

## Synthesis and characterizat on of some new coordination compounds of boron with mixed azines

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**Abstract:** Some new boron complexes have been synthesized by the reaction of triisopropoxyborane with the mixed azines, prepared by the condensation of salicylaldehyde and hydrazine with aldehydes/ketones in a 1:1:1 mole ratio to give a new series of  $(OPr^i)_2B(\overline{NO})$  type of complexes. Their structures were confirmed on the basis of elemental analyses, ultraviolet, infrared,  $^1H$ -NMR and  $^{11}B$ -NMR spectral studies. The ligands and their boron complexes were also screened for their antifungal activity. Several of these complexes were found to be quite active in this respect.

**Keywords:** mixed azines, aldehydes/ketones, triisopropoxyborane, spectral studies, antifungal activity.

### INTRODUCTION

Azines containing the N, O donor system are an important class of ligands and have found wide application in various fields.<sup>1–7</sup> Continuing earlier research<sup>8–13</sup> on biologically active complexes, an attempt has now been made to synthesize mixed azines derived from salicylaldehyde and hydrazine with aldehydes/ketones and their complexes with triisopropoxyborane. The mixed azines used in this study are shown in Fig. 1.

### EXPERIMENTAL

All the chemicals used in this work are of AR grade and the solvents were dried by standard methods. All reactions were carried out under an anhydrous atmosphere. The electronic spectra were recorded on the Pye-Unicam SP-8-100 spectrophotometer with 1 cm quartz cells in the range 800–200 nm. The infrared spectra were obtained on a Perkin–Elmer 577 grating spectrophotometer in the region  $4000$ – $200\text{cm}^{-1}$  as KBr pellets. The  $^1H$  NMR spectra were recorded on a Perkin–Elmer RB-12 spectrometer in  $DMSO-d_6$  using TMS as an external standard at 90 MHz.  $^{11}B$ -NMR of the resulting boron derivatives were recorded on the FX 90Q Jeol spectrometer using  $BF_3 \cdot Et_2O$  as the external standard.

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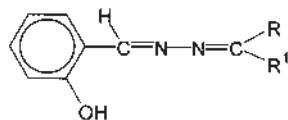
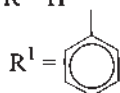
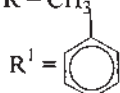
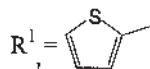
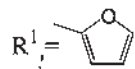
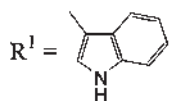
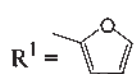
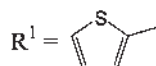
For ligand  $C_{14}H_{12}N_2O$  $(L^1H)$  $R = H$ For ligand  $C_{15}H_{14}N_2O$  $(L^2H)$  $R = CH_3$ For ligand  $C_{12}H_{10}N_2OS$  $(L^3H)$  $R = H$ For ligand  $C_{13}H_{12}N_2O_2$  $(L^4H)$  $R = CH_3$ For ligand  $C_{16}H_{13}N_3O$  $(L^5H)$  $R = H$ For ligand  $C_{12}H_{10}N_2O_2$  $(L^6H)$  $R = H$ For ligand  $C_{13}H_{12}N_2OS$  $(L^7H)$  $R = CH_3$ 

Fig. 1. Mixed azines used as ligands in this work.

The mixed azines were synthesized by the condensation of salicylaldehyde and hydrazine with aldehydes/ketones, *viz.* benzaldehyde, acetophenone, thiophene, 2-aldehyde, 2-furyl methyl ketone, indol 3-carboxaldehyde, furfuraldehyde and 2-acetylthiophene, in a 1:1:1 mole ratio using ethanol as the reaction medium ( $\approx 50$  ml) and then refluxing for 4–5 h. Subsequently, the solvent was removed in vacuo. The obtained solids were recrystallised from ethanol. Their elemental analyses and physical properties are given in Table I.

#### Synthesis of the boron complexes

The calculated amount of the appropriate ligand in a 1:1 mole ratio was added to a weighed amount of triisopropoxy borane in dry benzene ( $\approx 40$ –50 ml). The reactants were refluxed under a fractionating column for about 8 h to complete the reaction. The liberated 2-propanol in the reaction was removed azeotropically with benzene. After cooling and removing the excess solvent under reduced pressure, the final product was dried under vacuum for 2–3 h. The synthesis and analytical data of the resulting complexes are presented in Table II.

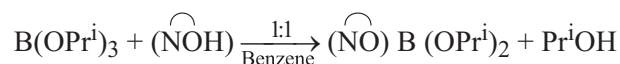
TABLE I. Physical properties and characteristics of the mixed azines

S. No.	Ligand	Colour and State	M.P./°C	Elemental analysis/%				Mol. wt. Found (Calcd.)
				C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	S Found (Calcd.)	
1.	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O (L <sup>1</sup> H)	Lemon yellow, shiny crystal	152	74.82 (74.98)	5.24 (5.39)	12.32 (12.49)	–	216.88 (224.24)
2.	C <sub>15</sub> H <sub>14</sub> N <sub>2</sub> O (L <sup>2</sup> H)	Yellow, shiny crystal	163	75.66 (75.76)	5.82 (5.92)	11.66 (11.76)	–	224.76 (238.27)
3.	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> OS (L <sup>3</sup> H)	Greenish brown, shiny crystal	166	62.44 (62.59)	4.24 (4.38)	12.04 (12.16)	13.76 (13.92)	218.11 (230.27)
4.	C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> (L <sup>4</sup> H)	Reddish brown, solid	181	68.32 (68.41)	5.22 (5.30)	12.11 (12.27)	–	220.64 (228.23)
5.	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O (L <sup>5</sup> H)	Light Red, solid	175	72.86 (72.99)	4.80 (4.98)	15.88 (15.96)	–	250.67 (263.28)
6.	C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> (L <sup>6</sup> H)	Reddish brown needle-like crystal	198	67.20 (67.28)	4.58 (4.71)	12.96 (13.08)	–	202.12 (214.20)
7.	C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> OS (L <sup>7</sup> H)	Brown, solid	172	63.82 (63.91)	4.79 (4.95)	11.32 (11.47)	13.02 (13.12)	236.32 (244.30)



## RESULTS AND DISCUSSION

The reaction of triisopropoxyborane with these ligands in a 1:1 mole ratio in benzene medium on refluxing for about 8 h can be represented as follows:



The resulting complexes were obtained as coloured solids. The low value of the molar conductance ( $10\text{--}15 \text{ S cm}^2 \text{ mol}^{-1}$ ) showed that these complexes are non electrolytes. The molecular weight of these complexes determined by the Rast camphor method<sup>14</sup> corresponding to the formula weight indicated their monomeric nature.

*Electronic spectra*

Two bands were observed at  $\approx 320 \text{ nm}$  and  $\approx 380 \text{ nm}$  in the spectra of all ligands. The band at  $\approx 320 \text{ nm}$  is due to the  $\pi - \pi^*$  transition within the aromatic ring and remains almost unchanged in the spectra of the boron complexes. Another band due to  $n - \pi^*$  transition within the  $>\text{C}=\text{N}$  chromophore<sup>15</sup> of the ligand at  $\approx 380 \text{ nm}$  shifts to a shorter wavelength in the complexes and appears at  $\approx 350 \text{ nm}$ . This indicates the coordination of the azomethine nitrogen to the boron atom.

*IR Spectra*

The infrared spectra of the ligands as well as the corresponding boron complexes were recorded (Table III) and some important features may be summarized as follows. The IR spectra of ligands show a broad and strong absorption band in the region  $\approx 3150\text{--}2850 \text{ cm}^{-1}$ , attributable to the  $\nu(\text{OH})$  mode, indicating that the hydroxyl groups are strongly hydrogen bonded with the azomethine nitrogen.<sup>16</sup> This band disappears in the spectra of the metal complexes, suggesting deprotonation of this functional group. One strong band in the IR spectra of all the ligands at  $\approx 1620 \text{ cm}^{-1}$ , due to  $\nu(\text{C}=\text{N})$  splits into two sharp bands at  $\approx 1630 \text{ cm}^{-1}$  and  $\approx 1600 \text{ cm}^{-1}$  on complex formation. The band at  $\approx 1630 \text{ cm}^{-1}$  in the metal complexes, indicates the coordination of the azomethine nitrogen to the boron atom,<sup>17</sup> whereas the other one is due to uncoordinated azomethine groups.

TABLE III. Important IR spectral data ( $\text{cm}^{-1}$ ) of the ligands and their boron complexes

Compounds	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{B}-\text{O})$	$\nu(\text{B}\leftarrow\text{N})$
L <sup>1</sup> H	3150-2880	1620	—	—
L <sup>1</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	—	1630 and 1600	1360	1555
L <sup>2</sup> H	3120-2850	1615	—	—
L <sup>2</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	—	1626 and 1600	1370	1540
L <sup>3</sup> H	3130-2870	1618	—	—
L <sup>3</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	—	1630 and 1605	1340	1550
L <sup>4</sup> H	3150-2850	1620	—	—
L <sup>4</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	—	1632 and 1608	1350	1530

TABLE III. Continued

Compounds	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{B}-\text{O})$	$\nu(\text{B}\leftarrow\text{N})$
L <sup>5</sup> H	3140-2860	1620	–	–
L <sup>5</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	–	1635 and 1605	1345	1525
L <sup>6</sup> H	3140-2850	1616	–	–
L <sup>6</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	–	1628 and 1598	1355	1540
L <sup>7</sup> BH	3130-2860	1618	–	–
L <sup>7</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	–	1632 and 1595	1360	1550

The phenolic  $\nu(\text{C}-\text{O})$  and  $\nu(\text{N}-\text{N})$  at  $\approx 1260$  and  $\approx 970$   $\text{cm}^{-1}$ , respectively, are also shifted to higher frequency region as a result of complex formation.<sup>18</sup>

The appearance of new strong and medium intensity bands in the spectra of the complexes in the regions,  $\approx 1555$ – $1525$   $\text{cm}^{-1}$  and  $\approx 1370$ – $1345$   $\text{cm}^{-1}$  may be attributed to  $\nu(\text{B}\leftarrow\text{N})$ <sup>19</sup> and  $\nu(\text{B}-\text{O})$ ,<sup>20</sup> respectively.

#### <sup>1</sup>H-NMR Spectra

The proton signal of the azomethine moiety ( $-\text{HC}=\text{N}$ ) is observed at  $\delta$  8.80 ppm in the spectra of the ligand and is shifted downfield in the spectra of the boron complexes, which is attributed to the donation of the lone pair of electrons by the azomethine nitrogen to the boron atom. The aromatic proton signal at  $\delta$  7.75–7.10 ppm remains almost unchanged. The proton signals observed at  $\delta \approx 1.0$  and  $\delta \approx 3.9$  ppm in the spectra of the metal complexes are due to the methyl and methine protons of the isopropoxy groups, respectively. Furthermore, the broad signal observed at  $\delta \approx 12.60$  ppm due to OH protons in the ligands are not observed in the spectra of the corresponding boron complexes, thereby showing the chelation of the ligand moiety through the deprotonated phenolic oxygen. The <sup>1</sup>H-NMR data for the ligands and their corresponding boron derivatives are given in Table IV.

TABLE IV. <sup>1</sup>H-NMR Spectra data ( $\delta$ , ppm) of the mixed azine ligands and their corresponding boron complexes

Compounds	–OH	HC=N	Aromatic protons	Isopropoxy	
				CH	CH <sub>3</sub>
L <sup>1</sup> H	12.60 <i>s</i>	8.87 <i>s</i>	7.75–7.10 <i>m</i>	–	–
L <sup>1</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	–	9.08 <i>s</i>	7.72–7.15 <i>m</i>	3.90 <i>m</i>	1.00 <i>d</i>
L <sup>2</sup> H	12.75 <i>s</i>	8.80 <i>s</i>	7.70–7.02 <i>m</i>	–	–
L <sup>2</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	–	9.04 <i>s</i>	7.75–7.08 <i>m</i>	3.88 <i>m</i>	1.10 <i>d</i>
L <sup>3</sup> H	12.50 <i>s</i>	8.84 <i>s</i>	7.77–7.17 <i>m</i>	–	–
L <sup>3</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	–	8.92 <i>s</i>	7.82–7.22 <i>m</i>	3.97 <i>m</i>	1.21 <i>d</i>
L <sup>4</sup> H	12.70 <i>s</i>	8.78 <i>s</i>	7.69–7.12 <i>m</i>	–	–
L <sup>4</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	–	8.84 <i>s</i>	7.78–7.15 <i>m</i>	3.92 <i>m</i>	1.14 <i>d</i>
L <sup>5</sup> H	12.55 <i>s</i>	8.90 <i>s</i>	7.65–7.10 <i>m</i>	–	–

TABLE IV. Continued

Compounds	-OH	HC=N	Aromatic protons	Isopropoxy	
				CH	CH <sub>3</sub>
L <sup>5</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	–	9.10 <i>s</i>	7.70–7.14 <i>m</i>	3.90 <i>m</i>	1.12 <i>d</i>
L <sup>6</sup> H	12.52 <i>s</i>	8.82 <i>s</i>	7.72–7.12 <i>m</i>	–	–
L <sup>6</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	–	8.95 <i>s</i>	7.84–7.15 <i>m</i>	3.94 <i>m</i>	1.16 <i>d</i>
L <sup>7</sup> H	12.62 <i>s</i>	8.92 <i>s</i>	7.75–7.10 <i>m</i>	–	–
L <sup>7</sup> B(OPr <sup>i</sup> ) <sub>2</sub>	–	9.05 <i>s</i>	7.86–7.15 <i>m</i>	3.90 <i>m</i>	1.1 <i>d</i>

*<sup>11</sup>B-NMR Spectra*

The <sup>11</sup>B-NMR spectra give signals ranging around δ 5.20 ppm, suggesting the coordination number 4 around the boron atom.

Based on the above findings, the resulting coordination compounds may be represented by the structure given in Fig. 2.

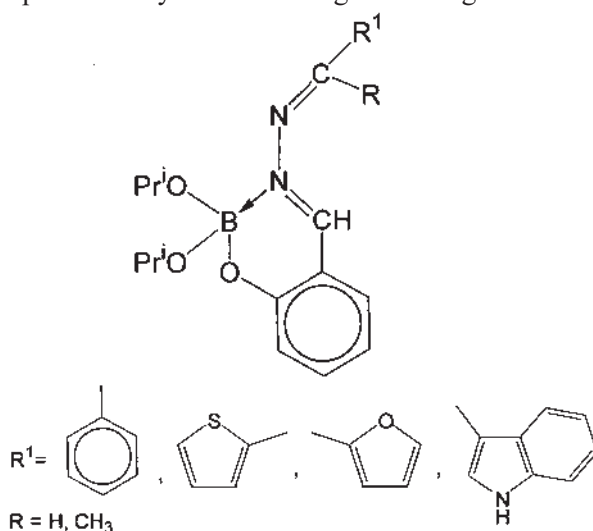


Fig. 2. Coordination compounds prepared in this work.

*Antifungal activity*

Some boron derivatives have recently been reported as effective bactericides, fungicides and trichomonacides. Organoboranes as insecticides and plant growth regulators have also been mentioned. Boron complexes are more potent in their inhibition properties than the free ligands. The pathogenic fungi used in these experiments were *Macrophomina phaseolina*, *Fusarium oxysporum* and *Aspergillus niger*. The radial growth method was used for the determination of the antifungal activity. The method used was potato dextrose agar (composition : potato slices – 200g, Dextrose – 20g, Agar-agar 15g and distilled water 1000 ml). The compounds were directly mixed with the medium in different concentrations (50, 100 and 200 ppm). The studies were carried out *in vitro* and the results are quite encour-

aging. The newly synthesized complexes were more active in inhibiting the growth of fungi compared with their corresponding ligands. The complexes exhibited remarkable activity even at lower concentrations. The increased biocidal activity after complexation can be explained on the basis of the chelation theory.

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## ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА НЕКИХ НОВИХ КООРДИНАЦИОНИХ  
ЈЕДИЊЕЊА БОРА СА МЕШОВИТИМ АЗИНИМА

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Добијени су нови комплекси бора реакцијом триизопророксиборана са мешовитим азинима, припремљеним кондензацијом салицилалдехида и хидридина са алдехидима/кетонима у молском односу 1:1:1, при чему настаје нова серија  $(OPr^i)_2B(NO)$  типа комплекса. Њихове структуре су одређене на основу елементалне анализе, UV, IR,  $^1H$ -NMR и  $^{11}B$ -NMR спектралног проучавања. Тестирана је такође и антигљивична активност лиганда и његових комплекса са бором. За неколико ових комплекса је нађена знатна активност.

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