

Elemento(III) Derivatives of N-(2-Hydroxy-6-Methyl Benzyl) Alanine

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Several elemento(III) viz. boron, aluminium, iron, arsenic and antimony derivatives of N-(2-hydroxy-6-methyl benzyl) alanine have been prepared by the interaction of the corresponding elemento (III) isopropoxide with the latter in 1:1, 1:2 and 1:3 molar ratios in benzene medium and characterized by azeotrope, elemental analysis and by IR and PMR spectra.

INTRODUCTION

The preparation of several metallo-organic/organometallic derivatives of N-(*o*-hydroxy substituted benzyl) alanines by alcoholysis reactions involving the interaction of the corresponding metal isopropoxide and the latter has been reported^{1,2}. The work described here relates to the preparation of elemento(III) viz. boron, aluminium, iron, arsenic and antimony derivatives of N-(2-hydroxy-6-methyl benzyl) alanine (H₃hmba-6) (Fig. 1) adopting identical procedure involving the reactivity of the corresponding elemento(III) isopropoxide with H₃hmba-6 in 1:1, 1:2 and 1:3 molar ratios in benzene medium.

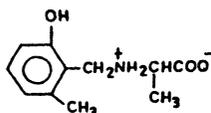


Fig. 1

EXPERIMENTAL

Necessary precautions were taken to exclude moisture throughout the experiments, as before^{1,2}. The other details are described in an earlier paper³.

Reaction between B(OPrⁱ)₃ and H₃hmba-6; 1:1 molar ratio

A mixture of B(OPrⁱ)₃ (0.8000 g; 3.45 mmole) and H₃hmba-6 (0.7170 g; 3.43 mmole) suspended in dry benzene (60 mL) taken in an R.B. flask was refluxed on a wax bath (95–100°C), using a fractionating column 30 cm. long. After *ca.* 5 h of reflux, the isopropanol liberated during the course of reaction was fractionated out azeotropically and estimated by an oxidimetric method, as before¹. On completion of the reaction, the excess of solvent from the reaction mixture was removed *in vacuo*, when the product, B(OPrⁱ) (Hhmba-6) isolated as a brownish white solid, which was washed with dry benzene (3–4 times) followed by dry ether (2–3 times) to remove excess of B(OPrⁱ)₃ and then dried under suction. The product was found to be soluble in DMF and DMSO but

insoluble in other organic solvents like ethanol, benzene, toluene, carbon tetrachloride and chloroform etc.

It may be mentioned here that since $B(OPr^i)_3$ is soluble in benzene, while $H_3hmba-6$ 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 unreacted $H_3hmba-6$. The amount of isopropanol liberated was, therefore, calculated according to the amount of $H_3hmba-6$ taken.

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

TABLE-1
ANALYTICAL DETAIL OF THE VARIOUS ELEMENTO (III) DERIVATIVES OF
N-(2-HYDROXY-6-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-6) (1:1) (brownish white)	180	0.70 (0.72)	60.52 (60.67)	7.20 (7.27)	4.98 (5.05)	3.82 (3.90)
B(OPr ⁱ)(H ₂ hmba-6) ₂ (1:2) (brownish white)	142	1.16 (1.18)	61.57 (61.73)	7.18 (7.25)	5.70 (5.76)	2.20 (2.22)
B(OPr ⁱ)(H ₂ hmba-6) ₃ (1:3) (brownish white)	135	0.46 (0.48)	62.48 (62.56)	6.62 (6.68)	6.58 (6.63)	1.68 (1.71)
Al(hmba-6) (1:1) (light brown)	197	0.25 (0.26)	56.43 (56.65)	5.10 (5.19)	5.90 (6.01)	11.42 (11.57)
Al(H ₂ hmba-6)(Hhmba-6) (1:2) (light brown)	175	0.29 (0.30)	59.60 (59.72)	6.70 (6.83)	6.28 (6.33)	6.00 (6.10)
Al(H ₂ hmba-6) ₃ (1:3) (light brown)	178	0.70 (0.71)	60.56 (60.82)	6.35 (6.50)	6.20 (6.45)	4.00 (4.14)
Fe(OPr ⁱ)(Hhmba-6) (1:1) (light brown)	145	0.40 (0.41)	52.05 (52.19)	6.18 (6.26)	4.27 (4.35)	17.25 (17.34)
Fe(OPr ⁱ)(H ₂ hmba-6) ₂ (1:2) (light brown)	140	0.42 (0.43)	56.38 (56.50)	6.53 (6.64)	5.15 (5.27)	10.38 (10.51)
Fe(H ₂ hmba-6) ₃ (1:3) (light brown)	148	0.48 (0.49)	58.18 (58.24)	6.15 (6.22)	6.10 (6.17)	8.10 (8.21)
As(OPr ⁱ)(Hhmba-6) (1:1) (light brown)	165	0.49 (0.51)	49.21 (49.27)	5.84 (5.91)	4.00 (4.11)	21.83 (21.95)
As(OPr ⁱ)(H ₂ hmba-6) ₂ (1:2) (light brown)	140	0.98 (0.99)	54.40 (54.55)	6.32 (6.41)	4.92 (5.09)	13.48 (13.61)
Sb(OPr ⁱ)(Hhmba-6) (1:1) (brown)	250	0.64 (0.65)	43.25 (43.33)	5.15 (5.19)	3.57 (3.61)	31.30 (31.37)
Sb(OPr ⁱ)(H ₂ hmba-6) ₂ (1:2) (brown)	160	0.41 (0.44)	50.22 (50.27)	5.87 (5.91)	4.64 (4.69)	20.30 (20.30)
Sb(OPr ⁱ)(H ₂ hmba-6) ₃ (1:3) (brown)	170	0.48 (0.49)	53.02 (53.10)	5.62 (5.67)	5.59 (5.63)	16.27 (16.31)

Abbreviations: $OPr^i = OC_3H_7$, $H_3hmba-6 = CH_3C_6H_3(OH)CH_2NH_2CH(CH_3)COO^-$

TABLE-2
 CHARACTERISTIC INFRARED FREQUENCY (cm^{-1}) OF THE VARIOUS ELEMENTO (III) DERIVATIVES OF
 N-(2-HYDROXY-6-METHYL BENZYL) ALANINE

Compound	$\nu(\text{OH})$	$\nu(\text{N-H})$ and aromatic $\nu(\text{C-H})$	$\nu(\text{C-H})$ of $-\text{CH}_3$ and $-\text{CH}_2$ groups	$\nu(\text{C=O})$ (ester)	$\nu_{\text{asym}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$	$\Delta\nu(\text{COO})$	$\nu(\text{C-N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
B(OPr ⁺)(Hmba-6)	—	3300-3100 (b)	2980 (w) 2940 (w)	—	1630 (s)	1390 (w)	240	1265 (m)	1375 (w)	1520 (m)
B(OPr ⁺)(H ₂ hmba-6) ₂	3550-3000 (vb)	3150-3000 (b)	2940 (w) 2920 (w) 2860 (wb)	1740 (s)	1600 (s)	1375* (s)	225	1250 (m)	—	—
B(H ₂ hmba-6) ₃	3600-3300 (vb)	3200-3000 (b)	2960 (m) 2930 (w) 2850 (m)	1750 (s)	1630 (s)	1380* (sh)	250	1250 (m)	—	—
Al(hmba-6)	—	3250-3000 (b)	2920 (m) 2885 (m) 2845 (m)	—	1680 (b)	1375 (b)	245	1265 (m)	680 (m) 600 (mb)	470 (w) 450 (m)
Al(H ₂ hmba-6)(Hhmba-6)	3500-3300 (b)	3100-3000 (mb)	2990 (s) 2940 (w)	—	1625 (s)	1390 (mb)	235	1265 (m)	690 (m) 665 (m)	580 (m) 540 (m)
Al(H ₂ hmba-6) ₃	3500-3400 (mb)	3200-3000 (mb)	2960 (w) 2930 (m) 2850 (m)	—	1630 (vs)	1390 (m)	240	1260 (w)	690 (m)	580 (m) 550 (m) 490 (m)

Compound	$\nu(\text{OH})$	$\nu(\text{N—H})$ and aromatic $\nu(\text{C—H})$	$\nu(\text{C—H})$ of $-\text{CH}_3$ and $-\text{CH}_2$ groups	$\nu(\text{C=O})$ (ester)	$\nu_{\text{asym}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$	$\Delta\nu(\text{COO})$	$\nu(\text{C—N})$	$\nu(\text{M—O})$	$\nu(\text{M—N})$
$\text{Fe}(\text{OPr}^i)(\text{H}_2\text{hmba-6})$	—	3200–3000 (b)	2950 (m) 2850 (m)	—	1615 (s)	1370 (mb)	245	1250 (m)	480 (m)	420 (m) 430 (w)
$\text{Fe}(\text{OPr}^i)(\text{H}_2\text{hmba-6})_2$	3400–3300 (vb)	3200–3020 (mb)	2910 (m) 2850 (m)	1680 (b)	1620 (s)	1375 (b)	255	1250 (b)	535 (s) 440 (s)	—
$\text{Fe}(\text{H}_2\text{hmba-6})_3$	3500–3200 (b)	3200–3000 (mb)	2920 (m) 2850 (w)	—	1620 (sb)	1375 (m)	245	1265 (s)	540 (s) 440 (s)	405 (s)
$\text{As}(\text{OPr}^i)(\text{Hhmba-6})$	—	3200–3000 (b)	2960 (m) 2925 (w) 2850 (m)	—	1610 (s)	1380 (m)	230	1260 (m)	560 (m)	470 (m) 410 (m)
$\text{As}(\text{OPr}^i)(\text{H}_2\text{hmba-6})_2$	3500–3300 (b)	3180–3030 (m)	2940 (m) 2850 (m)	1700 (s)	1620 (s)	1375 (sb)	245	1250 (s)	605 (s)	—
$\text{Sb}(\text{OPr}^i)(\text{Hhmba-6})$	—	3300–3000 (b)	2950 (mb) 2885 (w)	—	1610 (s)	1375 (sb)	235	1260 (s)	590 (s)	485 (s) 420 (m)
$\text{Sb}(\text{OPr}^i)(\text{H}_2\text{hmba-6})_2$	3400–3340 (b)	3200–3000 (mb)	2985 (m) 2860 (m)	—	1620 (s)	1395 (s)	225	1265 (vs)	585 (s)	485 (s) 430 (w)
$\text{Sb}(\text{H}_2\text{hmba-6})_3$	3500–3000 (b)	3140–3000 (b)	2940 (m) 2860 (m)	—	1630 (sb)	1390 (m)	240	1265 (m)	590 (s)	495 (s) 420 (s)

Abbreviations: s = strong, m = medium, w = weak, vsb = very strong broad, sb = strong broad, mb = medium broad.

*Overlapping of $\nu_{\text{sym}}\text{COO}$ and $\nu(\text{B—O})$

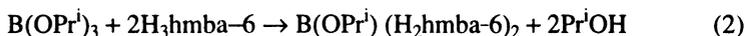
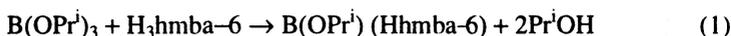
TABLE-3
 PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ VALUE) OF SEVERAL ELEMENTO (III) DERIVATIVES OF
 N-(2-HYDROXY-6-METHYL BENZYL)ALANINE

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)(Hhmba-6)	6.40–7.20 (m)	—	3.50–4.00 (bm)	3.00 (s)	2.20 (s)	2.05 (d)	1.25 (bs)	0.85 (d)
2.	Al(H ₂ hmba-6)(Hhmba-6)	6.40–7.00 (m)	6.25 (s)	3.50–3.90 (m)	3.20 (s)	2.20 (s)	2.00 (d)	1.20 (d)	—
3.	Fe(H ₂ hmba-6) ₃	6.25–7.30 (m)	6.00 (s)	3.55–4.00 (m)	3.34 (s)	2.35 (s)	2.00 (d)	1.25 (d)	—
4.	As(OPr ⁱ)(H ₂ hmba-6) ₂	6.45–7.25 (m)	—	3.60–4.00 (m)	3.00 (s)	2.25 (s)	2.00 (d)	1.30 (d)	0.75 (d)
5.	Sb(H ₂ hmba-6) ₃	6.30–7.00 (m)	6.00 (s)	3.50–4.00 (m)	3.34 (h)	2.10 (s)	2.00 (d)	1.20 (d)	—

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

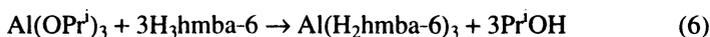
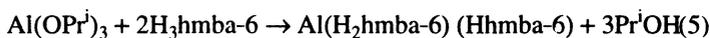
RESULTS AND DISCUSSION

The various reactions occurring between boron tri-isopropoxide and H₃hmba-6 may be illustrated as:



Identical reaction 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 H₃hmba-6 may be illustrated as under.



Infrared Spectra

The appearance of a broad band between 3300–3100 cm⁻¹ in B(OPrⁱ)(Hhmba-6) may be assigned to the overlapping of ν(N—H) and aromatic ν(C—H)^{4,5}. The band corresponding to the phenolic νOH, as observed in H₃hmba-6, is found to be absent here indicating the participation of the phenolate oxygen in bonding with boron. The presence of ν(N—H) in the lower region suggests possible bonding of nitrogen to boron^{6,7}. The weak absorptions at 2980 cm⁻¹ and 2940 cm⁻¹ may be ascribed to ν(C—H) of the —CH₂— and —CH₃ groups. The absence of any characteristic band corresponding to ν(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 boron. A strong band at 1630 cm⁻¹ may be attributed to the overlapping of ν_{asym}(COO), aromatic ν(C=C) and N—H deformation⁸. The medium band at 1520 cm⁻¹ may be attributed to ν(B—N)^{8,9}, while the others at 1490 cm⁻¹ and 1460 cm⁻¹ correspond to the aromatic skeletal vibrations^{5,9}. Further, instead of peak at 1405 cm⁻¹, as noted in H₃hmba-6, here the occurrence of a weak band around 1390 cm⁻¹ may be assigned to the overlapping of ν_{sym}(COO) and (C—H) bending of the *gem*-dimethyl structure of the isopropoxy group. A shift of 15 cm⁻¹ in ν_{sym}(COO), as compared to H₃hmba-6, indicates the bonding of the carboxylate oxygen with boron. The separation value, Δν(COO) of 240 cm⁻¹ suggests the absence of a bridged or coordinated carboxylate group^{6,10}. The weak absorption at 1375 cm⁻¹ arises due to ν(B—O)¹¹. A medium band due to the overlapping of ν(C—N) and ν(C—O) at 1265 cm⁻¹ instead of a weak absorption at 1250 cm⁻¹ corresponding to ν(C—N), as noted in case of H₃hmba-6, shows possible bonding of nitrogen to boron. The strong band at 1160 cm⁻¹ and medium bands at 1110 cm⁻¹ and 1040 cm⁻¹ may be assigned to the aromatic C—H in-plane bending modes⁵, while the

medium bands at 960 cm^{-1} , 870 cm^{-1} and 810 cm^{-1} correspond to the aromatic C—H out-of-plane bending modes expected of a trisubstituted benzene ring⁵. On the basis of the above observations it appears that the boron atom in $\text{B}(\text{OPr}^j)(\text{Hhmba-6})$ [Structure II] shows tetra-coordination^{8,12}, as a result of bonding with one of the oxygens from carboxylate group, the nitrogen from imino group and the oxygen from the phenolate group, along with an isopropoxy group.

Proton Magnetic Resonance Spectra

The PMR spectrum of $\text{B}(\text{OPr}^j)(\text{Hhmba-6})$ displays a multiplet between $\delta\ 6.40\text{--}7.20$ which may be assigned to the aromatic ring protons. A singlet at $\delta\ 6.55$ due to the phenolic group proton, as noted in $\text{H}_3\text{hmba-6}$, disappears here showing the deprotonation of the phenolic group as a result of bonding of the phenolate oxygen with boron. The hump in the region $\delta\ 3.00\text{--}3.30$ due to the protons of the $>\text{NH}_2$ group, as observed in $\text{H}_3\text{hmba-6}$, is found to be absent here, while the appearance of a new signal at $\delta\ 3.00$ corresponds to the proton of the $>\text{NH}$ group obtained as a result of deprotonation of the $>\text{NH}_2$ group. A broad multiplet between $\delta\ 3.50\text{--}4.00$ occurs because of the $>\text{CH}$ — group proton of the alanine part of $\text{H}_3\text{hmba-6}$, while the signals due to the protons of the $-\text{CH}_3$ and $-\text{CH}_2-$ groups attached with the benzene ring appear in form of a singlet at $\delta\ 2.20$ and a doublet at $\delta\ 2.05$, respectively. A broad singlet at $\delta\ 1.25$ and doublet at $\delta\ 0.85$ corresponds to the protons of the $-\text{CH}_3$ group of the alanine part of $\text{H}_3\text{hmba-6}$ and the *gem*-dimethyl protons of the isopropoxy group, respectively. Hence, the conclusions drawn here are in conformity to those inferred from the IR measurements earlier.

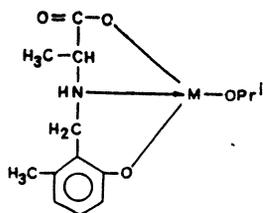
The IR and PMR spectral data were similarly interpreted in respect of the other derivatives and the main findings in the context of their structures are as under:

The derivatives, $\text{B}(\text{OPr}^j)(\text{Hhmba-6})$, $\text{Fe}(\text{OPr}^j)(\text{Hhmba-6})$, $\text{As}(\text{OPr}^j)(\text{Hhmba-6})$, $\text{Sb}(\text{OPr}^j)(\text{Hhmba-6})$ [Structure II] possess a tetra-coordinated boron, iron, arsenic or antimony atom in each case 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. However, the aluminium atom in the derivative, $\text{Al}(\text{hmba-6})$ [Structure III] exhibits trivalency as a consequence 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.

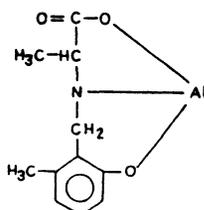
The boron, iron or arsenic atom in $\text{B}(\text{OPr}^j)(\text{H}_2\text{hmba-6})_2$, $\text{Fe}(\text{OPr}^j)(\text{H}_2\text{hmba-6})_2$ and $\text{As}(\text{OPr}^j)(\text{H}_2\text{hmba-6})_2$ [Structure IV] shows trivalency in the corresponding case, as a result of bonding with one of the oxygens from each of the two carboxylate groups available from two moles of $\text{H}_3\text{hmba-6}$ through a normal ester type of linkage, along with an isopropoxy group. However, the derivative, $\text{Sb}(\text{OPr}^j)(\text{H}_2\text{hmba-6})_2$ [Structure V] contains a pentacoordinated antimony atom 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 $H_3hmba-6$. Again, the aluminium atom in the derivative, $Al(H_2hmba-6)(Hhmba-6)$ [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 the phenolate group from the first mole of $H_3hmba-6$ and one of the oxygens from the carboxylate group, and the nitrogen from the imino group from the second mole of $H_3hmba-6$.

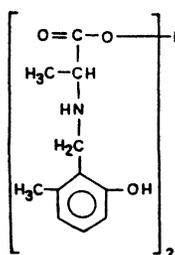
The boron atom in the derivative $B(H_2hmba-6)_3$ [Structure VII] displays trivalency by way of bonding with one of the oxygens from each of the three carboxylate groups available from three moles of $H_3hmba-6$ through a normal ester type of linkage. However, the aluminium, iron or antimony atom in $Al(H_2hmba-6)_3$, $Fe(H_2hmba-6)_3$ and $Sb(H_2hmba-6)_3$ [Structure VIII] shows hexa-coordination in the cooresponding case by way of bonding with one of the



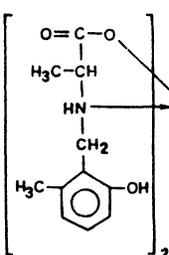
Where M = B Fe As Sb
(II)



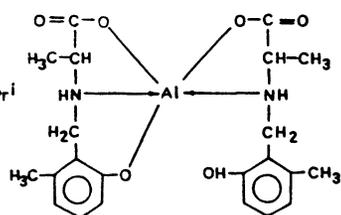
(III)



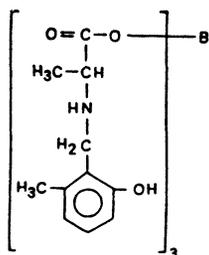
Where M = B As Fe
(IV)



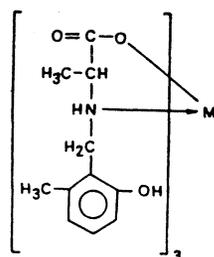
(V)



(VI)



(VII)



Where M = Al Fe Sb

(VIII)

oxygens from each of the three carboxylate groups and the nitrogen from each of the three imino groups available from three moles of H₃hmba-6.

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High Swelling Gels

36TH MICROSYMPOSIUM ON MACROMOLECULES: HIGH SWELLING GELS

PRAGUE, CZECH REPUBLIC

July 10–14, 1995

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