instead of a singlet at δ 3.65 due to the $>\overset{+}{N}H_2$ protons, as observed in H_3hmbg-6, here the singlet appearing at δ 3.55 suggests possible coordination of nitrogen from the >NH group to tin. The singlets at δ 3.15 and δ 2.40 may be assigned to the protons associated with —CH_2—

groups attached with benzene ring and the glycine part of H_3hmbg-6, respectively. A singlet at δ 2.10 corresponds to the protons of the —CH_3 group attached with the benzene ring, while the doublet at δ 1.20 occurs due to the dimethyl protons of the isopropoxy groups.

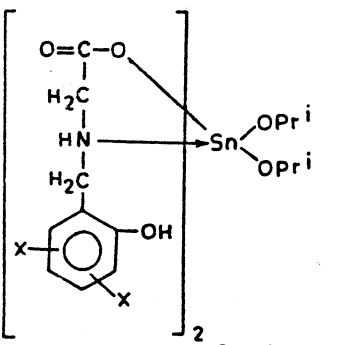
The IR and PMR data in respect of the other derivatives were interpreted similarly and the main findings relating to their structures are as under:

The derivatives, $Sn(OPr^i)_2$(Hhbg), $Sn(OPr^i)_2$(Hhmbg-3) and $Sn(OPr^i)_2$ (Hhmbg-5) contain a *penta*-coordinated tin atom in each case, displaying similar modes of bonding as those observed in $Sn(OPr^i)_2$(Hhmbg-6) (Structure-II).



(Where X = -H or-CH_3)

(II)



(Where X = -H or-CH_3)

(III)

The tin atom in $Sn(OPr^i)_2(H_2hbg)_2$, $Sn(OPr^i)_2(H_2hmbg\text{-}3)_2$, $Sn(OPr^i)_2$ $(H_2hmbg\text{-}6)_2$ and $Sn(OPr^i)_2(H_2hmbg\text{-}5)_2$ displays *hexa*-coordination in each case by way of bonding with one of the oxygens from each of the two carboxylate groups and the nitrogen from each of the two imino groups available from two moles of I, along with two isopropoxy groups (Structure-III).

REFERENCES

1. P. Sivadasan and M. Chandra, *Asian J. Chem.*, **6**, 498 (1994).
2. _____, *Chim. Acta Turcica*, **22**, 225 (1994).
3. R. Aman, Ph.D. Thesis, Kumaun University, Nainital (1991).
4. A.I. Vogel, A Text Book of Practical Organic Chemistry, 4th Edn., Longmans, London (1978).
5. D.C. Bradley, D.P. Gaur and R.C. Mehrotra, Metal Alkoxides, Academic Press, London (1978).
6. A.I. Vogel, Quantitative Inorganic Analysis, Longmans, London (1975).
7. D.C. Bradley, F.M.A. Halim and W. Wardlaw, *J. Chem. Soc.*, 3450 (1950).
8. R.C. Mehrotra, *J. Indian Chem. Soc.*, **31**, 904 (1954).
9. R.M. Silverstein, G. Bassler and T.C. Morrill, Spectroscopic Identification of Organic Compounds, John Wiley, New York (1981).
10. L.J. Bellamy, Infrared Spectra of Complex Molecules, Methuen, London (1962).
11. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley, New York (1978).
12. Asahi Research Centre Co. Ltd., Tokyo (Ed.), Hand Book of Proton NMR Spectra and Data, Vols. I–III, Academic Press, Japan (1985).

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