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Synthesis and characterisation of boron complexes with Schiff bases rearranged from benzothiazolines

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ABSTRACT

The present paper is a report on the synthesis of some new coordination compounds by the reactions of triisopropoxyborane with sulfur containing ligands. Ligands used in these reactions are benzothiazolines prepared by the reaction of p-tolualdehyde, 4-acetylbiphenyl, 9-anthraldehyde, 4-fluoroacetophenone and 2-acetylfluorene with o-aminothiophenol which on reaction with metal ion rearrange to Schiff bases. Characterization and structure elucidation of the complexes are achieved by elemental analysis, electronic, infrared, ¹H spectral studies. The potency of the synthesized compounds have been assessed by growth inhibiting potential of the complexes against variety of fungal and bacterial strains.

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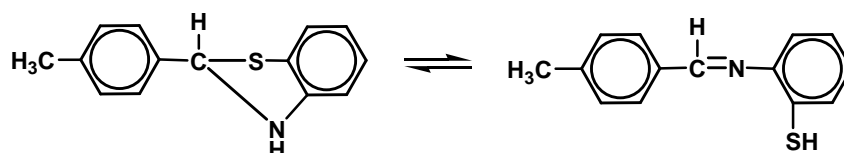
KEYWORDS

Triisopropoxyborane;
o-aminothiophenol;
Benzothiazolines;
Spectral studies.

INTRODUCTION

The condensation of o-aminothiophenol with the carbonyl compounds should form the Schiff base, but we get the benzothiazoline. These benzothiazolines when react with metal salts rearrange into Schiff base with the formation of their coordination compounds. *Duatti et al.*^[1] reported that even in the absence of metal ion the condensation product of aldehyde and ketone with o-aminothiophenol forms a mixture of benzothiazoline and the Schiff base and equilibrium may exist between the two as shown below.

Several workers have shown that in presence of metal ion, the cyclic structure of the thiazoline or benzothiazoline rearranges to give the Schiff base metal complex quantitatively. Tandon et al have also studied the reactions of these ligands with transition metals and the geometry of metal complexes has been deduced on the basis of various spectral studies. Metal complexes of such ligands and particularly of sulfur containing ligands are drawing enormous attention mainly due to their practical utility^[2-5]. They are active against tuberculosis, cancer, viruses, malaria, smallpox and certain kinds of tumor.



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TABLE 1 : Elemental analysis and physical properties of benzothiazolines

S. No.	Ligands	Colour & State	Melting point (°C)	Analysis : Found (Calcd.) (%)				Molecular weight: Found (Calcd.)
				C	H	N	S	
1.	C ₂₁ H ₁₅ NS (L ¹ H) 2-acetyl fluorine benzothiazoline	Green crystalline solid	80°	69.99 (70.01)	5.80 (5.87)	5.40 (5.44)	12.42 (12.45)	252.36 (257.34)
2.	C ₁₄ H ₁₂ NSF (L ² H) 4-fluoro acetophenone benzothiazoline	Light brown crystalline solid	85°	73.09 (73.69)	4.99 (5.15)	4.71 (4.77)	10.90 (10.92)	283.40 (293.38)
3.	C ₁₈ H ₁₅ NS (L ³ H) 9-anthraldehyde benzothiazoline	Brown powdered solid	45°	73.09 (73.69)	4.99 (5.15)	4.71 (4.77)	10.90 (10.92)	283.40 (293.38)
4.	C ₁₄ H ₁₃ NS (L ⁴ H) p-tolualdehyde benzothiazoline	Light cream powdered solid	135°	73.90 (73.93)	5.75 (5.76)	6.15 (6.16)	14.08 (14.10)	207.33 (227.32)
5.	C ₂₀ H ₁₇ NS (L ⁵ H) 4-acetylbiphenyl benzothiazoline	Yellow powdered solid	65°	78.99 (79.17)	5.09 (5.64)	4.60 (4.61)	10.50 (10.56)	298.43 (303.42)

TABLE 2 : Synthesis new coordination compounds of triisopropoxyborane with benzothiazolines.

Reactant metal	Ligand	Molar ratio	Product	Colour and State	M.P.C°	Mol. wt. found (Calcd.)	% Analysis found (Calcd.)		
							N Found (Calcd.)	S Found (Calcd.)	B Found (Calcd.)
B(OPr ⁱ) ₃	C ₂₁ H ₁₅ NS(L ¹ H)	1:1	[(Pr ⁱ O) ₂ B(C ₁₅ H ₁₄ NOS)]	Yellow solid	215	435.81 437.0	3.20 (3.28)	7.30 (7.32)	2.50 (3.00)
B(OPr ⁱ) ₃	C ₂₁ H ₁₅ NS(L ¹ H)	1:2	[(Pr ⁱ O)B(C ₁₅ H ₁₄ NOS) ₂]	Orange solid	250	505.0 (508.81)	5.00 (5.51)	12.00 (12.59)	1.90 (2.10)
B(OPr ⁱ) ₃	C ₂₁ H ₁₅ NS(L ¹ H)	1:3	[B(C ₁₅ H ₁₄ NOS)] ₃	Yellow solid	-	864.50 (865.81)	4.00 (4.85)	11.00 (11.09)	1.20 (1.20)
B(OPr ⁱ) ₃	C ₁₄ H ₁₂ NSF (L ³ H)	1:1	[(Pr ⁱ O) ₂ B(C ₁₈ H ₁₄ NOS)]	Orange solid	260	472.30 (473.00)	2.50 (2.95)	6.20 (6.76)	2.20 (2.30)
B(OPr ⁱ) ₃	C ₁₄ H ₁₂ NSF (L ³ H)	1:2	[(Pr ⁱ O)B(C ₁₈ H ₁₄ NOS) ₂]	Brown solid	-	543.50 (544.04)	5.00 (5.14)	11.50 (11.76)	2.00 (2.02)
B(OPr ⁱ) ₃	C ₁₄ H ₁₃ NS (L ⁴ H)	1:1	[(Pr ⁱ O) ₂ B(C ₁₄ H ₁₂ NS)]	Brown semi solid	290	422.00 (423.08)	3.0 (3.37)	7.50 (7.56)	2.40 (2.60)
B(OPr ⁱ) ₃	C ₁₄ H ₁₃ NS (L ⁴ H)	1:2	[(Pr ⁱ O)B(C ₁₄ H ₁₂ NS) ₂]	Brown solid	-	478.02 (480.04)	5.50 (5.83)	13.20 (13.33)	2.20 (2.29)

The role of metal chelates in all aspects of biological studies has gained considerable importance as these provide valuable approaches to the metabolic studies, oxidative phosphorylation, trans methylation and principles of chemotherapy. Recently, much interest has been shown in the synthesis of metal chelates of sulfur containing ligands and it is within this particular area that rather significant advances have been made^[6-8]. It was, therefore, considered worthwhile to synthesize such type of complexes by the reactions of triisopropoxyborane with benzothiazolines.

EXPERIMENTAL

All the reactions were carried out in strictly anhydrous condition using quick fit apparatus. All reagents were obtained commercially as analytical grade and

were used without further purification.

Analytical methods and physical measurements

Boron was estimated gravimetrically as triisopropoxyborane. Nitrogen and sulphur were estimated by Kjeldahl's method and Messenger's method, respectively^[9-12]. The IR spectra were recorded on FT IR spectrophotometer using a model A-8400 S, Shimadzu in KBr pellets. ¹H spectra were recorded on JEOLAL-300 spectrometer. Molecular weight determinations were carried out by the Rast Camphor Method. Molar conductance measurements were made in anhydrous dimethyl formamide at 36±1°C using a model 305 systronics conductivity bridge. The purity of the compounds were checked by thin layer chromatography.

Synthesis of ligands

The ligands were synthesized by the condensation of

TABLE 3: Selected infrared vibrations (in cm^{-1}) of ligands and their corresponding boron complexes.

S. No.	Compounds	$\nu\text{C}=\text{N}$	$\nu\text{NH}/\nu\text{OH}$	$\nu\text{B? N}$	$\nu\text{B-O}$
1	L ¹ H	1600	3260	-	-
2	B.3(L ¹ H)	1580	-	1525w	1360w
3	L ² H	1600	3220	-	-
4	B.3(L ² H)	1540	-	1530w	1370w
5	L ³ H	1608	3240	-	-
6	B.3(L ³ H)	1588	-	1550w	1340w

aldehydes / ketones viz. 9-anthraldehyde, 4-acetyl- biphenyl, 4-fluoroacetophenone and p-tolualdehyde with o-aminothiophenol in 1:1 molar ratio using absolute alcohol as the reaction medium. The mixture was heated on a water bath for about half an hour and then allowed to cool at room temperature. The crystals that separated out were recrystallized from the same solvent. The physical properties and analytical data are recorded in TABLE 1.

Synthesis of Boron (III) complexes

A weighed amount of triisopropoxyborane was added to the calculated amount of benzothiazoline in a molar ratios 1:1, 1:2 & 1:3 in dry benzene and refluxed under a fractionating column. The isopropanol liberated during the reaction by deprotonation of the ligand was removed azeotropically with benzene. After the complexation of the reaction the products were dried under reduced pressure and analysed. The purity of the compounds was checked by TLC using silica gel-G as an adsorbent. The physical properties and analytical data are recorded in TABLE 2.

Biological activity

The antimicrobial activity of ligands and their corresponding boron(III) complexes are tested against fungi and bacteria (*R.phaseoli*, *F. oxysporum*, *S. aureus*, *E. coli*, *P.fluorescens* etc.). The results also show that the resulting products are lipophilic in nature. The complexes are found to possess higher activity than ligands. The results of these studies show that the metal complexes are more active than the ligands. The fungi toxicity of the compounds increase with increase in concentration.

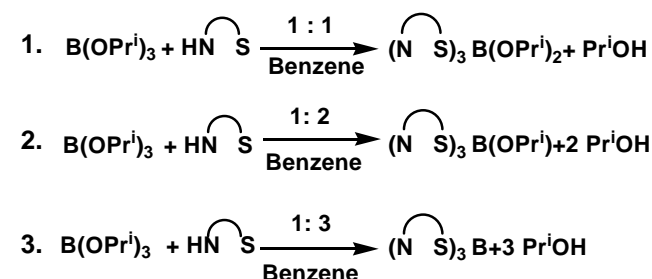
RESULTS AND DISCUSSION

The reactions of triisopropoxyborane with

TABLE 4 : Nuclear magnetic resonance data for the Schiff bases and the corresponding boron complexes in δ ppm.

Compound	H-C=N	NH ₂	Aromatic protons
L ¹ H (C ₁₄ H ₁₃ NS) ₃ B	- 9.26	5.80 -	7.90-6.80 7.95-6.79
L ² H (C ₂₀ H ₁₇ NS) ₃ B	- 9.60	5.90 -	7.72-7.15 7.75-7.10
L ³ H (C ₂₁ H ₁₅ NS) ₃ B	- 9.25	5.80 -	7.80-7.20 7.90-7.15
L ⁴ H (C ₁₄ H ₁₂ NSF) ₃ B	- 8.86	5.75 -	7.80-7.25 7.90-7.15

benzothiazolines in 1:1, 1:2 & 1:3 molar ratio proceed in following manner:



where $\begin{array}{c} \curvearrowright \\ \text{N S} \end{array}$ represents the donor sets of ligands.

Electronic spectra

The electronic spectra of the ligands exhibit two bands near 250 nm and 315 nm consistent with the typical spectrum of a benzothiazoline (cyclic form) moiety^[13-15]. These bands may be attributed to the $\phi-\phi^*$ and $\pi \rightarrow \pi^*$ benzenoid transitions. In the corresponding boron (III) complexes, an additional band around 410 nm due to $\pi \rightarrow \pi^*$ transition of the azomethine group is also observed. The formation of this new band may be due to the isomerization of benzothiazoline into Schiff bases.

Infrared spectra

In the solid state IR spectra of benzothiazoline, the presence of a strong and broad band due to νNH group in the region 3300-3100 cm^{-1} and absence of νSH at $\sim 2500\text{-}2600 \text{ cm}^{-1}$ is indicative of the benzothiazoline rather than the Schiff-base structure. A new band at 1605 cm^{-1} is observed in the spectra of metal complexes due to the presence of $\nu(\text{C}=\text{N})$ vibrations. The appearance of this band suggests that the complexes are metal Schiff base derivatives as the benzothiazoline

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TABLE 5.1 : Antifungal activity of the ligands and their boron (III) complexes.

Microorganisms		L ² H		B.3L ² H		L ³ H		B.3L ³ H		L ⁵ H		B.3L ⁵ H	
		100	200	100	200	100	200	100	200	100	200	100	200
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
<i>A. flavus</i>	IZ (AI)	26 (0.81)	38 (0.79)	18 (0.69)	24 (1.20)	14 (0.53)	22 (1.10)	20 (0.76)	20 (1.00)	18 (0.56)	28 (0.58)	16 (0.62)	24 (1.20)
<i>F. oxysporum</i>	IZ (AI)	24 (0.80)	38 (0.90)	18 (0.82)	18 (0.43)	12 (0.54)	20 (1.25)	16 (0.72)	18 (0.69)	22 (0.73)	38 (0.90)	16 (0.73)	20 (1.25)
<i>R. phaseoli</i>	IZ (AI)	22 (1.00)	34 (1.54)	18 (0.82)	20 (0.91)	22 (1.00)	34 (1.54)	26 (1.18)	36 (1.63)	24 (1.09)	42 (1.90)	18 (0.82)	24 (1.09)

IZ = Inhibition zone (diameter in mm); AI = Activity index (Inhibition zone of test compounds/Inhibition zone of standard). L²H = C₁₆H₁₃N₃S; L³H = C₁₅H₁₅N₃O; L⁵H = C₉H₁₀N₃OF

TABLE 5.2 : Antibacterial activity of the ligands and their boron(III) complexes.

Microorganisms		L ² H		B.3L ² H		L ³ H		B.3L ³ H		L ⁵ H		B.3L ⁵ H	
		100 ppm	200 ppm	100 ppm	200 ppm	100 ppm	200 ppm	100 ppm	200 ppm	100 ppm	200 ppm	100 ppm	200 ppm
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
<i>S. aureus</i>	IZ (AI)	16 (0.88)	38 (1.11)	18 (1.00)	24 (0.70)	10 (0.55)	22 (0.64)	16 (0.88)	26 (0.76)	20 (1.11)	36 (1.05)	20 (1.11)	20 (0.58)
<i>E. coli</i>	IZ (AI)	20 (1.00)	38 (1.00)	22 (1.10)	24 (0.63)	12 (1.65)	20 (0.52)	18 (0.47)	20 (0.52)	18 (0.90)	42 (1.10)	18 (0.90)	24 (0.63)

IZ = Inhibition zone (diameter in mm); AI = Activity index (Inhibition zone of test compounds/Inhibition zone of standard). L²H = C₁₆H₁₃N₃S; L³H = C₁₅H₁₅N₃O; L⁵H = C₉H₁₀N₃OF

ring rearranges to give the Schiff-base derivatives in the presence of metal ion. Data are given in TABLE 3.

¹H NMR spectra

The proton magnetic resonance spectra of benzothiazolines show the N–H proton signals at δ 5.8 ppm which disappear on complexation, indicating that the rearrangement of benzothiazoline form to the Schiff base form has occurred. The ligand shows a complex multiplet in the region δ 7.40–6.40 ppm for the benzene protons and these remains at almost the same position in the spectra of complexes. Data are given in TABLE 4.

BIOLOGICAL ACTIVITY

In vitro antifungal and antibacterial activity of the ligands and the complexes were tested using the paper disc diffusion method at a concentration of 1 mg/disc. Micostatin and Streptomycin were used as reference compounds for antifungal and antibacterial activities, respectively. The data have been recorded in TABLE 5.1 and 5.2. The antifungal activity of some ligands and their corresponding lead complexes are screened *in vitro* against *Aspergillus flavus*, *Fusarium oxysporum* etc. For antifungal activity, radial growth method was used. All the complexes showed high activity against some pathogenic fungi even at lower concentrations and the

inhibition of fungal growth was found to be dependent on the concentration of the compounds^[16–20].

All boron (III) coordination compounds were tested against gram positive (*Staphylococcus aureus*) and gram negative (*Escherichia coli*) bacteria and it was found that the metal complexes are much more active than the ligands. Although, all the complexes were found to be fairly active against gram positive bacteria, some of them could inhibit the growth of gram negative bacteria^[21–25].

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