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

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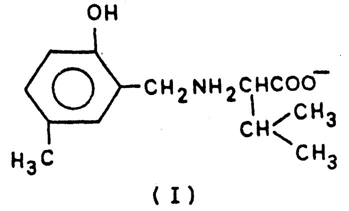
Boron(III), aluminium(III), iron(III), arsenic(III) or antimony(III) derivatives of N-(2-hydroxy-5-methyl benzyl) valine have been prepared by the reactivity of the corresponding elemento (III) isopropoxide with the latter in 1 : 1, 1 : 2 or 1 : 3 molar ratios in benzene medium which were characterized by azeotrope and elemental analyses, as well as by spectral measurements.

INTRODUCTION

The elemento(III) derivatives of N-(2-hydroxy-3-methyl benzyl)-and N-(2-hydroxy-6-methyl benzyl) valine have been reported earlier.[1, 2] In continuation, the work described here relates to the preparation of boron(III), aluminium(III), iron(III), arsenic(III) and antimony(III) derivatives of N-(2-hydroxy-5-methyl benzyl) valine (H_3hmbv-5) (I) involving the interaction of the corresponding elemento(III) isopropoxides with H_3hmbv-5 in 1 : 1, 1 : 2 or 1 : 3 molar tatios in benzene medium. The various compounds thus prepared were obtained as coloured solids and amongst them those containing isopropoxy group were found to be hygroscopic. All these compounds were characterised by azeotrope and elemental analyses, as well as by IR and PMR spectral measurements.



(I)

EXPERIMENTAL

Stringent precautions were taken to exclude moisture throughout the experiments, as before.[1, 2] The other details are described earlier.[1, 2]

Preparation of N-(2-hydroxy-5-methyl benzyl)valine

N-(2-hydroxy-5-methyl benzyl)valine was prepared adopting procedures identical to those employed for the preparation of the other similar derivatives.[1, 2] To a mixture of equimolar amounts of *p*-cresol (E. Merck), valine (Loba) and sodium acetate trihydrate (Sarabhai GR) in acetic acid (Sarabhai GR) medium was added an equimolar amount of formaldehyde solution (Sarabhai GR) and the contents were heated at 60–80°C till a viscous mass was obtained. The viscous mass was poured dropwise with brisk stirring in an excess of water, when the free acid precipitated which was filtered under suction and washed thoroughly with water. The crude product thus obtained was purified by dissolving it in a requisite quantity of sodium hydroxide solution, followed by its reprecipitation by 50% hydrochloric acid. The mother liquor was decanted and the precipitate was freed from chloride ions by washing it with water. Finally, it was filtered through a sintered funnel and air dried.

Preparation of elemento(III) derivatives of H_3hmbv-5

General Procedure: A mixture of elemento(III) isopropoxide and H_3hmbv-5 taken in suitable stoichiometry in dry benzene was refluxed on a wax bath (95–100°C). After several hours of reflux, the isopropanol-benzene azeotrope was fractionated out and the amount of isopropanol liberated was estimated oxidimetrically[1, 2] to monitor the completion of the reaction. Upon completion of the reaction, the excess of solvent from the reaction mixture was removed *in vacuo* and the product was washed with dry benzene (3–4 times) followed by dry ether (2–3 times) to remove unreacted elemento(III) isopropoxide. The product was finally dried under vacuum which was found to be soluble in dimethylsulphoxide, but insoluble in other common organic solvents like ethanol, benzene, toluene, chloroform and carbon tetrachloride.

It may be mentioned here that since elemento(III) isopropoxides are soluble in benzene, while H_3hmbv-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_3hmbv-5. The amount of isopropanol liberated was, therefore, calculated according to the amount of H_3hmbv-5 taken.

The relevant analytical details, the characteristic IR frequencies and PMR spectral data are summarized in Tables 1–3, respectively.

RESULTS AND DISCUSSION

The analysis of IR and PMR spectral data indicates that H_3hmbv-5 exists in zwitterionic form [Structure (I)] similarly as the other such derivatives.[1, 2]

The reaction occurring between the various elemento(III) isopropoxides and H_3hmbv-5 may be illustrated as follows:

$$B(OPr^i)_3 + H_3\text{hmbv-5} \rightarrow B(\text{hmbv-5}) + 3Pr^iOH$$

$$B(OPr^i)_3 + 2H_3\text{hmbv-5} \rightarrow B(OPr^i)(H_2\text{hmbv-5})_2 + 2Pr^iOH$$

$$B(OPr^i)_3 + 3H_3\text{hmbv-5} \rightarrow B(H_2\text{hmbv-5})_3 + 3Pr^iOH$$

$$Al(OPr^i)_3 + H_3\text{hmbv-5} \rightarrow Al(\text{hmbv-5}) + 3Pr^iOH$$

$$Al(OPr^i)_3 + 2H_3\text{hmbv-5} \rightarrow Al(H\text{hmbv-5})(H_2\text{hmbv-5}) + 3Pr^iOH$$

TABLE-1
ANALYTICAL DETAILS OF N-(2-HYDROXY-5-METHYL BENZYL) VALINE AND ITS VARIOUS ELEMENTO(III) DERIVATIVES

S. No	Compound/ (Colour)	Yield (%)	m.p. (°C)	Analysis % found (calcd.)			
				C	H	N	M
1.	H_3hmbv-5	62.1	120	65.50	7.92	5.85	—
	Light almond brown			(65.82)	(8.01)	(5.90)	
2.	B(hmbv-5)	94.3	140	64.00	6.50	5.60	3.63
	Light almond brown			(64.19)	(6.58)	(5.76)	(3.70)
3.	B(OPr^i)(H_2hmbv–5)$_2$	93.1	144	64.20	5.72	5.09	1.66
	Light almond brown			(64.44)	(5.76)	(5.16)	(1.67)
4.	B(H_2hmbv–5)$_3$	94.4	159	65.02	7.51	5.82	1.25
	Light almond brown			(65.27)	(7.53)	(5.86)	(1.26)
5.	Al(hmbv-5)	92.3	152	59.52	6.10	5.31	10.28
	Light almond brown			(59.77)	(6.13)	(5.36)	(10.34)
6.	Al(Hhmbv-5) (H_2hmbv-5)	92.5	156	62.42	7.00	5.60	5.38
	Light almond brown			(62.65)	(7.02)	(5.62)	(5.41)
7.	Al(H_2hmbv–5)$_3$	94.3	155	63.41	7.30	5.65	3.58
	Light almond brown			(63.67)	(7.35)	(5.71)	(3.61)
8.	Fe(hmbv-5)	93.7	147	53.72	5.50	4.80	18.90
	Light almond brown			(53.97)	(5.53)	(4.84)	(19.03)
9.	Fe (Hhmbv-5) (H_2hmbv-5)	92.2	142	59.01	6.60	5.28	10.37
	Light almond brown			(59.31)	(6.65)	(5.32)	(10.45)
10.	Fe(H_2hmbv–5)$_3$	95.0	149	62.01	7.05	5.48	7.15
	Light almond brown			(62.33)	(7.07)	(5.50)	(7.20)
11.	As (OPr^i) (Hhmbv-5)	94.2	165	51.88	6.45	3.77	20.15
	Light almond brown			(52.03)	(6.50)	(3.79)	(20.32)
12.	As (OPr^i) (H_2hmbv–5)$_3$	93.1	168	57.19	7.05	4.58	12.27
	Light almond brown			(57.42)	(7.09)	(4.62)	(12.37)
13.	Sb (OPr^i) (Hhmbv-5)	94.8	195	46.00	5.71	3.34	29.16
	Light almond brown			(46.15)	(5.76)	(3.36)	(29.32)
14.	Sb (OPr^i) (H_2hmbV–5)$_2$	93.7	192	53.66	6.55	4.25	18.60
	Light almond brown			(53.29)	(6.58)	(4.28)	(18.68)
15.	Sb(H_2hmbv–5)$_3$	94.5	189	56.12	6.47	5.02	14.64
	Light almond brown			(56.38)	(6.50)	(5.06)	(14.69)

Abbreviations: $OPr^i = OC_3H_7$, H_3hmbv–5 = $CH_3C_6H_3(OH)CH_2\overset{+}{N}H_2CHCH(CH_3)_2COO^-$

TABLE-2
CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) OF N-(2-HYDROXY-5-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-5	3700–3000 (vb)	—	2940 (s) 2850 (w)	—	1600 (sb)	1410 (s)	—	1230 (m)	—	—
B(hmbv-5)	—	3360–3000 (b)	2980 (s) 2860 (w)	—	1620 (sb)	1390 (m)	250	1230 (m)	1370 (m)	1500 (w)
B(OPr^i) (H_2hmbv–5)$_2$	3700–3400 (vb)	3400–3000 (b)	2980 (s) 2860 (w)	1720 (m)	1620 (s)	1365 (m)*	255	1230 (s)	1365 (m)	—
B(H_2hmbv–5)$_3$	3700–3400 (vb)	3400–3000 (b)	2980 (s) 2860 (w)	1700 (w)	1620 (s)	1370 (m)*	250	1230 (s)	1370 (m)	—
Al(hmbv-5)	—	3400–3000 (b)	2980 (s) 2880 (w)	—	1610 (sb)	1370 (m)	250	1250 (s)	660 (w)	480 (w)
Al (Hhmbv-5) (H_2hmbv-5)	3700–3400 (vb)	3400–3000 (b)	2980 (s) 2880 (w)	—	1610 (sb)	1380 (m)	240	1260 (s)	670 (s)	490 (w) 540 (m)
Al(H_2hmbv–5)$_3$	3700–3400 (vb)	3400–3000 (b)	2980 (s) 2880 (w)	—	1610 (sb)	1380 (m)	240	1250 (s)	660 (m)	480 (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-5)	—	3360–3000 (b)	2980 (s) 2880 (w)	—	1630 (sb)	1370 (m)	270	1240 (s)	480 (w)	410 (w)
Fe(Hhmbv-5) (H_2hmbv-5)	3700–3400 (vb)	3400–3000 (b)	2980 (s) 2880 (w)	—	1620 (sb)	1370 (m)	250	1245 (s)	485 (m)	425 (w)
Fe(H_2hmbv–5)$_3$	3690–3380 (vb)	3380–3000 (b)	2980 (s) 2890 (w)	—	1610 (sb)	1390 (m)	220	1250 (s)	530 (m) 440 (m)	410 (m)
As(OPr^i)(Hhmbv–5)	—	3400–3000 (b)	2980 (s) 2880 (w)	—	1600 (sb)	1360 (m)	240	1250 (s)	580 (m)	480 (s)
As(OPr^i)(H_2hmbv–5)$_2$	3700–3400 (vb)	3400–3000 (b)	2920 (s) 2860 (w)	—	1600 (sb)	1370 (s)	230	1250 (s)	580 (s)	470 (w)
Sb(OPr^i)(Hhmbv–5)	—	3400–3000 (b)	2980 (s) 2880 (w)	—	1600 (sb)	1380 (m)	220	1250 (s)	560 (w)	460 (m)
Sb(OPr^i)(H_2hmbv–5)$_2$	3700–3400 (vb)	3400–3000 (b)	2980 (s) 2880 (w)	—	1610 (sb)	1300 (m)	225	1260 (s)	540 (m)	480 (m)
Sb(H_2hmbv–5)$_3$	3700–3400 (vb)	3400–3000 (b)	2980 (s) 2880 (w)	—	1610 (sb)	1385 (m)	225	1260 (s)	580 (s)	450 (m)

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

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

TABLE-3
PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ VALUE) OF N-(2-HYDROXY-5-METHYL BENZYL) VALINE AND ITS VARIOUS ELEMENTO(III) DERIVATIVES

Compound	Aromatic ring	Phenolic (—OH)	>CH—groups (of valine part)	>NH	—CH_3 (attached with the benzene ring)	—CH_2— (attached with the benzene ring)	*gem*-dimethyl
H_3hmbv-5	6.60–6.80 (m)* 6.90–7.00 (d)* 6.80–6.90 (d)*	6.20 (s)	3.45–3.96 (m)	3.04–3.43 (h)	2.18 (s)	2.10 (d)	0.91 (s) 0.80–0.82 (d)
B(hmbv-5)	6.10–6.90 (m)	—	3.25–4.00 (m)	—	2.25 (s)	1.95 (d)	1.05 (s)
Al(Hhmbv-5)(H_2 hmbv-5)	6.20–6.85 (m)	6.92 (s)	3.35–4.00 (m)	3.20 (s)	2.20 (s)	2.10 (d)	0.95 (s)
Fe(H_2hmbv-5)$_3$	6.00–7.20 (m)	6.93 (s)	3.30–4.30 (m)	3.10 (s)	2.23 (s)	2.00–2.30 (d)	0.50–1.30 (bs)
Sb(H_2hmbv–5)$_3$	5.80–7.10 (m)	6.90 (s)	3.30–4.30 (m)	3.00 (s)	2.20 (s)	2.00–2.25 (a)	0.60–1.20 (m)

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

*Corresponds to the protons at positions 6, 3 and 4 of the trisubstitued benzene ring.

$Al(OPr^i)_3 + 3H_3hmbv\text{-}5 \rightarrow Al(H_2hmbv\text{-}5)_3 + 3Pr^iOH$

$Fe(OPr^i)_3 + H_3hmbv\text{-}5 \rightarrow Fe(hmbv\text{-}5) + 3Pr^iOH$

$Fe(OPr^i)_3 + 2H_3hmbv\text{-}5 \rightarrow Fe(Hhmbv\text{-}5)(H_2hmbv\text{-}5) + 3Pr^iOH$

$Fe(OPr^i)_3 + 3H_3hmbv\text{-}5 \rightarrow Fe(H_2hmbv\text{-}5)_3 + 3Pr^iOH$

$As(OPr^i)_3 + H_3hmbv\text{-}5 \rightarrow As(OPr^i)(Hhmbv\text{-}5) + 2Pr^iOH$

$As(OPr^i)_3 + 2H_3hmbv\text{-}5 \rightarrow As(OPr^i)(H_2hmbv\text{-}5)_2 + 2Pr^iOH$

$Sb(OPr^i)_3 + H_3hmbv\text{-}5 \rightarrow Sb(OPr^i)(Hhmbv\text{-}5) + 2Pr^iOH$

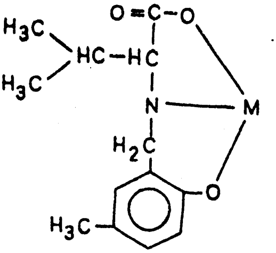
$Sb(OPr^i)_3 + 2H_3hmbv\text{-}5 \rightarrow Sb(OPr_i)(H_2hmbv\text{-}5)_2 + 2Pr^iOH$

$Sb(OPr^i)_3 + 3H_3hmbv\text{-}5 \rightarrow Sb(H_2hmbv\text{-}5)_3 + 3Pr^iOH$

The 1 : 3 reaction in case of arsenic(III) did not proceed even after prolonged reflux and fractionation.

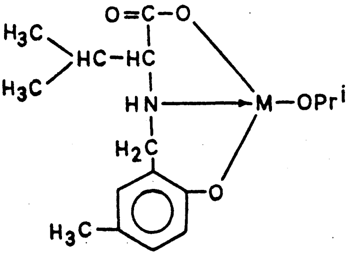
Based on azeotrope and elemental analysis, as well as the spectral data[3–8] in respect of the various derivatives prepared, the main findings relating to their structures are as under:

The boron, aluminium or iron atom in B(hmbv-5), Al(hmbv-5) and Fe(hmbv-5) [Structure (II)] displays trivalency in the corresponding case as a result 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. However, the arsenic or antimony atom in $As(OPr^i)$ (Hhmbv-5) and $Sb(OPr^i)$ (Hhmbv-5) [Structure (III)] shows tetra-coordination in the corresponding case as a result 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.



Where M= B, Al, Fe

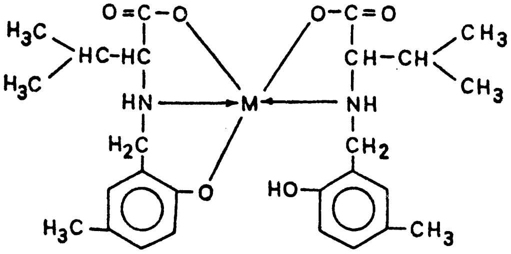
(II)



Where M=As, Sb

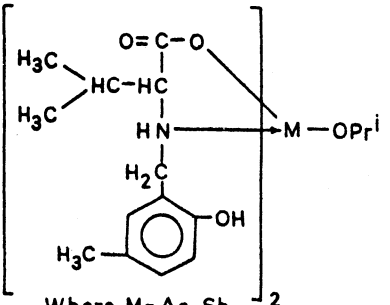
(III)

The aluminium or iron atom in Al(Hhmbv-5) (H_2hmbv-5) and Fe(Hhmbv-5) (H_2hmbv-5) [Structure (IV)] exhibits penta-coordination in the corresponding case 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_3hmbv-5 and the oxygen from the carboxylate group, the nitrogen from the imino group from the second mole of the H_3hmbv-5. However, the derivatives, As(OPr^i)(H_2hmbv-5)$_2$ and Sb(OPr^i)(H_2hmbv-5)$_2$ [Structure (V)] possess penta-coordinated arsenic or antimony atom in the corresponding 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 H_3hmbv-5, along with an isopropoxy group. However, the boron atom in B(OPr^i)(H_2hmbv-5)$_2$ [Structure (VI)] displays trivalency as a result of bonding with one of the oxygens from each of the two carboxylate groups available from two moles of H_3hmbv-5 through a normal ester type of linkage, along with an isopropoxy group.



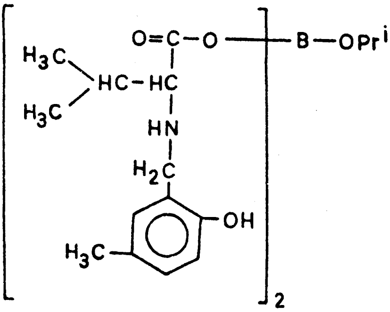
Where M= Al,Fe

(IV)



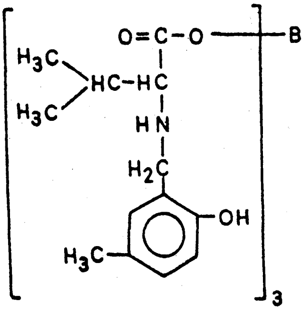
Where M=As,Sb

(V)

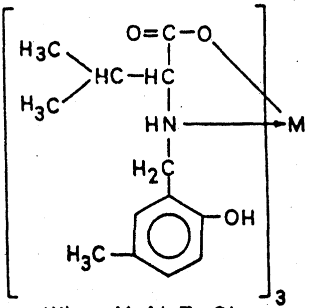


(VI)

The boron atom in B(H_2hmbv-3)$_3$ [Structure (VII)] shows trivalency by way of bonding with one of the oxygens from each of the three carboxylate groups available from three moles of the H_3hmbv-5 through a normal ester type of linkage. However, the aluminium, iron or antimony atom in Al(H_2hmbv–5)$_3$, Fe(H_2hmbv-5)$_3$ and Sb(H_2hmbv–5)$_3$ [Structure (VIII)] exhibits hexa-coordination in the corresponding 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_3hmbv-5.



(VII)



Where M = Al, Fe, Sb

(VIII)

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