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Some new N-protected amino acid derivatives of phenylboronic acid: preparation, structural chemistry and insight into structural aspects based on spectroscopic studies

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Abstract

Some new 1,3-dihydro-1,3-dioxo-α-substituted-2H-isoindole-2-acetic acid derivatives of phenylboronic acid of compositions $PhBOH[O_2CCH(R)NC(O)C_6H_4C(O)]$ and $PhB[O_2CCH(R)NC(O)C_6H_4C(O)]_2$ [where $-CH(R)=-CH_2CH_2-$, $R=-CH_2-C_6H_5$, $-CH(CH_3)_2$, and $-CH(CH_3)C_2H_5$] have been prepared by the reaction of phenylboronic acid with N-protected amino acids in 1:1 and 1:2 molar ratios in dry refluxing benzene. Plausible structures of these newly synthesized N-protected amino acid derivatives of phenylboronic acid have been proposed on the basis of physicochemical and spectroscopic studies. ^{11}B NMR data reveal the presence of tetracoordinated boron centers in these N-protected amino acid derivatives of phenylboronic acid.

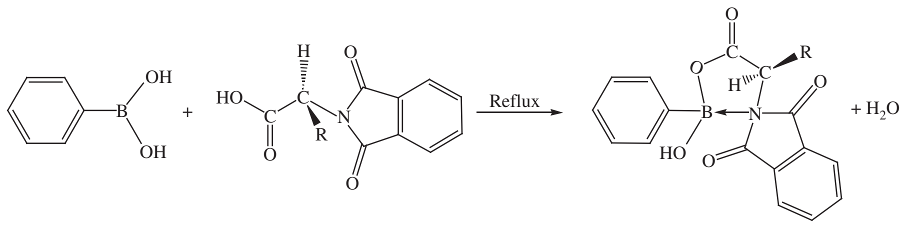
Keywords: N-protected amino acids; phenylboronic acid; spectroscopic studies.

Introduction

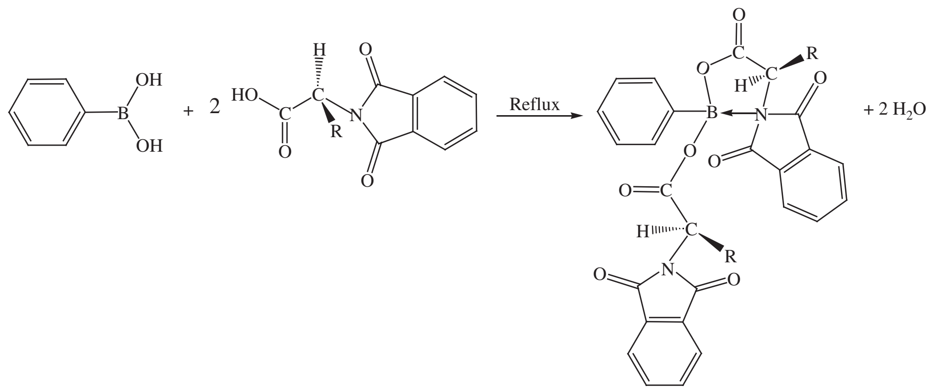
The chemistry of organic derivatives of boron has been extensively studied. The amino acid derivatives of boron possessing B←N bond (Mancilla et al., 2005) have attracted much attention because of the fact that boronated phenyl alanine (Bendel, 2005) has been used as boron neutron capture therapy. Boron-nitrogen-carbon (BNC) compounds are important materials owing to their technological applications. These compounds possess favorable properties for various device applications (Morant et al., 2006; Ying et al., 2007). Recently, superior mechanical, chemical, electrical and optical properties of ternary phases $B_XC_YN_Z$ have been studied. The plasma assisted chemical vapor deposition technique has been used for obtaining BNC coatings with superior mechanical and tribological properties. BNC films were also synthesized by inductively coupled plasma chemical vapor deposition (Chowdhury et al., 2008). The electrospinning technique has been used for the preparation of boron doped nickel/zinc (Ni/Zn) metal fibers. The preparation of boron doped Ni/Zn acetate nanofibers has also been reported (Uslu et al., 2009). The addition of boron to metal acetate increases the thermal stability and diameters of the fibers. Some organoboron compounds such as boric acid esters and arylboronic acid derivatives are used as antioxidants (König et al., 1988). Phenylboronic acid derivatives are also used as applications in medical and agrochemical fungicides (Freeman et al., 2003). Some new azacyclo organoborinates derivatives of piperidinyl and pyridinyl alcohols exhibit anticoccidial activity (Tabuchi et al., 2003). It has been reported that some novel boronic-chalcone derivatives exhibit antitumor activity (Kumar et al., 2003). A novel glucose sensor system has been developed which is capable of detecting dynamic changes in glucose concentration. The hologram is received within a biocompatible hydrogel matrix which contains phenylboronic acid derivatives (Kabilan et al., 2005). Various potential organic ligands have been used for the synthesis of organic derivatives of organoboron(III) (Singh et al., 2005; Swami et al., 2009; Yadav et al., 2010). N-Protected amino acids are an important class of organic ligands which display a diversified mode of bonding (Saxena et al., 1991, 1992; Surana and Saxena, 1996; Verma et al., 2004; Joshi et al., 2005; Sharma et al., 2007; Gupta et al., 2009) and their metal complexes exhibit significant biological activities (Saxena et al., 1991). In view of the interesting results obtained in our previous communications (Gupta et al., 2010a,b; Sharma et al., 2010) and as an extension of our ongoing research work concerning the synthesis of organic derivatives of some trivalent and tetravalent elements, it was considered relevant to study the ligating capability of N-protected amino acids towards $PhB(OH)_2$. These interesting results fostered the idea to modify the reactivity of $PhB(OH)_2$ by reacting it with N-protected amino acids. The presence of $-CH(R)=-CH_2CH_2-$, and $R=-CH_2C_6H_5$, $-CH(CH_3)_2$, and $-CH(CH_3)-C_2H_5$ groups on $HO_2CCH(R)NC(O)C_6H_4C(O)$ provides an opportunity to study the steric and electronic effects on the structures and properties of these N-protected amino acids modified-$PhB(OH)_2$ products.

Results and discussion

N-Protected amino acid derivatives of phenylboronic acid with compositions, $PhBOH[O_2CCH(R)NC(O)C_6H_4C(O)]$ and $PhB[O_2CCH(R)NC(O)C_6H_4C(O)]_2$, were prepared by the



Scheme 1 Derivative [PhB(OH)L], where -CHR=-CH_2CH_2; derivative 1, [PhB(OH)L_1]; R=-$CH_2C_6H_5$; derivative 2, [PhB(OH)L_2]; R=-CH$(CH_3)_2$; derivative 3, [PhB(OH)L_3]; R=-CH(CH_3)C_2H_5; derivative 4, [PhB(OH)L_4].



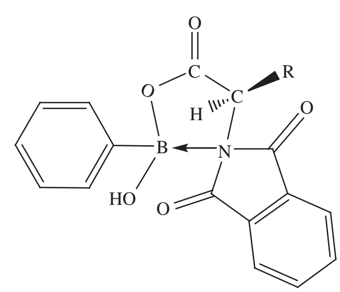
Scheme 2 Derivative [PhB$(L)_2$] where -CHR=-CH_2CH_2; derivative 5, [PhB$(L_1)_2$]; R=-$CH_2C_6H_5$; derivative 6, [PhB$(L_2)_2$]; R=-CH$(CH_3)_2$; derivative 7, [PhB$(L_3)_2$]; R=-CH(CH_3)C_2H_5; derivative 8, [PhB$(L_4)_2$].

reaction of phenylboronic acid with N-protected amino acids in 1:1 and 1:2 molar ratios in dry refluxing benzene solution as outlined in Schemes 1 and 2, respectively.

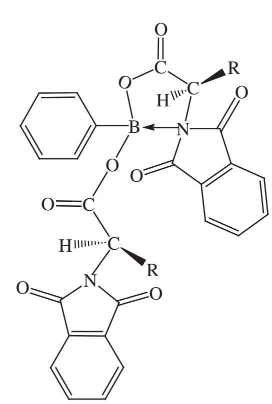
The reactions of phenylboronic acid with N-protected amino acids were carried out on a fractionating column and were completed in ~12 h of refluxing. The liberated water during the reaction was fractionated off azeotropically with benzene. After removal of the excess solvent under reduced pressure, white solid products were obtained which were found to be soluble in benzene and tetrahydrofuran. These solid products were purified by recrystallization from a benzene-hexane mixture and exhibited sharp melting points. The molecular weight measurements revealed the monomeric nature of these N-protected amino acid derivatives of phenylboronic acid. These products were further subjected to spectroscopic studies.

Conclusion

The molecular weight measurements revealed the monomeric nature of N-protected amino acid derivatives of phenylboronic acid of the types [PhB(OH)L] and [PhB$(L)_2$]. The following plausible structures (Structures 1 and 2) were suggested for the derivatives [PhB(OH)L] and [PhB$(L)_2$], respectively, with the aid of physicochemical and spectral [IR and NMR (^{1}H, ^{13}C and ^{11}B)] studies.



Structure 1



Structure 2

The spectral evidence suggests the unidentate nature of N-protected amino acids and the presence of B←N bond in these borole derivatives. ^{11}B NMR chemical shift values (δ 2.00–2.79 ppm) indicate the presence of tetracoordinated boron centers and a tetrahedral geometry may be suggested for these borole derivatives.

Experimental

The ligands and N-protected amino acids were prepared by a previously reported method (Sheehan et al., 1952). $PhB(OH)_2$ was commercially available. Strict precautions were taken to exclude atmospheric moisture throughout the whole experimental work. The solvents used were dried by standard methods (Furniss et al., 1989). Boron was estimated volumetrically by the Thomas method (Thomas, 1946). Molecular weights of these N-protected amino acid derivatives of phenylboronic acid were determined cryoscopically in dry benzene solution. IR (4000–400 cm^{-1}) spectra of the samples were recorded on a SHIMADZU (Tokyo, Japan), FTIR-8400 spectrophotometer and samples were prepared as KBr pellets. ^{1}H and ^{13}C NMR spectra of the samples were recorded in $CDCl_3$ and DMSO-d_6 solutions using TMS as an internal reference on a JEOL-FT (Tokyo, Japan) AL300 NMR spectrometer operating at 300 and 75.45 MHz, respectively. ^{11}B NMR spectra of N-protected amino acid derivatives of phenylboronic acid were recorded using methylborate as an external standard. These derivatives were prepared by a common method. Hence, the experimental details of a representative derivative are described.

Preparation of $PhB(OH)[O_2CCH(CH_2C_6H_5)$-$NC(O)C_6H_4C(O)]$, $[PhB(OH)L_2]$

To a dry benzene solution of phenylboronic acid (0.30 g, 2.49 mmol), a dry benzene solution of 1,3-dihydro-1,3-dioxo-α-(benzyl)-2H-isoindole-2-acetic acid (0.73 g, 2.49 mmol) was added. The reaction mixture was refluxed on a fractionating column for ~12 h. During the reaction, water was formed which was removed azeotropically with benzene. After completion of the reaction, the excess solvent was removed under reduced pressure. A white solid was isolated which was recrystallized from a benzene-hexane mixture. The physicochemical properties and analytical data of N-protected amino acid derivatives of phenylboronic acid are given in Table 1.

Spectral studies

IR spectra In the IR spectra of N-protected amino acids, the broad absorption band appearing in the region ~2900–3400 cm^{-1} may be assigned to the carboxylic-OH of the ligands. This band was absent in the IR spectra of N-protected amino acid derivatives of phenylboronic acid which indicates the deprotonation of the ligands. The appearance of new medium intensity bands in the region 1345–1365 cm^{-1} in boron derivatives clearly shows the formation of B-O bond (Yadav and Singh, 2011). In the IR spectra of the ligands, the bands observed at ~1780 cm^{-1} and at 1390±10 cm^{-1} may be attributed to imido $\upsilon(CO)_{asym}$ and $\upsilon(COO)_{sym}$ vibrations, respectively. $\upsilon(CO)_{sym}$ and $\upsilon(COO)_{asym}$ bands are merged and appeared as a broad band at ~1690 cm^{-1}. In the IR spectra of boron derivatives, this band

Table 1 Physical and analytical data of N-protected amino acid derivatives of phenylboronic acid.

Derivative no.	Product formula	Reagents in g/mmol		Molar ratio	Physical state color	Mol. wt. found (calc.)	B % found (calc.)	M.P. °C	% Yield[a]
		$PhB(OH)_2$	LH						
1	$[PhB(OH)L_1]$	0.57	1.03	1:1	White	320	3.32	110	84
	$BC_{17}H_{14}O_5N$	(4.67)	(4.67)		solid	(323.02)	(3.34)		
2	$[PhB(OH)L_2]$	0.30	0.73	1:1	White	394	2.70	140	87
	$BC_{23}H_{18}O_5N$	(2.49)	(2.49)		solid	(399.09)	(2.70)		
3	$[PhB(OH)L_3]$	0.40	0.82	1:1	White	350	3.06	86	78
	$BC_{19}H_{18}O_5N$	(3.33)	(3.33)		solid	(351.04)	(3.07)		
4	$[PhB(OH)L_4]$	0.42	0.91	1:1	White	360	2.94	78	84
	$BC_{20}H_{20}O_5N$	(3.49)	(3.49)		solid	(365.05)	(2.96)		
5	$[PhB(L_1)_2]$	0.26	0.95	1:2	White	523	2.04	120	80
	$BC_{28}H_{21}O_8N_2$	(2.17)	(4.35)		solid	(524.15)	(2.06)		
6	$[PhB(L_2)_2]$	0.31	1.50	1:2	White	674	1.59	130	82
	$BC_{40}H_{29}O_8N_2$	(2.54)	(5.08)		solid	(676.29)	(1.59)		
7	$[PhB(L_3)_2]$	0.22	0.91	1:2	White	575	1.84	80	86
	$BC_{32}H_{29}O_8N_2$	(1.84)	(3.68)		solid	(580.20)	(1.86)		
8	$[PhB(L_4)_2]$	0.35	1.50	1:2	White	600	1.76	84	84
	$BC_{34}H_{33}O_8N_2$	(2.88)	(5.76)		solid	(608.23)	(1.77)		

[a] Yield of the recrystallized products.

L_1H=$HOOCCH_2CH_2NC(O)C_6H_4C(O)$
$C_{11}H_9O_4N$
L_2H=$HOOCCH(CH_2C_6H_5)NC(O)C_6H_4C(O)$
$C_{17}H_{13}O_4N$
L_3H=$HOOCCH[CH(CH_3)_2]NC(O)C_6H_4C(O)$
$C_{13}H_{13}O_4N$
L_4H=$HOOCCH[CH(CH_3)C_2H_5]NC(O)C_6H_4C(O)$
$C_{14}H_{15}O_4N$

shifts in the region 1725±5 cm^{-1} which indicates the unidentate nature of the ligands (Verma et al., 2004). The unidentate nature of N-protected aminoacids is further supported by the magnitude of Δυ [$\Delta\upsilon=\upsilon(COO)_{asym}$ -$\upsilon(COO)_{sym}$] calculated for these boron derivatives. The value of Δυ for these boron derivatives was in the range 335–350 cm^{-1}. The appearance of medium intensity bands in the regions 1500–1505 cm^{-1} and 1240–1260 cm^{-1} may be assigned to υB N and υPh-B vibrations, respectively (Saxena et al., 1993; Al-Masri et al., 2005).

^{1}H NMR spectra The ^{1}H NMR spectra of N-protected amino acid derivatives of phenylboronic acid and N-protected amino acids were recorded in $CDCl_3$ and DMSO-d_6/$CDCl_3$ solution using tetramethylsilane as an internal standard and are summarized in Table 2.

In the ^{1}H NMR spectra of the ligands, the signal due to carboxylic-OH proton was observed in the region δ 8.44–10.62 ppm. This signal disappeared from the ^{1}H NMR spectra of N-protected amino acid derivatives of phenylboronic acid which clearly indicates the deprotonation of the parent ligands and formation of B-O bonds. The aromatic protons of N-protected amino acids of these derivatives were observed as a complex pattern in the region δ 7.07–8.05 ppm. The phenyl protons attached to boron are overlapping with aromatic protons of the ligands in the same region. The -OH proton signal of the derivatives of the type [PhB(OH)L] was overlapping with the signals of DMSO-d_6 solvent. In the ^{1}H NMR spectra of these derivatives, a small shift in the position of -CH(R)N< proton signal was observed as compared to its position in the corresponding ligands which indicates the involvement of very poorly nucleophilic imido nitrogen in bonding.

^{13}C NMR spectra The ^{13}C NMR spectra of N-protected amino acid derivatives of phenylboronic acid of the types [PhB(OH)L] and [PhB$(L)_2$] and their parent ligands were recorded in $CDCl_3$ and DMSO-d_6/$CDCl_3$ solution and are summarized in Table 3.

In the ^{13}C NMR spectra of N-protected amino acids, the carboxylic carbon signal appeared in the region δ 170.85–176.33 ppm. In the ^{13}C NMR spectra of these derivatives, the carboxylic carbon signal undergoes a significant upfield shift (Table 3) as compared to its position in the parent ligands which shows the unidentate nature of the carboxylic group of N-protected amino acids in these derivatives. There is some downfield shift (Table 3) in the position of -CH(R)N< carbon signal as compared to its position in the parent ligands which suggests the involvement of nitrogen in bonding. The imido carbon signal appeared at δ 167.60–167.98 ppm in the ^{13}C NMR spectra of the free ligands. This carbon signal experiences some downfield shift in its position in the ^{13}C NMR spectra of these derivatives.

^{11}B NMR spectra ^{11}B NMR spectra of some of the representative N-protected amino acid derivatives of phenylboronic acid with compositions [PhBOH(O_2CCH(R)NC(O)C_6H_4C(O)] where CHR=-CH_2CH_2; derivative 1, [PhB(OH)L_1]; R=-$CH_2C_6H_5$; derivative 2, [PhB(OH)L_2]; R=-$CH(CH_3)_2$; derivative 3, [PhB(OH)L_3];

Table 2 ^{1}H NMR data of N-protected amino acid derivatives of phenylboronic acid (in δ ppm).

Derivative no.	Ligands and derivatives	C(O)C_6H_4C(O)NCH(R)COOH, (LH)					
		-OH	-C_6H_5/>C_6H_4	CH	CH_2	CH_3	Ph-B
	L_1H	9.51	7.28–8.13 (m)		2.80 (t) 4.00 (t)		
1	[PhB(OH)L_1]	–	7.84–7.37 (m)		2.65 (t) 3.85 (t)		a
	L_2H	8.44 (bs)	7.09–7.80 (m)	5.22 (t)	3.57 (d)		
2	[PhB(OH)L_2]	–	7.07–7.75 (m)	5.07 (t)	3.42 (d)		a
	L_3H	8.90 (bs)	7.28–7.89 (m)	4.63 (d) 2.76 (m)		0.90 (d) 1.71 (d)	
3	[PhB(OH)L_3]	–	7.12–7.89 (m)	4.33 (d) (unresolved) 2.49 (m) (unresolved)		0.87 (d) (unresolved) 1.14 (d) (unresolved)	a
	L_4H	10.62 (bs)	7.28–7.88 (m)	4.76 (d) 2.55 (m)	1.54 (m)	0.86 (t) 1.12 (d)	
4	[PhB(OH)L_4]	–	7.32–7.86 (m)	4.52 (d) 2.58 (m)	1.49 (m)	0.84 (t) 1.11 (d)	a
5	[PhB$(L_1)_2$]	–	7.18–8.05 (m)		2.27 (t) 3.67 (t)		a
6	[PhB$(L_2)_2$]	–	7.09–7.71 (m)	5.10 (t)	3.56 (d)		a
7	[PhB$(L_3)_2$]	–	7.23–7.79 (m)	4.46 (d) 2.49 (m) (unresolved)		0.69 (d) 0.96 (d)	a
8	[PhB$(L_4)_2$]	–	7.23–7.77 (m)	4.35 (d) 2.42 (m) (unresolved)	1.38 (m) (unresolved)	0.78 (t) 0.92 (d)	a

[a]Merged with phenyl proton of N-protected amino acid.
Note: (s), singlet; (d), doublet; (t), triplet; (q), quartet; (m), multiplet; (bs), broad singlet.

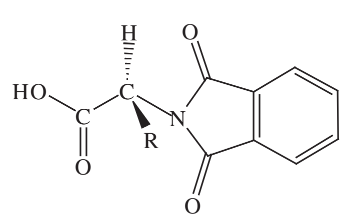
Table 3 [13]C NMR data of N-protected amino acid derivatives of phenylboronic acid (in δ ppm).

Derivative no.	Ligands and derivatives	$\overline{C(O)C_6H_4C(O)N}CH(R)COOH$, (LH)							
		>COO	CO	CH	CH_2	CH_3	$-C_6H_5$	$>C_6H_4$	Ph-B
	L_1H	176.33	167.98		33.34			123.38	
					32.53			131.89	
								134.08	
1	$[PhB(OH)L_1]$	173.21	168.40		34.23			123.61	128.16
					33.03			130.88	128.94
								134.71	131.95
									135.04
	L_2H	170.85	167.60	53.37	34.44		134.01	137.12	
							128.73	131.51	
							128.45	123.29	
							126.64		
	L_3H	173.82	167.87	57.49		20.94		134.52	
				(CH-N)		19.46		131.53	
				28.42				123.64	
3	$[PhB(OH)L_3]$	170.82	168.40	57.79		21.48		134.78	128.21
				(CH-N)		19.82		131.58	128.97
				28.69				124.11	130.94
									135.59
	L_4H	174.61	167.80	56.97	25.82	16.80		134.29	
				(CH-N)		10.90		131.59	
				34.33				123.65	

Complex no.	Ligands and complexes	$\overline{C(O)C_6H_4C(O)N}CH(R)COOH$, (LH)							
		>COO	CO	CH	CH_2	CH_3	$-C_6H_5$	$>C_6H_4$	Ph-B
4	$[PhB(OH)L_4]$	170.70	168.28	57.04	25.91	16.22		135.58	[a]
				(CH-N)		11.77		131.43	
				35.15				124.04	
5	$[PhB(L_1)_2]$	172.42	167.72		33.65			123.05	[a]
					32.66			130.01	
								134.07	
6	$[PhB(L_2)_2]$	170.20	167.00	52.87	33.94		136.69	133.57	[a]
							133.57	130.97	
							128.21	122.74	
							126.15		
7	$[PhB(L_3)_2]$	170.62	168.30	57.65		21.39		135.60	[a]
				(CH-N)		19.73		131.43	
				28.55				124.06	
8	$[PhB(L_4)_2]$	170.74	168.42	57.07	25.93	17.39		135.65	134.65
			168.34	(CH-N)		11.80		131.43	130.86
				34.39				124.09	128.94
									128.15

[a]Merged with phenyl carbon of N-protected amino acid.

LH =



where $-CHR=-CH_2CH_2(L_1H)$, $R=-CH_2C_6H_5(L_2H)$, $-CH(CH_3)_2(L_3H)$, $-CH(CH_3)C_2H_5(L_4H)$.

$R=-CH(CH_3)C_2H_5$; derivative 4, $[PhB(OH)L_4]$ and $PhB[O_2CCH(R)\text{-}\overline{NC(O)C_6H_4C(O)}]_2$ where $R=-CH(CH_3)_2$; derivative 7, $[PhB(L_3)_2]$; $R=-CH(CH_3)C_2H_5$; derivative 8, $[PhB(L_4)_2]$ were recorded in $CDCl_3$/DMSO-d_6 solution using methylborate as an external reference and exhibited signals in the region δ 2.00–2.79 ppm and are summarized in Table 4.

These [11]B NMR chemical shift values reveal the presence of tetracoordinated boron centers (Pandey and Singh, 1999; Barba et al.,

Table 4 ^{11}B NMR data of N-protected amino acid derivatives of phenylboronic acid (in δ ppm).

Derivative no.	Derivatives product formula	^{11}B NMR chemical shift values
1	$[PhB(OH)L_1]$	2.46
2	$[PhB(OH)L_2]$	2.21
3	$[PhB(OH)L_3]$	2.39
4	$[PhB(OH)L_4]$	2.00
7	$[PhB(L_3)_2]$	2.56
8	$[PhB(L_4)_2]$	2.79

2005) in these derivatives. The observed ^{11}B NMR chemical shift values are in agreement with the reported values for tetracoordinated derivatives of boron.

References

Al-Masri, H. T.; Sieler, J.; Blaurock, S.; Lönnecke, P.; Junk, P. C.; Hawkins, E. H. Synthesis and characterization of novel intramolecularly base-stabilized boron halides. Molecular structures of 1-X2BOCR1R2-2-NMe2C6H4 [R1=R2=Ph, X=Cl or F; R1=R2=Cy, X=Cl] and [1-LiN(Ph)C(H)Ph-2-NMe2C6H4]2. *Z. Anorg. Allg. Chem*. **2005**, *631*, 518–523.

Barba, V.; Santillan, R.; Farfán, N. Dimeric boronates derived from the reaction of Schiff bases and boronic acids. *J. Mex. Chem. Soc*. **2005**, *49*, 211–217.

Bendel, P. Biomedical applications of ^{10}B and ^{11}B NMR. *NMR Biomed.* **2005**, *18*, 74–82.

Chowdhury, M. P.; Dalui, S.; Chakraborty, B. R.; Mukherjee, A.; Pal, A. K. Effect of carbon content on the mechanical properties in ternary BCN compound prepared by ICP-CVD technique. *Indian J. Pure Appl. Phys*. **2008**, *46*, 776–782.

Freeman, A.; Segal, R.; Dror, Y. Phenylboronic acid derivatives as medical and agrochemical fungicides. *PCT Int. Appl. CODEN:PIXXD2*, **2003**, 34.

Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. Vogel's Text Book of Practical Organic Chemistry, 5th Edition. Pearson, Harlow, 1989, 395–469.

Gupta, R. K.; Jain, A.; Saxena, S. Some new hexacoordinated aluminium(III) complexes of sterically hindered heterocyclic β-diketones and N-protected amino acids: preparation and structural considerations based upon spectral [IR and NMR (1H, 13C and 27Al)] studies. *Main Group Met. Chem.* **2009**, *32*, 65–78.

Gupta, R. K.; Jain, A.; Saxena, S. New organic-inorganic hybrid complexes of aluminium (III) of β-diketones and sterically demanding heterocyclic β-diketones: synthesis, structural aspects and spectroscopic [Ir and Nmr (1h, 13c and 27al)] characterization. *Main Group Met. Chem.* **2010a**, *33*, 9–24.

Gupta, R. K.; Jain, A.; Saxena, S. Certain new organic-inorganic hybrid complexes of monobutyltin(Iv) of β-diketones/fluorinated β-diketone and sterically congested heterocyclic β-diketones: preparation, structural chemistry and structural elucidation based upon spectroscopic [Ir and Nmr (1H, 13C and 119Sn)] studies. *Main Group Met. Chem.* **2010b**, *33*, 167–182.

Joshi, A.; Verma, S.; Jain, A.; Saxena, S. Preparation, structural aspects and spectroscopic [IR, NMR (1H, 13C and 119Sn)] characterization of certain new penta-coordinated mixed ligand complexes of dibutyltin(IV) of β-diketones, fluorinated β-diketones and 1,3-dihydro-1,3-dioxo α-substituted-2H-isoindole-2-acetic acids. *Main Group Met. Chem*. **2005**, *28*, 31–40.

Kabilan, S.; Marshall, A. J.; Sartain, F. K.; Lee, M.-C.; Hussain, A.; Yang, X.; Blyth, J.; Karangu, N.; James, K.; Zeng, J.; Smith, D.; Domschke, A.; Lowe, C. R. Holographic glucose sensors. *Biosens. Bioelectr.* **2005**, *20*, 1602–1610.

König, T.; Männel, D.; Habicher, W. D.; Schwetlick, K. Organoboron antioxidants: Part 1 – Boric acid derivatives as primary antioxidants. *Polym. Degrad. Stabil.* **1988**, *22*, 137–145.

Kumar, S. K.; Hager, E.; Pettit, C.; Gurulingappa, H.; Davidson, N. E.; Khan, S. R. Design, synthesis, and evaluation of novel boronic-chalcone derivatives as antitumor agents. *Med. Chem*. **2003**, *46*, 2813–2815.

Mancilla, T.; Zamudio-Rivera, L. S.; Beltrán, H. I.; Santillan, R.; Farfán, N. Synthesis and characterization of new (N→B) phenyl substituted [N-benzyliminodiacetate-O,O′,N]boranes. *Arkivoc* **2005**, *vi*, 366–376.

Morant, C.; Prieto, P.; Bareño, J.; Sanz, J. M.; Elizalde, E. Hard BCxNy thin films grown by dual ion beam sputtering. *Thin Solid Films* **2006**, *515*, 207–211.

Pandey, T.; Singh, R. V. Unsymmetrical borole complexes of monobasic bidentate benzothiazolines. *Main Group Met. Chem.* **1999**, *22*, 221–226.

Saxena, A. K.; Saxena, S.; Rai, A. K. The structure-activity relationships of some cyclopentadienyltitanium (IV) complexes of 1, 3-dihydro-1, 3-dioxo-α-(substituted)-2H-isoindole-2-acetates. *Appl. Organomet. Chem.* **1991**, *5*, 65–67.

Saxena, A. K.; Saxena, S.; Rai, A. K. Seven coordinated organotin(IV) complexes of 1,3-dihydro-1,3-dioxo-α-(substituted)-2H-isoindole-2-acetic acids. *Indian J. Chem*. **1992**, *31A*, 469–471.

Saxena, C.; Sharma, D. K.; Singh, R. V. Fluoro-boron complexes as antifungal and antibacterial agents. *Main Group Met. Chem.* **1993**, *16*, 345–354.

Sharma, S.; Jain, A.; Saxena, S. N-Protected amino acids and ketooximes-modified dibutyltindichloride: synthetic strategy and structural aspects based upon spectral [IR,NMR (1H,13C & 119Sn)] studies. *Main Group Met. Chem*. **2007**, *30*, 63–74.

Sharma, S.; Jain, A.; Saxena, S. Facile incorporation of Bu3Sn(IV) into sterically congested Schiff bases of heterocyclic β-diketones: synthetic route and structural considerations based upon multinuclear (1H, 13C and 119Sn) NMR studies. *Main Group Met. Chem*. **2010**, *33*, 253–263.

Sheehan, J. C.; Chapman, D. W.; Roth, R. W. The synthesis of stereochemically pure peptide derivatives by the phthaloyl method. *J. Am. Chem. Soc.* **1952**, *74*, 3822–3825.

Singh, R. V.; Biyala, M. K.; Fahmi, N. Important properties of sulfur-bonded organoboron (iii) complexes with biologically potent ligands. *Phosphor. Sulf. Silicon* **2005**, *180*, 425–434.

Surana, C.; Saxena, S. Synthesis and spectral studies of some aluminum(III) complexes of N-protected amino acids. *Indian J. Chem.* **1996**, *35A*, 620–622.

Swami, M.; Mahajan, K.; Gupta, N.; Singh, R. V.; Arya, S.; Kushwah, S. Synthesis, spectroscopic characterization, and in vitro antimicrobial potency of sulfur-bonded complexes of boron(III). *Phosphor. Sulf. Silicon* **2009**, *184*, 2125–2139.

Tabuchi, H.; Kawaguchi, H.; Taniguchi, H.; Imazaki, H.; Hayase, Y. Anticoccidial activity of some azacyclo organoborinates. *Heterocycles* **2003**, *60*, 177–182.

Thomas, L. H. The preparation of simple organic orthoborates. *J. Chem. Soc.* **1946**, 820–822.

Uslu, I.; Öztürk, M. K.; Aksu, M. L.; Gökme, F. Synthesis and reactivity in inorganic, metal-organic, and nano-metal chemistry.

Synth. React. Inorg. Met.-Org. Nano-Met. Chem. **2009**, *39*, 199–203.

Verma, S.; Joshi, A.; Jain, A.; Saxena, S. New mixed ligand complexes of dicyclopentadienyl titanium(IV) derived from sterically congested heterocyclic β-diketones and N-protected amino acids. *J. Chem. Res.* **2004**, *Nov*. 768–772.

Yadav, S.; Singh, R. V. Ferrocenyl-substituted Schiff base complexes of boron: synthesis, structural, physico-chemical and biochemical aspects. *Spectrochim. Acta A* **2011**, *78*, 298–306.

Yadav, S.; Swami, M.; Singh, R. V. In vitro antibacterial and antifungal activities of some sulfur-nitrogen-oxygen and oxygen-nitrogen-oxygen donor bifunctional tridentate Schiff bases and their boron(III) complexes. *Phosphor. Sulf. Silicon* **2010**, *185*, 394–401.

Ying, Z. F.; Yu, D.; Ling, H.; Xu, N.; Lu, Y. F.; Sun, J.; Wu, J. D. Synthesis of BCN thin films by nitrogen ion beam assisted pulsed laser deposition from a B4C target. *Diam. Relat. Mater.* **2007**, *16*, 1579–1585.