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

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Several elemento(III) viz. boron, aluminium, iron, arsenic and antimony derivatives of N-(2-hydroxy-6-methyl benzyl) valine have been prepared by alcoholysis reactions involving the interaction of the corresponding elemento(III) isopropoxide and the latter in 1 : 1, 1 : 2 and 1 : 3 molar ratios in benzene medium. The compounds thus prepared were obtained as coloured solids and out of them those containing isopropoxy group were found to be hygroscopic. All these compounds were characterized by azeotrope and elemental analyses, as well as by IR and PMR spectral measurements.

INTRODUCTION

In continuation to the studies on elemento(III) derivatives of N-(2-hydroxy-methyl substituted benzyl) valines[1], the work described here deals with the preparation and characterization of boron, aluminium, iron, arsenic and antimony derivatives of N-(2-hydroxy-6-methyl benzyl) valine (H_2hmbv-6).

EXPERIMENTAL

Benzene (BDH, AR), isopropanol (BDH Glaxo AnalaR) and solvent ether (E. Merck) were dried by reported methods[1]. The various elemento(III) isopropoxides were prepared and the amount of the corresponding trivalent element content in each case, wherever necessary, was estimated, as before[1]. The details of the various glass assemblies and instruments used were identical to those reported earlier[1]. The alcoholysis reactions were performed in a moisture-free atmosphere, as before[1].

The procedures for the preparation of H_3hmbv-6(using *m*-cresol; E. Merck) and its purification have been the same as those employed in respect of the analogous derivative, N-(2-hydroxy-3-methyl benzyl) valine[1].

The various elemento(III) derivatives of H_3-hmbv-6 were prepared and purified similarly as those of the corresponding derivatives of N-(2-hydroxy-3-methyl benzyl) valine[1]. These derivatives were found to be soluble in dimethyl formamide and dimethyl sulphoxide, sparingly soluble in chloroform but insoluble in other common organic solvents like ethanol, benzene, toluene and carbon tetrachloride etc.

The relevant analytical details, characteristic IR frequencies and PMR spectra

data of the various compounds prepared are summarized in Tables 1-3, respectively.

TABLE-1
ANALYTICAL DETAILS OF N-(2-HYDROXY-6-METHYL BENZYL) VALINE AND ITS VARIOUS ELEMENTO(III) DERIVATIVES

Compound (molar ratio) (colour)	m.p. (°C)	Elemental analysis, % Found (Calcd.)			
		C	H	N	M
H_3hmbv-6 (Light almond brown)	140	65.60 (65.82)	8 .13 (8.10)	5.88 (5.90)	–
B(hmbv-6) (1 : 3) (Light almond brown)	189	63.95 (64.19)	6.56 (6.58)	5,74 (5.76)	3.68 (3.70)
B(OPr^i)(H_2hmbv-6)$_2$ (1 : 2) (Light almond brown)	182	64.10 (64.44)	5.73 (5.76)	5.14 (5.16)	1.68 (1.67)
B(H_2hmbv-6)$_3$ (1 : 3) (Light almond brown)	188	65.05 (65.27)	7.50 (7.53)	5.83 (5.86)	1.26 (1.26)
Al(hmbv-6) (1 : 1) (Light almond brown)	198	59.55 (59.77)	6.11 (6.13)	5.33 (5.36)	10.30 (10.34)
Al(Hhmbv-6)(H_2hmbv-6) (1 : 2) (Light almond brown)	195	62.43 (62.65)	7.00 (7.02)	5.60 (5.62)	5.40 (5.42)
Al(H_2hmbv-6)$_3$ (1 : 3) (Light almond brown)	180	63.40 (63.67)	7.34 (7.35)	5.69 (5.71)	3.59 (3.61)
Fe(hmbv-6) (1 : 1) (Light brownish pink)	180	53.65 (53.97)	5.50 (5.53)	4.82 (4.84)	19.00 (19.03)
Fe(Hhmbv-6)(H_2hmbv-6) (1 : 2) (Light brownish pink)	182	59.18 (59.31)	6.62 (6.65)	5.30 (5.32)	10.41 (10.45)
Fe(H_2hmbv-6)$_3$ (1 : 3) (Light brownish pink)	188	61.11 (61.33)	7.04 (7.07)	5.48 (5.50)	7.00 (7.20)
As(OPr^i)(H_2hmbv-6) (1 : 1) (Light brownish pink)	210	52.31 (52.03)	6.48 (6.50)	3.79 (3.79)	20.29 (20.32)
As(OPr^i)(H_2hmbv-6)$_2$ (1 : 2) (Light brownish pink)	212	57.18 (57.42)	7.07 (7.09)	4.61 (4.62)	12.31 (12.37)
Sb(OPr^i)(Hhmbv-6) (1 : 1) (Light brownish orange)	260	46.40 (46.15)	5.74 (5.76)	3.35 (3.36)	29.30 (29.32)
Sb(OPr^i)(H_2hmbv-6)$_2$ (1 : 2) (Light brownish orange)	262	53.05 (53.29)	6.55 (6.58)	6.26 (6.28)	18.60 (18.68)
Sb(H_2hmbv-6)$_3$ (1 : 3) (Light brownish orange)	259	56.16 (56.38)	6.48 (6.50)	5.04 (5.06)	14.65 (14.69)

Abbreviations: $OPr^i = OC_3H_7$, H_3hmbv-6 = $CH_3C_6H_3(OH)CH_2\overset{+}{N}H_2CHCH(CH_3)_2COO^-$

TABLE-2
CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) OF N-(2-HYDROXY-6-METHYL BENZYL) VALINE AND ITS VARIOUS ELEMENTO(III) DERIVATIVES

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)
H_3hmbv-6	3670–3000 (vb)	—	2960 (s) 2840 (w)	—	1610 (sb)	1410 (m)	—	1260 (s)	—	—
B(Hhmbv-6)	—	3400–3000 (b)	2980 (s) 2860 (w)	—	1620 (sb)	1375 (m)	245	1260 (s)	1375 (m)	1520 (m)
B(OPr^i)(H_2hmbv-6)$_2$	3680–3400 (vb)	3400–3000 (b)	2980 (m) 2860 (w)	1720 (mb)	1620 (sb)	1380 (m)*	240	1260 (s)	1380 (m)	—
B(H_2hmbv-6)$_3$	3660–3300 (vb)	3300–3000 (mb)	2980 (s) 2860 (w)	1720 (mb)	1620 (sb)	1370 (m)*	250	1260 (m)	1370 (m)	—
Al (hmbv-6)	—	3400–3000 (b)	2980 (s) 2880 (w)	—	1620 (sb)	1380 (m)	240	1265 (s)	660 (m) 590 (m)	470 (w) 445 (m)
Al(Hhmbv-6)(H_2hmbv-6)	3680–3400 (vb)	3400–3000 (b)	2980 (s) 2880 (w)	—	1610 (sb)	1365 (m)	245	1270 (s)	675 (m)	490 (w)
Al(H_2hmbv-6)$_3$	3680–3400 (vb)	3400–3000 (b)	2980 (s) 2880 (w)	—	1620 (sb)	1370 (m)	250	1280 (s)	675 (m)	470 (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)
Fe(hmbv-6)	—	3380–3000 (b)	2970 (s) 2880 (w)	—	1620 (sb)	1380 (m)	240	1280 (s)	450 (w)	410 (w)
Fe(Hhmbv-6)(H_2hmbv-6)	3690–3350 (vb)	3350–3000 (b)	2980 (s) 2870 (w)	—	1610 (sb)	1380 (m)	230	1270 (s)	480 (m)	415 (m)
Fe(H_2hmbv-6)$_3$	3690–3360 (vb)	3360–3000 (b)	2980 (s) 2880 (w)	—	1620 (sb)	1360 (m)	260	1275 (s)	440 (m)	410 (w)
As(OPr^i)(Hhmbv-6)	—	3360–3000 (b)	2980 (s) 2875 (w)	—	1620 (sb)	1370 (m)	250	1270 (s)	590 (m)	480 (m)
As(OPr^i)(H_2hmbv-6)$_2$	3690–3360 (vb)	3360–3000 (b)	2980 (s) 2875 (w)	—	1620 (sb)	1375 (m)	245	1280 (s)	570 (m)	470 (m)
Sb(OPr^i)(Hhmbv-6)	—	3360–3000 (b)	2980 (s) 2880 (w)	—	1620 (sb)	1370 (m)	250	1270 (s)	620 (m)	460 (w)
Sb(OPr^i)(H_2hmbv-6)$_2$	3670–3360 (vb)	3360–3000 (b)	2980 (s) 2880 (w)	—	1620 (sb)	1370 (m)	250	1270 (s)	570 (m) 640 (m)	470 (m) 425 (w)
Sb(H_2hmbv-6)$_3$	3680–3360 (vb)	3360–3000 (b)	2980 (s) 2880 (w)	—	1620 (sb)	1380 (m)	240	1280 (s)	630 (m)	460 (m)

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

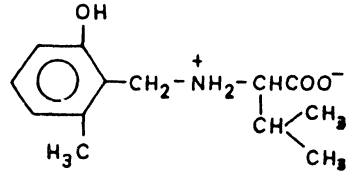
TABLE-3
PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ VALUE) OF N-(2-HYDROXY-6-METHYL BENZYL) VALINE AND ITS VARIOUS ELEMENTO(III) DERIVATIVES (DMSO-d_6)

S. No.	Compound	Aromatic ring	Pehnolic (—OH)	>CH— groups (of valine part)	>NH	—CH_3 (attached with the benzene ring)	—CH_2— (attached with the benzene ring)	*gem*-dimethyl
1.	H_3hmbv-6	6.60–6.72 (d)* 6.72–6.85 (t)* 6.94–7.00 (d)*	6.92 (s)	3.42–4.15 (m)	3.10–3.42 (h)	2.04–2.10 (d)	2.16 (s)	0.92 (s)
2.	B(H_2hmbv-6)$_3$	6.30–7.20 (m)	6.95 (s)	3.20–4.00 (m)	3.10 (s)	2.20 (s)	2.20-2.10 (d)	0.70–1.10 (d)
3.	Al (hmbv-6)	6.10–6.75 (m)	—	3.20–3.80 (m)	—	2.20 (s)	2.10 (s)	0.75–1.10 (d)
4.	Fe(Hhmbv-6)(H_2hmbv-6)	6.20–6.90 (m)	6.92 (s)	3.35–4.00 (m)	3.10 (s)	2.20 (s)	2.05 (s)	0.75–1.25 (d)
5.	As(OPr^i)(H_2hmbv-6)$_2$	5.90–6.95 (m)	7.00 (s)	3.30–4.00 (m)	3.00 (s)	2.15 (s)	2.00 (s)	0.75–1.25 (d)
6.	Sb(OPr^i)(H_2hmbv-6)$_2$	6.15–6.90 (m)	6.95 (s)	3.30–3.85 (m)	3.00 (s)	2.15 (d)	2.00 (s)	0.60–1.10 (d)

Abbrevations: s = singlet, d = doublet, m =multiplet, h = hump, t = triplet.
*Corresponds to the protons at positions 3, 4 and 5 of the trisubstituted benzene ring.

RESULTS AND DISCUSSION

The IR and PMR spectral data indicate that the H_3hmbv-6 exists in zwitterionic form (Structure I).



(I)

The reaction between $B(OPr^i)_3$ and H_3hmbv-6 in 1:1 molar ratio may be illustrated as

$$B(OPr^i)_3 + H_3hmbv\text{-}6 \rightarrow B(hmbv\text{-}6) + 3Pr^iOH$$

Identical reactions followed in case of iron(III) and aluminium(III). However, arsenic(III) and antimony(III) isopropoxides reacted differently as under:

$$As(OPr^i)_3 + H_3hmbv\text{-}6 \rightarrow As(OPr^i)(Hhmbv\text{-}6) + 2Pr^iOH$$

$$Sb(OPr^i)_3 + H_3hmbv\text{-}6 \rightarrow Sb(OPr^i)(Hhmbv\text{-}6) + 2Pr^iOH$$

The reaction between $B(OPr^i)_3$ and H_3hmbv-6, in 1:2 molar ratio, occurred as

$$B(OPr^i)_3 + 2H_2hmbv\text{-}6 \rightarrow B(OPr^i)(H_2hmbv\text{-}6) + 2Pr^iOH$$

Identical reactions followed in case of arsenic(III) and antimony(III). However, aluminium(III) and iron(III) isopropoxides reacted differently as under:

$$Al(OPr^i)_3 + 2H_2hmbv\text{-}6 \rightarrow Al(Hhmbv\text{-}6)(H_2hmbv\text{-}6) + 3Pr^iOH$$

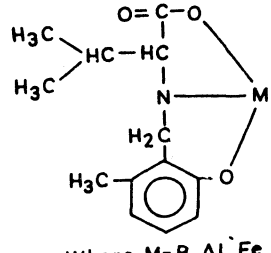
$$Fe(OPr^i)_3 + 2H_2hmbv\text{-}6 \rightarrow Fe(Hhmbv\text{-}6)(H_2hmbv\text{-}6) + 3Pr^iOH$$

The reaction between $B(OPr^i)_3$ and H_3hmbv-6 in 1:3 molar ratio may be illustrated as under

$$B(OPr^i)_3 + 3H_2hmbv\text{-}6 \rightarrow B(H_2hmbv\text{-}6)_3 + 3Pr^iOH$$

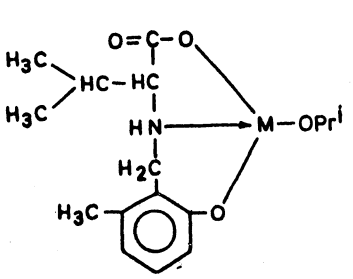
Identical reactions followed in case of aluminium(III), iron(III) and antimony(III). However, 1:3 reaction in case of arsenic(III) did not proceed even after prolonged reflux and fractionation.

Based on azeotrope and elemental analysis, as well as the spectral data[2–10], the structures [(II)-(VIII)] of the various derivatives prepared may be illustrated as under:

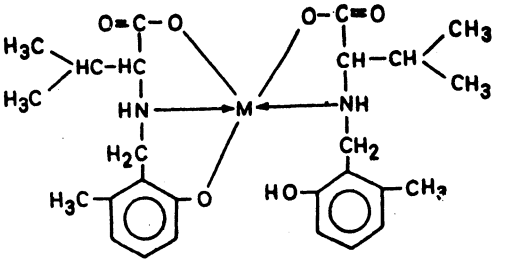


Where M=B, Al, Fe

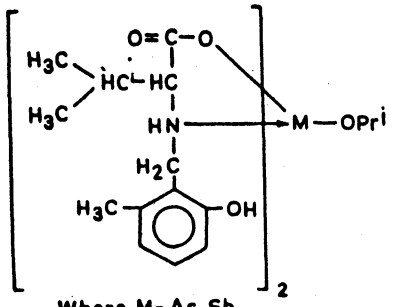
(II)



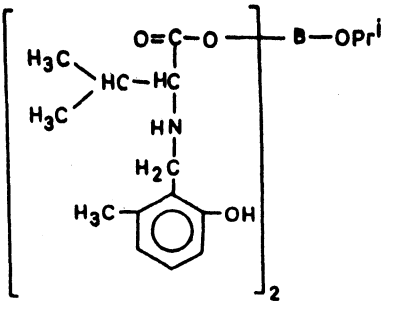
Where M=As, Sb
(III)



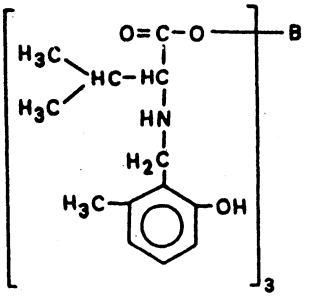
Where M=Al, Fe
(IV)



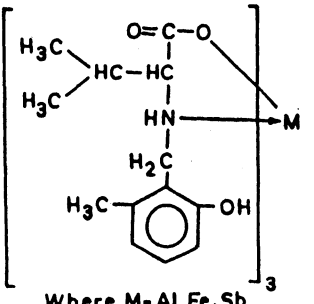
Where M=As, Sb
(V)



(VI)



(VII)



Where M=Al, Fe, Sb
(VIII)

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