Synthesis and Characterization of Boron Derivatives with N-(o-hydroxy substituted benzyl)phenylalanines

Anil Kumar*, Manju Kandpal, Supriya Verma, Seema Islam, Pradeep Bhatt

Department of Chemistry, IPGG (PG) College of Commerce, Affiliated to Kumaun University, Nainital, Uttarakhand, India

ABSTRACT

An efficient and general method has been developed for synthesis of boron derivatives of N-(o-hydroxy substituted benzyl) phenylalanines from boron triisopropoxide and protonated ligands H_3hmbpa-3[N-(2-hydroxy-3-methyl benzyl)phenylalanine], H_3hmbpa-6[N-(2-hydroxy-6-methyl benzyl)phenylalanine], and H_3hmbpa-5[N-(2-hydroxy-5-methyl benzyl)phenylalanine] in ratio of 1:1, 1:2, and 1:3 using a highly vacuumed assembly. Boron triisopropoxide was prepared using boric acid and isopropyl alcohol and the protonated ligands H_3hmbpa-3, H_3hmbpa-6, and H_3hmbpa-5 were prepared from reaction between o,m,p-cresol, formaldehyde, and phenylalanine. The structure of boron triisopropoxide, ligands, and boron derivatives is identified by H^1NMR, FT-IR, and elemental analysis. The elemental analysis, H^1NMR, and FT-IR data of boron derivatives proposed the boron: Ligands stoichiometry, molecular formulae, and coordination linkage of ligands with boron in 1:1, 1:2, and 1:3 ratio. The number of moles of isopropanol liberated during the preparation of boron derivatives in the binary azeotrope with benzene was estimated by the method described by Bradey *et al*. and Mehrotra.

Key words: Azeotrope, Boron triisopropoxide, H_3hmbpa-3,6,5, O,m,p-cresol, Phenylalanine, Stretching.

1. INTRODUCTION

One of the convenient methods of preparation of metallo-organic/organometallic derivatives is provided by the facile reactivity of metal alkoxide toward the various classes of organic compounds, and hence, this fascinating aspect of alkoxide chemistry has evoked considerable interest during the past decades as evident from a number of reviews and monograph appearing from time to time [1-8].

The reaction of boron alkoxide with a number of glycols such as propane-1,3-diol, propane-1,2-diol, and 2,2-dimethylpentane-2,4-diol was examined in 1:1 and 2:3 molar ratios, which resulted in the formation of the corresponding monoalkoxide monoglycolate and triglycolate bis borate, respectively [9].

Boron trimethoxide forms adduct with hydrazine [10]. The formation of these adducts was also achieved by the interaction of boron triethoxide or triisopropoxide with hydrazine in excess of methanol [11]. In absence of methanol, however, instead of complex formation, a replacement reaction occurred.

Boron aryloxide forms complex with amines more readily than the corresponding alkoxide derivatives, and thus numerous coordinating compounds prepared by the interaction of boron triphenoxide with several primary secondary and tertiary amines[12].

Tandon *et al*. [13] synthesized and characterized boron complexes of N, O, and S donar ligands in 1:1 and 1:2 molar ratios who further studied the binuclear semicarbazone complexes of boron having B-O-B linkage in each case.

Synthesis and characterization of boron derivatives with N-(o-hydroxy substituted benzyl) valines and alanines [14,15,16] have been studied.

The present study aims to synthesis of boron derivatives with N-(o-hydroxy substituted benzyl)phenylalnines from boron triisopropoxide and protonated ligands such as H_3hmbpa-3, H_3hmbpa-6, and

H_3hmbpa-5 and characterized by various physiochemical spectral data.

2. MATERIALS AND METHODS

All the chemicals, namely − phenylalanine o,m,p-cresol, sodium acetate trihydrate, formaldehyde solution 37% w/v, glacial acetic acid, boric acid anhydrous, benzene, isopropanol, potassium dichromate, and con.c sulfuric acid were of AnalaR grade (99% pure) used in the formation of borontriisopropoxide, N-(o-hydroxy substituted benzyl) phenylalanines such as H_3hmbpa-3, H_3hmbpa-6, H_3hmbpa-5, and boron derivatives of N-(o-hydroxy substituted benzyl)phenylalanines. Since boron triisopropoxide and its derivative are hygroscopic in nature hence isopropanol, benzene, other solvent, and reagent have been dried and distilled.

Elemental analysis of the prepared compounds was carried out using elemental Vario make EL-III model instrument at 950–1200°C temperature.

Perkin-Elmer spectrum-Two IR spectrometer is used for recording the IR data of prepared compound in the range of 4000–400 cm^{-1} using KBr pellet technique.

The H^1NMR spectra of prepared complexes were carried out by NMR

instrument in DMSO-d$_6$.

2.1. Synthesis of N-(O-Hydroxy Substituted Benzyl)Phenylalanines

H$_3$hmbpa-3, H$_3$hmbpa-6, and H$_3$hmbpa-5 compounds belonging to N-(o-hydroxy substituted benzyl)phenylalanines class were prepared adopting procedure similar to those employed for the preparation of the corresponding glycine derivatives) [11,14]. For the preparation of these compounds, in general, to a mixture of equimolar amounts of o,m,p-cresol (E.Merk) 54.0 g (0.5 mol), phenylalanine (Alfa) 82.5 g (0.5 mol), and sodium acetate tri hydrate (Fischer) 68 g (0.5 mol) in glacial acetic acid (Fischer) 250 ml medium were added an equimolar amount of formaldehyde solution (Fischer) and the content was heated at 60–80°C until a viscous mass was obtained. The viscous mass then poured, drop-wise 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 precipitate, now, washed by water and dried in desiccator under normal temperature. The yield of H$_3$hmbpa-3 (45 g), H$_3$hmbpa-6 (48 g), and H$_3$hmbpa-5 (52 g) was obtained.

Where x = H or -CH$_3$

2.2. Synthesis of Boron Triisopropoxide

Boron triisopropoxide was prepared by dehydration of a mixture of anhydrous boric acid and isopropanol in 1:3 molar ratio in benzene medium, according to the reaction.

$$H_3BO_3 + 3(CH_3)_2CHOH \qquad B[OHC(CH_3)_2]_3 + 3H_2O$$

Dried boric acid (15.30 g, 0.2549 mol) suspended in benzene (75 ml) was taken in a R.B. flask, and then, excess of isopropanol (100 ml) was added fractionated out azeotropically, and a colorless solution was obtained, when the entire boric acid changed in to boron triisopropoxide. The excess of solvent was distilled off and content of the flask was dried under vacuum. Boron triisopropoxide, thus formed, was purified by distillation, when it was obtained as a colorless liquid with yield (22.5 g).

2.3. Synthesis of Boron Derivatives of N-(O-Hydroxy Substituted Benzyl)Phenylalanines

The preparation of boron derivatives of N-(o-hydroxy substituted benzyl)phenylalanines was carried out under a fractionating column (30 cm. long) packed with Rasching rings and fitted to a total condensation variable take-off still head. The alcoholysis reaction is performed between boron triisopropoxide and H$_3$hmbpa-3, H$_3$hmbpa-6, and H$_3$hmbpa-5, in the molar ratio of 1:1, 1:2, and 1:3 with each ligands, respectively, in benzene medium at about 8–10 h depend on how much number of moles of isopropanol were liberated. The number of moles of isopropanol liberated in the binary azeotrope with benzene was estimated by the method described by Bradley and Halim and Mehrotra [17], which is modification of the one developed earlier by Adams and Nicholas.

3. RESULTS AND DISCUSSION

Newly prepared boron triisopropoxide, ligands, and boron derivatives are quite stable molecules. Based on the elemental analysis, it is suggested that the boron derivatives are conformable with the ratio

1:1, 1:2, and 1:3 for boron to ligands. Table 1 represents the physical properties and elemental analysis data of boron triisopropoxide and protonated ligands prepared.

3.1. IR Spectra

The IR and PMR data (after D$_2$O exchange) of the N-(o-hydroxy substituted benzyl)phenylalanines are shown in Figures 1 and 2, respectively. It may be mentioned here that the amino acids and their derivatives often exhibit zwitterionic behavior which has been confirmed in many cases by IR and PMR spectral measurement.

A very broad band between 3650 and 3000 cm^{-1} in spectrum of H$_3$hmbpa-3 [Figure 1] indicates the overlapping of the phenolic −OH and both aromatic ring C-H stretchings, while medium and weak absorptions at 2950 cm^{-1} and 2850 cm^{-1} occur due to the overlapping of C-H stretchings of both -CH$_2$- and -CH$_3$ group of cresol ring. A weak broad band at 2390 cm^{-1} corresponds to the N-H stretching of the >NH$\Box^+$ group, while a very strong broad band at 1630 cm^{-1} with a shoulder may be assigned to the possible overlapping with overlapping of the asymmetric O-C=O and aromatic C=C stretching. A weak absorption at 1495 cm^{-1} and a strong absorption at 1435 cm^{-1} show the overlapping of the aromatic C=C stretching and C-H bending of both -CH$_2$- and -CH$_3$ group of cresol ring. A medium broad band at 1385 cm^{-1} may be ascribed to the O-C=O stretching, while a medium broad band at 1320 cm^{-1} occurs due to the O-H bending of the phenolic group. A strong band at 1295 cm^{-1} appears due to the interaction of the O-H bending and C-O stretching of the phenolic group, while the another at 1235 cm^{-1} corresponds to the C-N stretching. A weak broad band at 1160 cm^{-1} may be attributed to the phenolic C-C-O stretching. The medium to weak band at 1116 cm^{-1}, 1033 cm^{-1}, and 975 cm^{-1} indicate the aromatic C-H in-plane bending modes, while those at 832 cm^{-1}, 748 cm^{-1}, and 680–600 cm^{-1} correspond to the characteristics C-H out of plane bending of a trisubstituted benzene ring of cresol part. The bands having intensities between 1250 and 1000 cm^{-1} correspond to the C-H in-plane bending and 900–670 cm^{-1} out of plane bending of C-H aromatic ring of phenylalanine part. The absorption below 600 cm^{-1} occur due to both the aromatic ring skeletal vibrations.

The occurrence of a broad band in region 3610–3000 cm^{-1} in case of H$_3$hmbpa-6 [Figure 1] may be ascribed to the overlapping to the phenolic -O-H and both aromatic ring C-H stretchings. The medium band at 2980 cm^{-1} and 2870 cm^{-1} indicates the overlapping of the C-H stretching of both -CH$_2$- and -CH$_3$ group of cresol ring, while another medium band at 2340 cm^{-1} corresponds to the N-H stretching of the >NH$_2^+$ group. The overlapping of the asymmetric O-C=O and aromatic
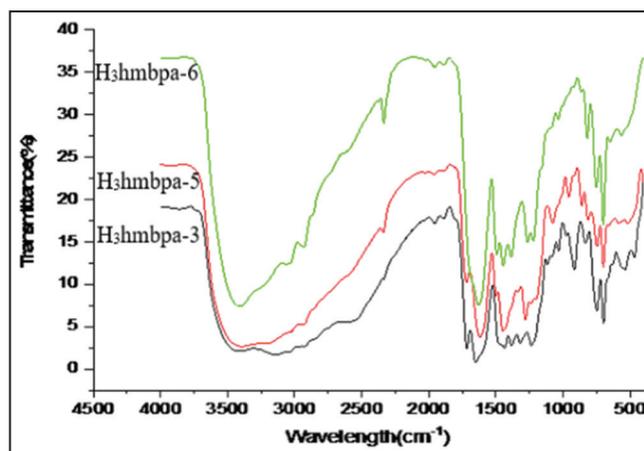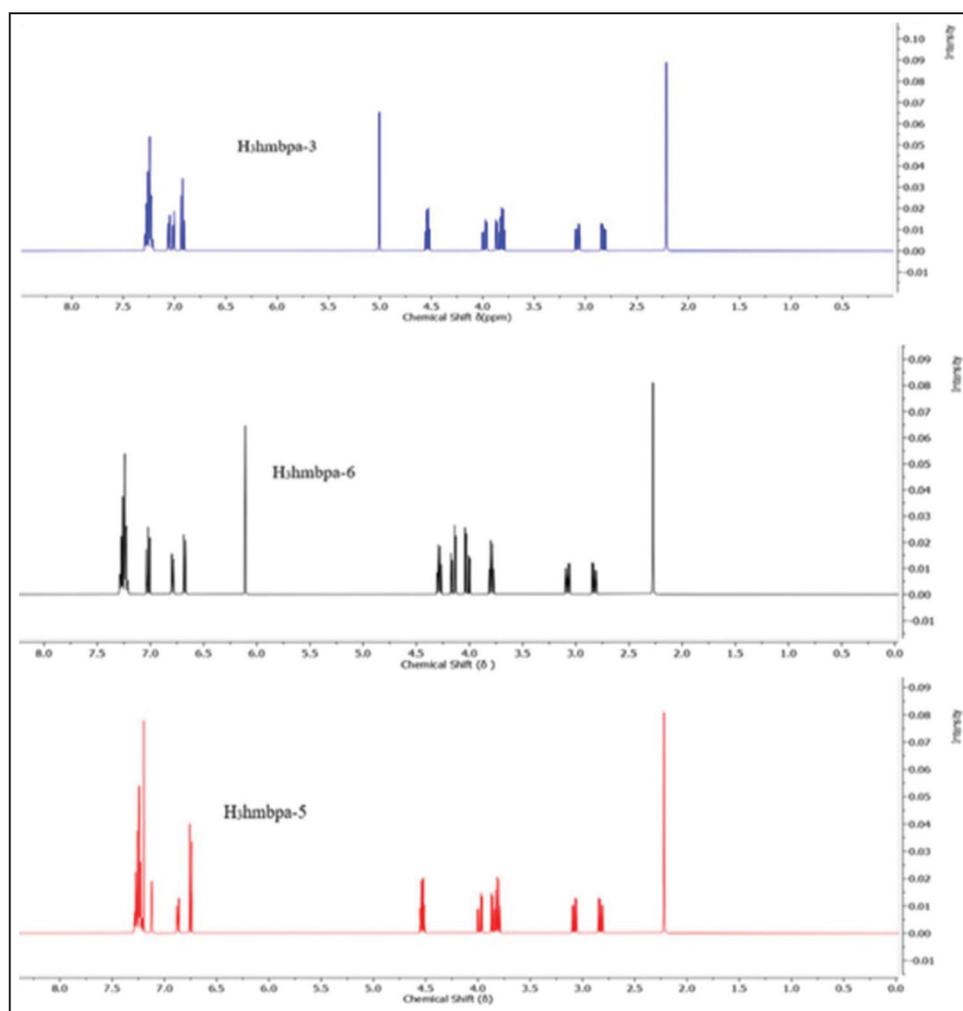

Figure 1: IR spectra of H$_3$hmbpa-3, H$_3$hmbpa-6, and H$_3$hmbpa-5.

Table 1: Analytical data of synthesized boron triisopropoxide and ligands

| S. No.	B (OPr^i)$_3$/ Ligands	M.W. (g/mol)	Color	Solubility	Elemental Analysis (%) Found (calcd.)				
					C	H	N	O	B
1.	B (OPr^i)$_3$	188.07	Colorless	DMF, DMSO	57.41 (57.44)	11.14 (11.17)	-	25.51 (25.53)	5.72 (5.75)
2.	H$_3$hmbpa-3	285	Light brown	DMF, DMSO	71.53 (71.57)	6.63 (6.67)	4.90 (4.91)	16.82 (16.84)	
3.	H$_3$hmbpa-6	285	Cream	DMF, DMSO	71.54 (71.57)	6.65 (6.67)	4.88 (4.91)	16.81 (16.84)	
4.	H$_3$hmbpa-5	285	Light brown	DMF, DMSO	71.52 (71.57)	6.64 (6.67)	4.89 (4.91)	16.83 (16.84)	

Figure 2: Proton NMR Spectra of H$_3$hmbpa-3, H$_3$hmbpa-6, and H$_3$hmbpa-5.
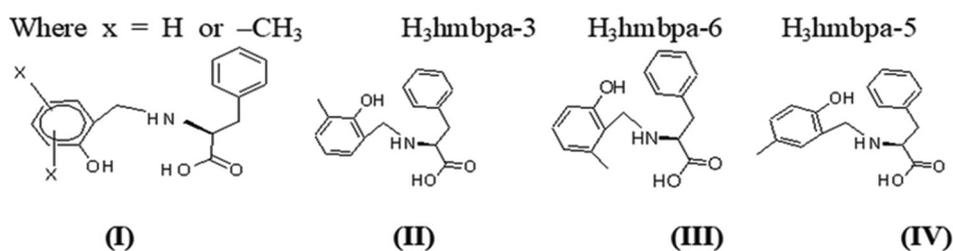
Figure 3: General structure of N-(o-hydroxy substituted benzyl)phenylalanines(i), H$_3$hmbpa-3(II), H$_3$hmbpa-6(III), and H$_3$hmbpa-5(IV).

C=C stretchings is identified here as a shouldered band at 1640 cm^{-1}. A medium band at 1497 cm^{-1} and sharp band at 1447 cm^{-1} correspond to the overlapping of the aromatic C=C stretching and C-H bending of both -CH$_2$- and -CH$_3$ group of cresol ring. A weak band at 1415 cm^{-1} may be assigned to the symmetric O-C=O stretching, while another at 1395 cm^{-1} shows the O-H bending of the phenolic group. A sharp band

Table 2: Analytical data of the synthesized boron derivatives

S. No.	Boron triisopropxide (QTY) (in g, mmol)	Ligands (QTY) (in g, mmol)	Molar Ratio (Reflux Time in) (h)	Boron Derivatives	Yield of Boron Derivativ-es found (calcd.)	Moles of Pr^iOH Obtai-ned	Azeotrope analysis of Pr^iOH (g) found (calcd.)	M.P. (°C)
1.	B(OPr^i)$_3$ (0.5640, 3.00)	H$_3$hmbpa-3 (0.8550, 3.00)	1:1 (8)	B(OPr^i)(Hhmbpa-3)	1.02 (1.05)	2	0.35 (0.36)	172
2.	B(OPr^i)$_3$ (0.4700, 2.50)	H$_3$hmbpa-3 (1.4250, 2.50)	1:2 (9)	B(OPr^i)(H$_2$hmbpa-3)$_2$	1.50 (1.59)	2	0.29 (0.30)	179
3.	B(OPr^i)$_3$ (0.3760, 2.00)	H$_3$hmbpa-3 (1.7100, 2.00)	1:3 (10)	B (H$_2$hmbpa-3)$_3$	1.71 (1.72)	3	0.35 (0.36)	181
4.	B(OPr^i)$_3$ (0.5640, 3.00)	H$_3$hmbpa-6 (0.8550,3.00)	1:1 (8)	B(OPr^i)(Hhmbpa-6)	0.98 (1.05)	2	0.35 (0.36)	175
5.	B(OPr^i)$_3$ (0.4700, 2.50)	H$_3$hmbpa-6 (1.4250, 2.50)	1:2 (10)	B(OPr^i)(H$_2$hmbpa-6)$_2$	1.49 (1.59)	2	0.29 (0.30)	171
6.	B(OPr^i)$_3$ (0.3760, 2.00)	H$_3$hmbpa-6 (1.7100, 2.00)	1:3 (11)	B (H$_2$hmbpa-6)$_3$	1.68 (1.72)	3	0.35 (0.36)	168
7.	B(OPr^i)$_3$ (0.5640, 3.00)	H$_3$hmbpa-5 (0.8550, 3.00)	1:1 (9)	B(OPr^i)(Hhmbpa-5)	1.00 (1.05)	2	0.35 (0.36)	161
8.	B(OPr^i)$_3$ (0.4700, 2.50)	H$_3$hmbpa-5 (1.4250, 2.50)	1:2 (10)	B(OPr^i)(H$_2$hmbpa-5)$_2$	1.51 (1.59)	2	0.29 (0.30)	157
9.	B(OPr^i)$_3$ (0.3760, 2.00)	H$_3$hmbpa-5 (1.7100, 2.00)	1:3 (10)	B (H$_2$hmbpa-5)$_3$	1.65 (1.72)	3	0.35 (0.36)	154
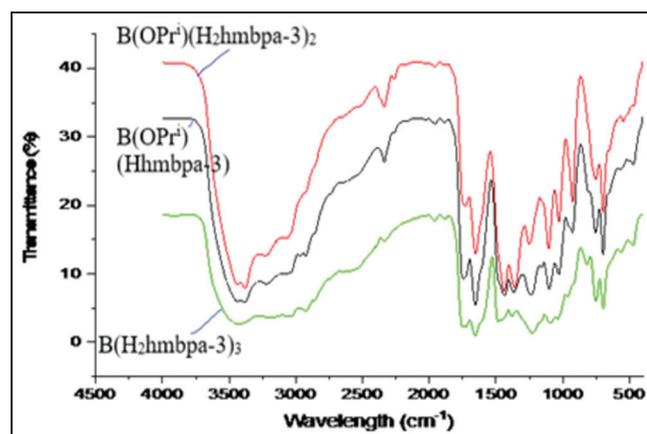
Figure 4: IR spectra of B(OPr^i)(Hhmbpa-3), B(OPr^i)(H$_2$hmbpa-3)$_2$, and B(H$_2$hmbpa-3)$_3$.
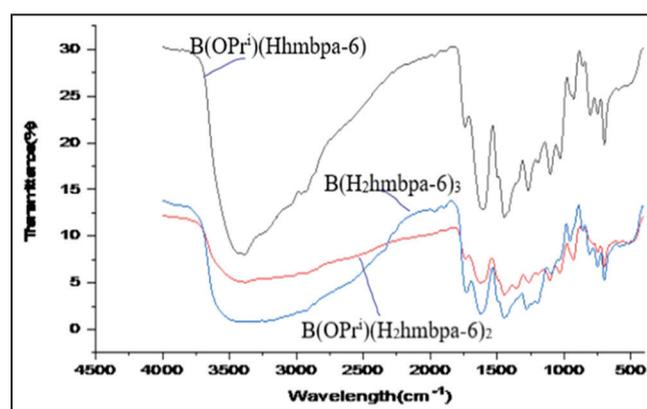
Figure 5: IR spectra of B(OPr^i)(Hhmbpa-6), B(OPr^i)(H$_2$hmbpa-6)$_2$, and B(H$_2$hmbpa-6)$_3$.
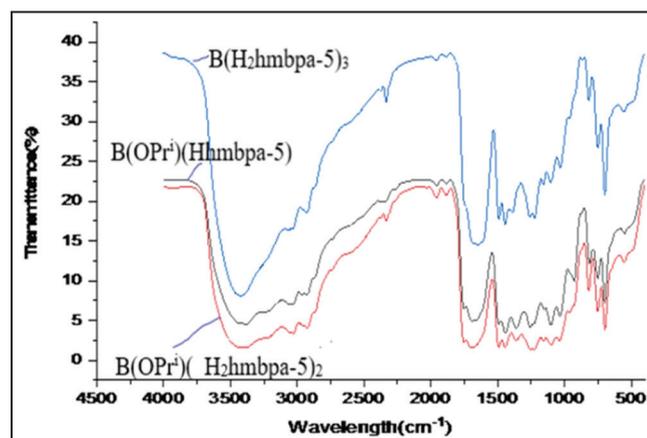
Figure 6: IR spectra of B(OPr^i)(Hhmbpa-5), B(OPr^i)(H$_2$hmbpa-5)$_2$, and B(H$_2$hmbpa-5)$_3$.

at 1280 cm^{-1} may be attributed to the interaction of C-O stretching and the O-H bending of the phenolic group, while the weak absorption at 1240 and 1110 cm^{-1} corresponds to the C-N stretching and phenolic C-C-O stretching, respectively. The medium bands at 1100 cm^{-1}, 1050 cm^{-1}, 970 cm^{-1}, and 940 cm^{-1} show the aromatic cresol ring C-H in-plane bending, while the absorptions due to the C-H out of plane bending 805 cm^{-1}, 765 cm^{-1}, and 650 cm^{-1}. The skeletal vibrations of both aromatic ring here too were identified below 600 cm^{-1}.

The appearance of a broad band in region 3640–3000 cm^{-1} in case

Table 3: Analytical data of the synthesized boron derivatives

S. No.	Boron Derivatives	Colour (Solid)	Solubility	Elemental Analysis (%) Found (Calcd.)				
				C	H	N	O	B
1.	B (OPr^i) (Hhmbpa-3)	Brownish White	DMF, DMSO	67.95 (67.99)	6.76 (6.79)	18.11 (18.13)	3.92 (3.96)	3.01 (3.06)
2.	B (OPr^i) (H$_2$hmbpa-3)$_2$	Brownish White	DMF, DMSO	66.17 (66.22)	6.89 (6.95)	19.88 (19.93)	4.94 (4.99)	1.87 (1.93)
3.	B (H$_2$hmbpa-3)$_3$	Brownish White	DMF, DMSO	65.82 (65.85)	6.46 (6.48)	20.23 (20.25)	5.89 (5.90)	1.51 (1.53)
4.	B (OPr^i) (Hhmbpa-6)	Brownish White	DMF, DMSO	67.93 (67.99)	6.72 (6.79)	18.10 (18.13)	3.92 (3.96)	3.02 (3.06)
5.	B (OPr^i) (H$_2$hmbpa-6)$_2$	Brownish White	DMF, DMSO	66.17 (66.22)	6.88 (6.95)	19.90 (19.93)	4.93 (4.99)	1.91 (1.93)
6.	B (H$_2$hmbpa-6)$_3$	Brownish White	DMF, DMSO	65.81 (65.85)	6.45 (6.48)	20.22 (20.25)	5.87 (5.90)	1.50 (1.53)
7.	B (OPr^i) (Hhmbpa-5)	Brownish White	DMF, DMSO	67.92 (67.99)	6.75 (6.79)	18.11 (18.13)	3.91 (3.96)	3.02 (3.06)
8.	B (OPr^i) (H$_2$hmbpa-5)$_2$	Brownish White	DMF, DMSO	66.19 (66.22)	6.93 (6.95)	19.91 (19.93)	4.93 (4.99)	1.89 (1.93)
9.	B (H$_2$hmbpa-5)$_3$	Brownish White	DMF, DMSO	65.79 (65.85)	6.44 (6.48)	20.23 (20.25)	3.92 (5.90)	1.50 (1.53)
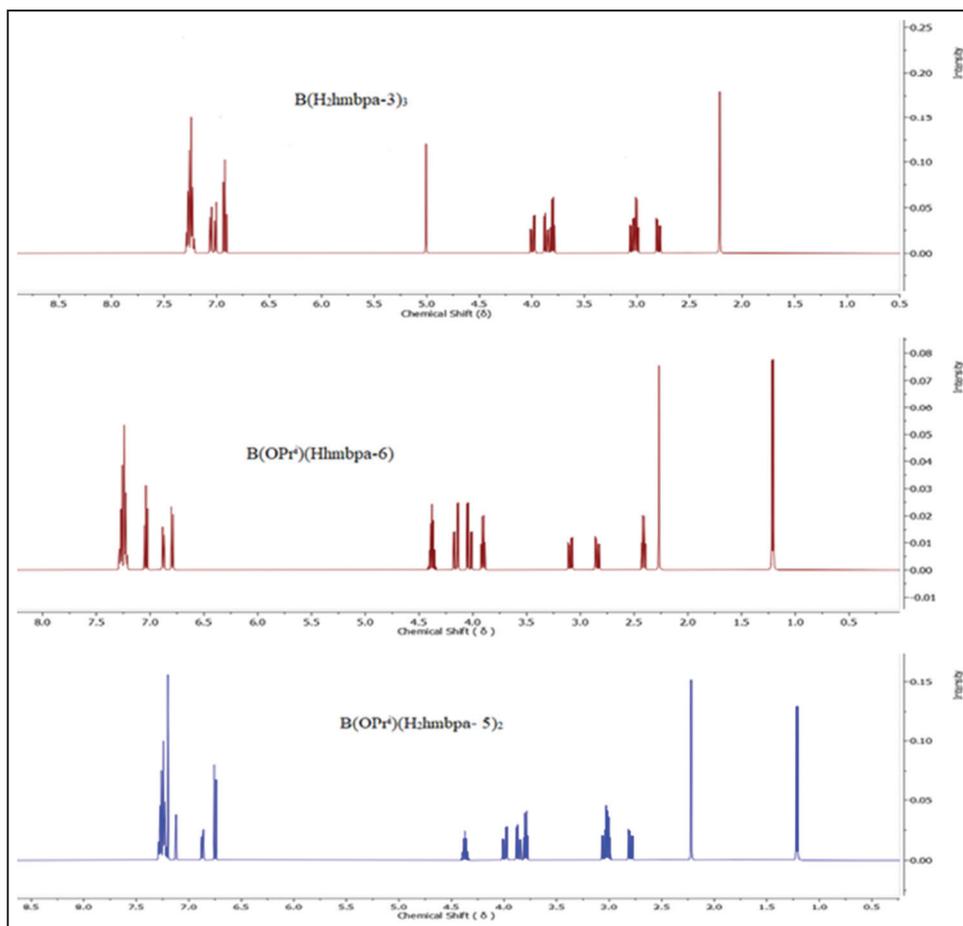
Figure 7: Proton NMR Spectra of B(H$_2$hmbpa-3)$_3$, B(OPr^i)(Hhmbpa-6), and B(OPr^i)(H$_2$hmbpa-5)$_2$.
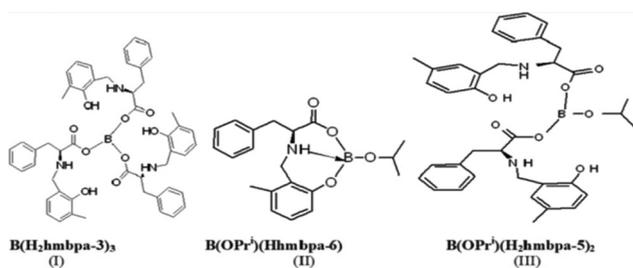
Figure 8: Structure of B(H$_2$hmbpa-3)$_3$, B(OPr^i)(Hhmbpa-6), and B(OPr^i)(H$_2$hmbpa-5)$_2$.

of H$_3$hmba-5 [Figure 1] shows the overlapping of the phenolic O-H and aromatic C-H stretchings. The medium and weak bands at 2930 cm^{-1} and 2850 cm^{-1}, respectively, may be assigned to C-H stretching of both -CH$_2$ and -CH$_3$ group of cresol ring. A weak broad band at 2350 cm^{-1} shows the N-H stretching of the >NH$_2$$^+$ group, while the appearance of a very strong broad band at 1625 cm^{-1} may be attributed C=C stretchings. The overlapping of aromatic C=C stretching and C-H bending of both -CH$_2$- and -CH$_3$ group of cresol ring is identified here by the appearance of strong bands at 1500 cm^{-1} and 1460 cm^{-1}, while a sharp band of medium intensity at 1380 cm^{-1} may be ascribed to the symmetric O-C=O stretching.

Table 4: Characteristics infrared frequency (cm^{-1}) of boron derivatives

S. No.	Boron Derivatives	ν_{O-H} of pheno-lic group	ν_{N-H} and ν_{C-H} of both aromatic ring	ν_{C-H} of -CH$_3$ and both -CH$_2$- group	ν_{asCOO}	ν_{sCOO}	ν_{COO}	ν_{C-N}	ν_{B-O}	ν_{B-N}	ν_{C-O} ester
1	B (OPr^i) (Hhmbpa-3)	-	3300–3050 (b)	2960 (mb) 2955 (w) 2850 (m)	1640 (sb)	1370 (w)	270	1251 (mb)	1370 (w)	1540 (mb)	-
2	B (OPr^i) (H$_2$hmbpa-3)$_2$	3500–3000 (vb)	3250–3000(mb)	2925 (wb) 2910 (b) 2880 (w)	1619 (s)	1380 (mb)	239	1233 (m)	1380 (mb)	-	1717 (s)
3	B (H$_2$hmbpa-3)$_3$	3500–3000 (b)	3280–3000(b)	2910 (m) 2850 (wb) 2820 (w)	1640 (sb)	1360 (s)	280	1236 (w)	1360 (s)	-	1752 (b)
4	B (OPr^i) (Hhmbpa-6)	-	3300–3100(vb)	2950 (m) 2900 (w) 2810 (wb)	1631 (sb)	1375 (s)	256	1263 (m)	1375 (s)	1530 (mb)	-
5	B (OPr^i) (H$_2$hmbpa-6)$_2$	3600–3350 (vb)	3150–3000(b)	2920 (w) 2830 (wb) 2810 (w)	1655 (s)	1370 (mb)	285	1265 (mb)	1370 (mb)	-	1719 (s)
6	B (H$_2$hmbpa-6)$_3$	3550–3300 (vb)	3300–3100(vb)	2900 (m) 2850 (w) 2830 (b)	1654 (s)	1380 (mb)	274	1279 (m)	1380 (mb)	-	1736 (s)
7	B (OPr^i) (Hhmbpa-5)	-	3250–3000(mb)	2980 (m) 2950 (m) 2810 (w)	1653 (s)	1370 (sh)	283	1257 (mb)	1370 (sh)	1535 (s)	-
8	B (OPr^i) (H$_2$hmbpa-5)$_2$	3570–3350 (b)	3300–3100(b)	2960 (w) 2910 (m) 2820 (w)	1618 (sb)	1397 (m)	121	1255 (s)	1397 (m)	-	1752 (s)
9	B (H$_2$hmbpa-5)$_3$	3500–3350 (b)	3252–3000(mb)	2930 (b) 2850 (wb) 2930 (m)	1633 (s)	1387 (m)	248	1260 (s)	1387 (w)	-	1750 (vs)

vb: Very broad, b: Broad, m: Medium, mb: Medium broad, w: Weak, wb: Weak broad, s: Sharp, vs: Very sharp, sb: Sharp broad, sh: Shoulder hump

The occurrence of a sharp band at 1280 cm^{-1} corresponds to the interaction of O-H bending and C-O stretching of the phenolic group, while medium bands at 1190 cm^{-1} and 1155 cm^{-1} may be attributed to the C-N stretching and phenolic C-C-O stretching, respectively. Here too, very weak absorptions below 600 cm^{-1} occur due to the both aromatic ring skeletal vibrations.

3.2. Proton Magnetic Resonance Spectra

The multiplet in the region δ7.21–7.29 appears in PMR spectra is for five aromatic proton of phenylalanine part of H$_3$hmbpa-3 in [Figure 2]. The multiplet in the region δ 6.90–6.93 and two doublet at δ7.01 and δ7.05 in the PMR spectrum of H$_3$hmbpa-3 may be assigned respectively to the protons of aromatic ring of cresol part of H$_3$hmbpa-3. A singlet at δ5.00 corresponds to the phenolic proton, while the broad multiplet

Table 5: Proton magnetic resonance data of boron derivatives

S. No.	Boron Derivatives	Proton of both aromatic ring	Phen-olic (OH)	>CH-	>NH	-CH$_3$ (attache-d with benzene ring)	-CH$_2$-attached with cresol	-CH$_2$-of phenylal-anine part	Gem Di methyl
1.	B (OPr^i) (Hhmbpa-6)	6.80–7.30 (m)	-	4.30–4.40 (m) 3.80–3.90 (m)	2.41 (m)	2.26 (s)	4.10 (d)	2.95 (d)	1.21 (d)
2.	B (OPr^i) (H$_2$hmbpa-5)$_2$	6.70–7.28 (m)	7.19 (s)	4.34–4.39 (m) 3.75–3.79 (m)	3.00 (m)	2.22 (s)	3.86 (d)	2.79 (d)	1.20 (d)
3.	B (H$_2$hmbpa-3)$_3$	6.90–7.30 (m)	5.00 (s)	3.78–3.82 (m)	3.05 (m)	2.20 (s)	3.99 (d)	3.05 (d)	-

between δ3.79 and 3.84 may be assigned to the protons associated with the >CH- group of H$_3$hmbpa-3. The appearance of a hump in association with the said multiplet between δ4.48 and 4.52 may be assigned to the protons of the >NH$_2^+$ group. A singlet at δ2.20 and a multiplet between δ3.86 and 4.00 corresponds, respectively, to the proton of -CH$_3$ and -CH$_2$- group. The signals at position δ2.90 appear due to the protons of the -CH$_2$- group of H$_3$hmbpa-3. The absence of any signal between 7.50 and 13.00 indicates the absence of free carboxylic acid group in the compound.

The singlet at δ5.0 and hump in the region δ4.48–4.52 upon D$_2$O exchange observed to disappear with the appearance of quartet in this region due to protons of the >C-H group which, further, confirms the presence of the phenolic –OH and >NH$_2^+$ groups. A new signal at δ4.40 possibly corresponds to HOD, as a consequence of D$_2$O exchange. Thus, from the foregoing considerations, it is reasonable to believe that H$_3$hmbpa-3 exists in zwitterionic form.

In case of H$_3$hmba-6 [Figure 2], the appearance of a triplet at δ7.02 and two doublet at δ6.79 and δ6.68 may be assigned, respectively, to the protons of the trisubstituted benzene ring. The multiplet in the region δ7.21–7.29 appears in PMR spectra is for five aromatic proton of phenylalanine part of H$_3$hmbpa-6. The singlet at δ6.11 may be assigned to the phenolic group proton. The broad multiplet in the regions δ3.77–3.81 corresponds to the proton of the >CH- group of H$_3$hmba-6, while a hump between δ4.27 and 4.30 may be attributed to the protons of the >NH$_2^+$ group. A singlet at δ2.72 and multiplet between at δ4.03 and 4.17 appear, respectively, due to the protons of the -CH$_3$ and -CH$_2$- groups. The signals at position δ2.90 appear due to the protons of the -CH$_2$- group of at position of H$_3$hmbpa-6.

On D$_2$O exchange, the disappearance of the singlet at δ6.11 and broad multiplet in the regions δ4.27–4.30 with the appearance of quartet between δ4.10 due to the protons of the >CH- group further confirms the presence of the phenolic and >NH$_2^+$ groups. Again, a new peak observed here at δ4.10 corresponds to HOD. These observations again suggest that H$_3$hmbpa-6 too exist in zwitterionic form.

The signals corresponding to the protons of the trisubstituted benzene ring in H$_3$hmbpa-5 [Figure 2] have been identified here by the appearance of a singlet at δ7.12 and doublets at δ6.75 and δ6.85, respectively. Similarly, the multiplet in the region δ7.21–7.29 appear in PMR spectra is for five aromatic proton of phenylalanine part of H$_3$hmbpa-3 in [Figure 2]. The singlet at δ7.20 occurs due to the pheonilc group proton. The broad multiplet between δ3.79 and 3.84 may be assigned to the proton of the >C-H group of H$_3$hmba-5, while a hump at δ4.48–4.52 corresponds to the protons of the >NH$_2^+$ group. A singlet at δ2.72 and multiplet between at δ4.03 and 4.17 appear, respectively, due to the protons of the -CH$_3$ and -CH$_2$- groups. The signals at position δ2.90 appear due to the protons of the -CH$_2$- group of H$_3$hmbpa-5.

The disappearance of the singlet at δ7.20 and hump at δ4.40 with the appearance of quartet in the region δ4.10 and 4.30 due to the protons of the >CH- groups on D$_2$O exchange confirms the presence of the phenolic and >NH$_2^+$ groups. The appearance of a new peak at δ4.20 corresponds to HOD. It is hence concluded that H$_3$hmbpa-5 also exists in zwitterionic form.

On the basis of elemental analysis data [Table 1], IR data [Figure 1], and NMR data [Figure 2], the general structure of N-(o-hydroxy substituted benzyl)phenylalanines, and specific structure of H$_3$hmbpa-3, H$_3$hmbpa-6, and H$_3$hmbpa-5 represents in Figure 3.

Calculative data for the synthesis of boron derivatives with the help of reaction between boron triisopropoxide and N-(o-hydroxy substituted benzyl)phenylalanines in the ratio of 1:1, 1:2, and 1:3, their physical properties and elemental analysis are shown in Tables 2 and 3. The IR data from [Figures 4-6] and NMR data from Figure 7 are shown in Tables 4 and 5.

On the basis of elemental analysis data from [Table 3] IR data from [Figures 4-6], Table 4 and NMR data from [Figure 7] and Table 5 the structure of B(H$_2$hmbpa-3)$_3$, B(OPr^i)(Hhmbpa-6), and B(OPr^i) (H$_2$hmbpa-5)$_2$ are shown in Figure 8.

4. CONCLUSION

The boron triisopropoxide, N-(o-hydroxy substituted benzyl) phenylalanines, and boron derivatives of N-(o-hydroxy substituted benzyl)phenylalanines were synthesized successfully using benzene as a solvent and characterized by elemental analysis, FT-IR and proton NMR techniques. The boron derivatives with N-(o-hydroxy substituted benzyl) phenylalanines were found to be stable but very hygroscopic in nature. Based on the elemental analysis, FT-IR and Proton NMR data are suggested that the boron derivatives are comfortable with the ratio 1:1, 1:2, and 1:3 ratio for boron to ligands.

5. ACKNOWLEDGMENT

6. CONFLICTS OF INTREST

Nil.

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*****Bibliographical Sketch*

Anil Kumar born in Jaspur U.S. Nagar, Uttarakhand, on 20-08-1990. Post Gratuated in 2013 from K.U. Nainital Uttarakhand. At present his research work is ongoing on organometallic chemistry under the supervision of Dr. Manju Kandpal assistant professor in chemistry from IPGGPG college of commerce, Haldwani Nainital. Presently working as lecturer in chemistry in Uttarakhand school education. Only one research paper in national journal is published till now. His research interests are synthesis of biologically active organometallic derivatives of metals etc.