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Elemento(III) Derivatives of N-(2-Hydroxy-5-Methyl Benzyl) Alanine

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Several elemento(III) *viz.* boron, aluminium, iron, arsenic and antimony derivatives of N-(2-hydroxy-5-methyl benzyl) alanine have been prepared *via* the reactivity of the corresponding elemento(III) isopropoxide with the latter in 1 : 1, 1 : 2 and 1 : 3 molar ratios in benzene medium. All these compounds have been characterized by azeotrope and elemental analyses, as well as by IR and PMR spectral measurements.

INTRODUCTION

In continuation to preparation of the various metallo-organic/organometallic derivatives of N-(*o*-hydroxy substituted benzyl) alanines[1,2] by alcoholysis reactions involving the interaction of the corresponding metal isopropoxide and the latter, the work described here deals with the preparation of several elemento(III) derivatives of N-(2-hydroxy-5-methyl benzyl) alanine (H_3hmba-5) (Fig. 1) on similar lines.

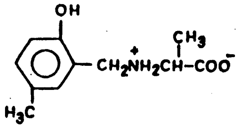


Fig. 1

EXPERIMENTAL

All the experiments were carried out in a moisture-free atmosphere, as before[1,2]. The other details are described in earlier paper[3].

Reaction between $Sb(OPr^i)_3$ and H_3hmba-5; 1 : 1 molar ratio

A mixture of $Sb(OPr^i)_3$ (0.7856 g; 2.63 mmole) and H_3hmba-5 (0.5412 g; 2.62 mmole) suspended in dry benzene (60 mL) taken in a R.B. flask was refluxed on a wax bath (95–100°C), using a fractionating column 30 cm long. After *ca.* 9 h of reflux, the isopropanol liberated during the course of reaction was fractionated out azeotropically and estimated by an oxidimetric method, as before[1,2]. On completion of the reaction, the excess of solvent from the reaction mixture was removed *in vacuo*, when the product, $Sb(OPr^i)(Hhmba\text{-}5)$ isolated as a brown solid which was washed with dry benzene (3–4 times) followed by dry ether (2–3 times) to remove excess of $Sb(OPr^i)_3$ and then dried under suction. The product was found to be soluble in dimethylformamide and dimethylsulphoxide but insoluble in other common organic solvents like ethanol, benzene, toluene, carbon tetrachloride and chloroform etc.

It may be mentioned here that since $Sb(OPr^i)_3$ is soluble in benzene, while $H_3hmba\text{-}5$ 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 unreacted $H_3hmba\text{-}5$. The amount of isopropanol liberated was, therefore, calculated according to the amount of $H_3hmba\text{-}5$ taken.

Identical procedure was adopted for the preparation and purification of other derivatives. The relevant analytical details, characteristic IR frequencies and PMR data are incorporated in Tables 1–3, respectively.

RESULTS AND DISCUSSION

The various reactions occurring between boron tri-isopropoxide and $H_3hmba\text{-}5$ may be illustrated as:

$$B(OPr^i)_3 + H_3hmba\text{-}5 \rightarrow B(OPr^i)(Hhmba\text{-}5) + 2Pr^iOH \qquad (1)$$

$$B(OPr^i)_3 + 2H_3hmba\text{-}5 \rightarrow B(OPr^i)(H_2hmba\text{-}5)_2 + 2Pr^iOH \qquad (2)$$

$$B(OPr^i)_3 + 3H_3hmba\text{-}5 \rightarrow B(H_2hmba\text{-}5)_3 + 3Pr^iOH \qquad (3)$$

Identical reactions followed in case of iron(III), arsenic(III) and antimony(III). However, 1 : 3 reaction in case of arsenic(III) did not proceed even after prolonged reflux and fractionation.

The various reactions occurring between aluminium tri-isopropoxide and $H_3hmba\text{-}5$ may be illustrated as under:

$$Al(OPr^i)_3 + H_3hmba\text{-}5 \rightarrow Al(hmba\text{-}5) + 3Pr^iOH \qquad (4)$$

$$Al(OPr^i)_3 + 2H_3hmba\text{-}5 \rightarrow Al(H_2hmba\text{-}5)(Hhmba\text{-}5) + 3Pr^iOH \qquad (5)$$

$$Al(OPr^i)_3 + 3H_3hmba\text{-}5 \rightarrow Al(H_2hmba\text{-}5)_3 + 3Pr^iOH \qquad (6)$$

Infrared Spectra

A medium broad band in the derivative $Sb(OPr^i)(Hhmba\text{-}5)$ in the region 3300–3030 cm^{-1} may be assigned to the overlapping of ν(N—H) and aromatic ν(C—H)[4,5]. The appearance of ν(N—H) in the lower region suggests possible bonding of nitrogen to antimony. The band due to ν(OH) of the phenolic group, as noted in $H_3hmba\text{-}5$, is found to be absent here, indicating the participation of the phenolate oxygen in bonding with antimony. The weak absorptions at 2920 cm^{-1} and 2890 cm^{-1} may be ascribed to ν(CH) of the $—CH_2—$ and $—CH_3$ groups.

TABLE-1
ANALYTICAL DETAILS OF THE VARIOUS ELEMENTO(III) DERIVATIVES OF N-(2-HYDROXY-5-METHYL BENZYL) ALANINE

Compound (molar ratio)/(colour)	m.p. (°C)	Azeotropic analysis Pr^{i}OH (g) found (calcd.)	Analysis % found (calcd.)			
			C	H	N	M
B(OPr^{i})(Hhmba-5) (1 : 1) (brownish white)	157	0.48 (0.50)	60.58 (60.67)	7.20 (7.27)	4.95 (5.05)	3.85 (3.90)
B(OPr^{i})(H$_2$hmba-5)$_2$ (1 : 2) (brownish white)	150	0.23 (0.25)	61.65 (61.73)	7.20 (7.25)	5.60 (5.76)	2.10 (2.22)
B(H$_2$hmba-5)$_3$ (1 : 3) (brownish white)	152	0.33 (0.35)	62.48 (62.56)	6.60 (6.68)	6.58 (6.63)	1.68 (1.71)
Al(hmba-5) (1 : 1) (light brown)	130	0.51 (0.52)	56.48 (56.65)	5.09 (5.19)	5.90 (6.01)	11.48 (11.57)
Al(H$_2$hmba-5)(Hhmba-5) (1 : 2) (light brown)	142	0.32 (0.33)	59.58 (59.72)	6.70 (6.83)	6.25 (6.33)	6.00 (6.20)
Al(H$_2$hmba-3)$_3$ (1 : 3) (light brown)	170	0.30 (0.31)	60.70 (60.82)	6.40 (6.50)	6.26 (6.45)	4.05 (4.14)
Fe(OPr^{i})(Hhmba-5) (1 : 1) (light brown)	145	0.37 (0.38)	52.05 (52.19)	6.15 (6.26)	4.27 (4.35)	17.26 (17.34)
Fe(OPr^{i})(H$_2$hmba-5)$_2$ (1 : 2) (light brown)	142	0.27 (0.28)	56.40 (56.50)	6.52 (6.64)	5.15 (5.27)	10.41 (10.51)
Fe(H$_2$hmba-5)$_3$ (1 : 3) (light brown)	145	0.29 (0.30)	58.18 (58.24)	6.18 (6.22)	6.10 (6.17)	8.12 (8.21)
As(OPr^{i})(Hhmba-5) (1 : 1) (light brown)	163	0.31 (0.32)	49.22 (49.27)	5.85 (5.91)	4.02 (4.11)	21.90 (21.95)
As(OPr^{i})(H$_2$hmba-5)$_2$ (1 : 2) (light brown)	162	0.28 (0.30)	54.50 (54.55)	6.33 (6.41)	5.00 (5.09)	13.55 (13.61)
Sb(OPr^{i})(Hhmba-5) (1 : 1) (brown)	185	0.30 (0.32)	43.27 (43.33)	5.13 (5.19)	3.56 (3.61)	31.30 (31.37)
Sb(OPr^{i})(H$_2$hmba-5)$_2$ (1 : 2) (brown)	142	0.26 (0.27)	50.20 (50.27)	5.86 (5.91)	4.62 (4.69)	20.32 (20.38)
Sb(H$_2$hmba-5)$_3$ (1 : 3) (brown)	172	0.32 (0.34)	53.01 (53.10)	5.63 (5.67)	5.56 (5.63)	16.25 (16.31)

Abbreviations: OPr^{i} = OC_3H_7, H$_3$hmba-5 = $CH_3C_6H_3(OH)CH_2\overset{+}{N}H_2CH(CH_3)COO^-$.

The absence of any characteristic band corresponding to $\nu(C{=}O)$ in the region 1750–1650 cm^{-1} rules out the possibility of a normal ester type of linkage between the carboxylate oxygen and antimony. A very strong band at 1600 cm^{-1} may be attributed to the overlapping of ν_{asym}(COO), aromatic C=C and (N—H) deformation, while the medium and broad bands at 1490 cm^{-1} and 1440 cm^{-1} correspond to the aromatic skeletal vibrations and C—H bonding of the —CH_2— and —CH_3 groups. Instead of a band at 1390 cm^{-1}, as noted in H$_3$hmba-5, here the appearance of a strong band at 1390 cm^{-1} shows the overlapping of ν_{sym}(COO) and C—H bending of the *gem*-dimethyl structure of

TABLE-2
CHARACTERISTIC INFRARED FREQUENCY (cm^{-1}) OF THE VARIOUS ELEMENTO(III) DERIVATIVES OF N-(2-HYDROXY-5-METHYL BENZYL) ALANINE

Compound	ν(OH)	ν(N—H) and aromatic ν(C—H)	ν(C—H) of —CH_3 and —CH_2 groups	ν(C=O) (ester)	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(M—O)	ν(M—N)
B(OPr^i)(Hhmba-5)	—	3250–3000 (b)	2950 (w) 2860 (w)	—	1630 (b)	1380 (mb)*	250	1260 (s)	—	1525 (s)
B(OPr^i)(H_2hmba-5)$_2$	3560–3340 (b)	3300–3100 (b)	2950 (m) 2840 (mb)	1670 (m)	1600 (s)	1370 (m)*	230	1220 (mb)	—	—
B(H_2hmba-5)$_3$	3500–3300 (b)	3200–3000 (mb)	2950 (m) 2920 (m)	1750 (vs)	1630 (s)	1380 (m)*	250	1220 (s)	—	—
Al(hmba-5)	—	3260–3000 (b)	2910 (m) 2845 (m)	—	1610 (sb)	1370 (s)	240	1250 (sb)	680 (m) 630 (m)	530 (m) 450 (m)
Al(H_2hmba-5)(Hhmba-5)	3500–3400 (b)	3200–3000 (mb)	2990 (m) 2945 (m)	—	1625 (s)	1390 (m)	235	1260 (s)	690 (m) 660 (m)	580 (m) 450 (w)
Al(H_2hmba-5)$_3$	3500–3330 (b)	3200–3000 (b)	2960 (w) 2930 (m)	—	1620 (s)	1400 (m)	220	1265 (m)	680 (m) 630 (s)	580 (m) 490 (w)
Fe(OPr^i)(Hhmba-5)	—	3200–3000 (b)	2960 (m) 2850 (m)	—	1615 (b)	1375 (m)	240	1260 (m)	520 (m) 450 (m)	430 (w)
Fe(OPr^i)(H_2hmba-5)$_2$	3520–3300 (vb)	3200–3010 (mb)	2900 (m) 2860 (m)	1680 (b)	1600 (b)	1375 (b)	225	1265 (s)	540 (s) 440 (b)	—
Fe(H_2hmba-5)$_3$	3500–3210 (b)	3200–3000 (mb)	2950 (m) 2850 (m)	—	1615 (vs)	1375 (mb)	240	1250 (s)	535 (s) 440 (s)	420 (m)
As(OPr^i)(Hhmba-5)	—	3200–3000 (b)	2965 (m) 2855 (w)	—	1620 (s)	1370 (s)	250	1250 (m)	610 (m) 590 (w)	475 (m) 405 (w)

Compound	ν(OH)	ν(N—H) and aromatic ν(C—H)	ν(C—H) of —CH_3 and —CH_2 groups	ν(C═O) (ester)	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(M—O)	ν(M—N)
As(OPr^i)(H_2hmba-5)$_2$	3500–3300 (b)	3200–3000 (m)	2950 (w) 2910 (m)	1710 (s)	1625 (s)	1375 (b)	250	1250 (s)	605 (s)	—
Sb(OPr^i)(Hhmba-5)	—	3300–3030 (mb)	2920 (w) 2890 (w)	—	1600 (vs)	1370 (s)	230	1255 (s)	590 (s)	480 (s) 430 (s)
Sb(OPr^i)(H_2hmba-5)$_2$	3460–3300 (b)	3200–3000 (mb)	2985 (m) 2920 (m)	—	1610 (b)	1390 (s)	220	1260 (b)	675 (m) 590 (m)	490 (s) 430 (s)
Sb(H_2hmba-5)$_3$	3440–3300 (b)	3200–3000 (b)	2950 (m) 2860 (m)	—	1630 (sh)	1400 (s)	230	1265 (m)	880 (m) 590 (s)	495 (m) 425 (w)

Abbreviations: b = broad, m = medium, mb = medium broad, s = strong, sh = shoulder, vb = very broad, vs = very strong, vw = very weak, w = weak.

*Overlapping of ν_{sym}(COO) and ν(B—O).

TABLE-3
PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ VALUE) OF SEVERAL ELEMENTO(III) DERIVATIVES OF N-(2-HYDROXY-6-METHYL BENZYL) ALANINE

S.No.	Compound	Aromatic ring	Phenolic —(OH)	>CH—	>NH—	—CH_3 attached with the benzene ring	—CH_2—	—CH_3 of the alanine part	*Gem*-dimethyl
1.	B(OPr^i)(H_2hmba-5)$_2$	6.60–7.20 (m)	6.90 (s)	3.60–4.00 (m)	3.20 (h)	2.15 (s)	2.00 (d)	1.20 (d)	1.00 (d)
2.	Al(hmba-5)	6.60–7.20 (m)	—	3.55–4.10 (bm)	—	2.15 (s)	2.00 (d)	1.25 (d)	—
3.	Fe(OPr^i)(H_2hmba-5)$_2$	6.40–7.10 (m)	6.05 (s)	3.60–4.00 (m)	3.40 (s)	2.10 (s)	2.00 (s)	1.30 (s)	0.82 (d)
4.	Sb(OPr^i)(Hhmba-5)$_2$	6.50–7.00 (m)	—	3.40–4.00 (bm)	3.00 (s)	2.15 (s)	2.00 (d)	1.25 (d)	1.00 (d)

Abbreviations: s = singlet, d = doublet, m = multiplet, h = hump, bs = broad singlet, bm = broad multiplet.

the isopropoxy group[5]. A shift of 20 cm^{-1} in $\nu_{sym}(COO)$, as compared to H_3hmba-5, indicates the bonding of the carboxylate oxygen with antimony. Further, the separation value, $\Delta\nu(COO)$, of 230 cm^{-1} suggests the absence of a bridged or coordinated carboxylate group[6, 7]. A strong band due to ν(C—N) occurring at 1255 cm^{-1} instead of 1220 cm^{-1} as noted in H_3hmba-5, suggests possible bonding of nitrogen to antimony. A weak band at 1210 cm^{-1} may be assigned to ν(C—O), while the other at 1150 cm^{-1} corresponds to ν(C—O) of the isopropoxy group. The absorptions due to the aromatic in-plane bending occur at 1100 cm^{-1}, 1030 cm^{-1} and 930 cm^{-1},[5, 8] while the bands at 830 cm^{-1}, 805 cm^{-1} and 765 cm^{-1} correspond to the characteristic C—H out-of-plane bending expected of a trisubstituted benzene ring[5]. A strong bond at 590 cm^{-1} corresponds to ν(Sb—O)[9, 10], while the others 480 cm^{-1} and 430 cm^{-1} show the ν(Sb—N). In view of the foregoing considerations, it is concluded that $Sb(OPr^i)$(Hhmba-5) [Structure (II)] contains a tetra-coordinated antimony atom by way of bonding with one of the oxygens from the carboxylate group, the nitrogen from the imino group and the oxygen from the phenolate group, along with an isopropoxy group.

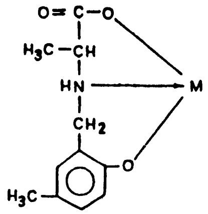
Proton Magnetic Resonance Spectra

The PMR spectra of $Sb(OPr^i)$(Hhmba-5) shows a multiplet in the region δ 6.50–7.00 which may be assigned to the aromatic ring protons, while the singlet at δ 6.90 due to the phenolic group proton, as noted in H_3hmba-5, disappears here indicating the deprotonation of the phenolic group as a result of bonding of the phenolate oxygen with antimony. The hump at δ3.20 due to the $>NH_2$ group protons, as observed in H_3hmba-5, disappears here with the appearance of a new singlet at δ3.00 which may be assigned to the >NH group proton obtained as a result of deprotonation of the $>NH_2$ group. A broad multiplet between δ3.40–4.00 shows the >CH— group proton of the alanine part of H_3hmba-5, while the signals due to the protons of the $—CH_3$ and $—CH_2—$ groups attached with the benzene ring appear in the form of a singlet at δ 2.15 and a doublet at δ 2.00, respectively. The doublet at δ 1.25 corresponds to the $—CH_3$ group protons of the alanine part of H_3hmba-5, while a new doublet observed at δ1.00 shows the presence of the *gem*-dimethyl protons of the isopropoxy group. Hence the conclusions drawn here are in conformity to those inferred from the IR measurements earlier.

The IR and PMR (wherever available) spectral data were similarly interpreted for the other derivatives and the main findings in context of their structures are as under:

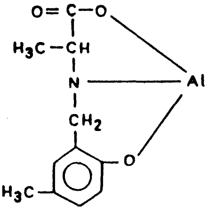
The derivatives, $B(OPr^i)$(Hhmba-5), $Fe(OPr^i)$(Hhmba-5), $As(OPr^i)$(Hhmba-5) and $Sb(OPr^i)$(Hhmba-5) [Structure (II)] contain a tetra-coordinated boron, iron, arsenic or antimony atom in the corresponding case, as a result of bonding with one of the oxygens from the carboxylate group, the nitrogen from the phenolate group, along with an isopropoxy group. However, the aluminium atom in the derivative, Al(hmba-5) [Structure (III)] displays trivalency by way of bonding with one of the oxygens from the carboxylate group, the nitrogen from the deprotonated imino group and the oxygen from the phenolate group.

The boron, iron or arsenic atom in $B(OPr^i)(H_2hmba\text{-}5)_2$, $Fe(OPr^i)(H_2hmba\text{-}5)_2$ and $As(OPr^i)(H_2hmba\text{-}5)_2$ [Structure (IV)] exhibits trivalency in the corresponding case, as a consequence of bonding with one of the oxygens from each of the two carboxylate groups available from two moles of H_3hmba-5 through a normal ester type of linkage, along with an isopropoxy group. However, the derivative, Sb(OPr^i)(H_2hmba-5)$_2$ [Structure (V)] possesses a penta-coordinated antimony atom as a consequence 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 H_2hmba-5, along with an isopropoxy group. The aluminium atom in Al(H_2hmba-5)(Hhmba-5) [Structure (VI)] displays penta-coordination as a result of bonding with one of the oxygens from the carboxylate group, the nitrogen from the imino group, as well as the oxygen from phenolate group from the first mole of H_3hmba-5 and one of the oxygens from the carboxylate group, and the nitrogen from the imino group from the second mole of H_3hmba-5.

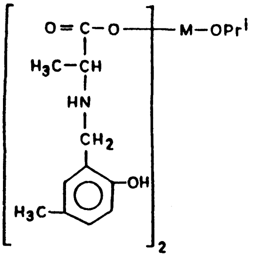


Where M = B Fe AS Sb

(II)

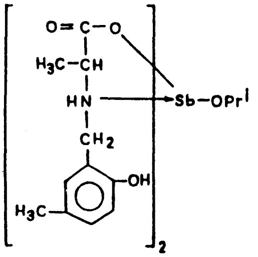


(III)



Where M = B Fe As

(IV)



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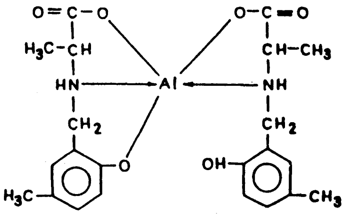
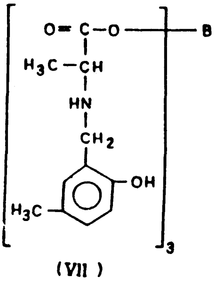
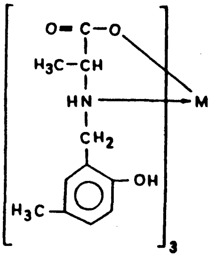


(VI)



(VII)



Where M = Al Fe Sb

(VIII)

The boron atom in the derivative, B(H_2hmba-5)$_3$ [Structure (VII)] shows trivalency by way of bonding with one of the oxygens from each of the three carboxylate groups available from three mole of H_3hmba-5 through a normal ester type of linkage. Again, the aluminium, iron or antimony atom in the derivatives Al(H_2hmba-5)$_3$, Fe(H_2hmba-5)$_3$ and Sb(H_2hmba-5)$_3$ [Structure (VIII)] exhibits hexa-coordination in the cooresponding case, as a consequence 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 moles of H_3hmba-5.

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