

# Synthesis and characterization of some 1,2,3-benzodioxaborole with N-alkyl-2-mercaptoacetamides: A studies on the steric effect of alkyl group on the coordination

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## I. Introduction

The ligands N-alkyl-2-mercaptoacetamides are known to exist in two isomeric forms<sup>1-4</sup> and behave as mono-dentate or mono-functional bi-dentate ligands depending upon the nature of the metal used in the complexation. The presence of O, N and S atoms at suitable positions in these ligands provide additional feature of linkage isomerism<sup>5-7</sup>.

Because of the interesting feature of the ligand N-alkyl-2-mercaptoacetamides, their reactions with 2-isopropoxy-1,3,2-benzodiazaborole in non-aqueous medium in 1:1 molar ratio have been carried out and the resulting boron complexes have been characterized and their structures have been postulated.

## Experimental

All the reactions were carried out under anhydrous conditions. Isopropyl borate (b.p. 139 ° C) was prepared by refluxing boric acid with isopropanol in benzene solution<sup>8</sup>. 2-isopropoxy-1,3,2-benzodiazaborole has been prepared by the interaction of isopropyl borate and catechol in 1:1 molar ratio in refluxing benzene solution. N-alkyl-2-mercaptoacetamides were synthesised by the condensation of thioglycolic acid and alkyl amines<sup>9</sup>. Boron, nitrogen and sulphur were analysed by literature method<sup>10</sup>. Molecular weight measurements were carried out on Knauer vapour pressure osmometer in methanol solution at 45°C. The IR spectra were recorded on Carl-Zeiss Specord M 80 as nujol mulls. The <sup>1</sup>H, <sup>13</sup>C & <sup>11</sup>B NMR spectra were recorded on Jeol FX 90 Q NMR spectrometer.

## General Method of Preparation of complexes

The Boron complexes are synthesised by the reaction of 2-isopropoxy-1,3,2-benzodiazaborole with N-alkyl-2-mercaptoacetamides in 1:1 molar ratio in benzene solution and therefore for brevity the synthetic procedure of a representative compound is being described.

## Synthesis of [2-mercapto-N-(ethyl)acetamidato]-1,3,2-benzodioxaborole

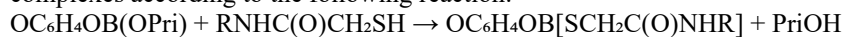
A Benzene solution of 2-isopropoxy-1,3,2-benzodioxaborole (0.98gm, 5.51mm) was added to the benzene solution of N-alkyl-2-mercaptoacetamide (0.65gm 5.46mm) with constant stirring. The reaction was found to be facile and the boron complexes separated out in ~ 15 minutes. To ensure the complexation of the reaction, the reaction mixture was stirred for another two hours at ambient temperature. The solvent was decanted off and the white compound was dried under reduced pressure (yield 98%) at the room temperature.

## II. Results and discussion

N-alkyl-2-mercaptoacetamides exist in following two isomeric forms<sup>1-4</sup>:



They interact with 2-isopropoxy-1,3,2-benzodioxaborole in a 1:1 molar ratio in benzene solution to yield complexes according to the following reaction:



where R = C<sub>2</sub>H<sub>5</sub>, n-C<sub>3</sub>H<sub>7</sub>, i-C<sub>3</sub>H<sub>7</sub>, n-C<sub>4</sub>H<sub>9</sub>, i-C<sub>4</sub>H<sub>9</sub>,

These complexes have been characterized by elemental analysis and spectral (IR,  $^1\text{H}$ ,  $^{13}\text{C}$  &  $^{11}\text{B}$  NMR) studies. The complexes appear to exist in two conformational isomeric forms,  $^{11}\text{B}$  NMR spectral evidences suggest the existence of three different complex species in solution. Two of them are four coordinated conformational isomers and the third one is tri-coordinated boron compound. Semi empirical calculations have been used to confirm the existence of these three forms and the steric effect of N-alkyl group in the coordination of Nitrogen with boron has been confirmed by semi empirical molecular orbital calculations.

### IR Spectra

The broad band observed at 2520-2500  $\text{cm}^{-1}$  in the IR spectra of the ligands and assigned for  $\nu$  SH mode was found to be missing from the spectra of the corresponding boron derivatives indicating the de-protonation of SH group and the formation of B-S bond. This has been further confirmed by the appearance of a new band at  $\sim 900\text{cm}^{-1}$  which may be assigned to  $\nu$  B-S bond.

The position of the amide bands in the I.R. spectra also play an important role in deciding the coordination sites. If a shift in the position of amide – I [ $\nu(\text{C} = \text{O})$ ] occurs after complexation, that implies the metal atom is bonded through carbonyl group of the ligand. On the other hand if this band is observed at the same position and the rest of the amide bands show a shift, the coordination through NH group is indicated instead of the Carbonyl group. Absence of any shift in the position of amide-I [ $\nu(\text{C} = \text{O})$ ] band ( $\sim 1640\text{cm}^{-1}$ ) indicates the non-participation of the carbonyl oxygen of the ligand moiety in bond formation with central boron atom. However appearance of a new band at  $\sim 1100\text{cm}^{-1}$  in all these complexes which may be assigned to  $\sim \text{B-N}^9$  confirms the NH group participation in the bonding. A shift of  $\sim 35\text{cm}^{-1}$  towards lower wave number of amido-II and the amide-III bands in comparison to their position in ligands further confirms the involvement of amido nitrogen in the bonding.

### $^1\text{H}$ NMR spectra

The  $^1\text{H}$  NMR of these complexes exhibits the characteristic resonance due to alkyl and aryl protons along with the NH proton. The signal for SH proton, which was observed in ligand at  $\sim \delta$  3 ppm is found to be absent in the corresponding boron derivatives, confirming the de-protonation of mercapto group and the formation of B-S bond. The spectra of the complexes as well as the corresponding ligands exhibit two signals for NH proton, the presence of two NH protons signals even after complexation indicates that the two isomeric forms of the ligands interact individually with the boron precursor leading to the formation of the corresponding boron derivatives. The signal for alkyl proton show considerable shift and splitting, confirming the involvement of NH group in the bond formation.

A down field shift of 0.1-0.3 ppm in the position of  $-\text{CH}_2\text{S}$  proton signals further support the B-S bond formation in the range  $\sim \delta$  6.52 to  $\sim \delta$  6.59 ppm as multiplet.

### $^{13}\text{C}$ NMR Spectra

A down field shifting the position of  $-\text{CH}_2\text{S}$  carbon further support the participation of sulphur atom in the bonding. In the alkyl carbon signals a little shifting and splitting show the participation of amido nitrogen in the bonding and the existence of isomers even in the complexes.

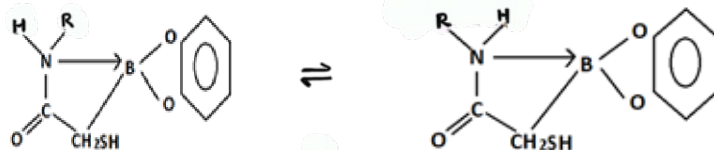
Comparison of the carbonyl signals with their position in the corresponding ligands signals does not show any appreciable shift confirming the non-participation of the carbonyl oxygen in the bonding. The presence of two signals for the carbonyl carbon further supports the existence of these complexes in two isomeric forms.

Signals for the phenyl carbon and C-O also appears as doublet. This indicates the existence of the phenyl group and C-O in two different environments, The pphenyl carbon signals have observed in the range of  $\sim 109.2$ - $120.0$  ppm and C-O at  $\sim 145.1$  and  $\sim 150.5$  ppm  $^{13}$  respectively

### $^{11}\text{B}$ NMR Spectra

The  $^{11}\text{B}$  NMR Spectra of boron derivatives exhibit three signals at  $\sim 9.0$ ,  $\sim 14.0$  and  $\sim \delta$  19.5 ppm. The appearance of these signals may be due to the presence of boron atoms in three different environments.

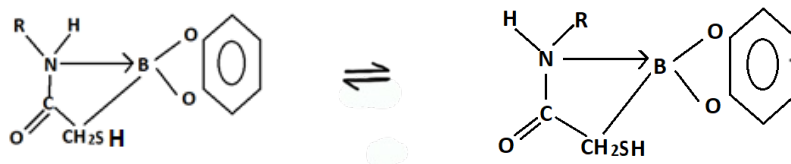
The signals observed at  $\sim 9.0$  and  $\sim \delta$  14.4 ppm have been assigned to tetra coordinated boron $^{14}$ . The appearance of these two signals confirms the existence of the boron compounds in two conformational isomeric forms as indicated by their  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.



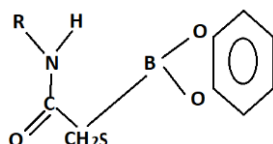
The third signal observed at  $\sim \delta 19.5$  ppm has been assigned to tri-coordinated boron atom $^{11}$  having  $\text{BO}_2\text{S}$  environment due to the weak coordination between boron and amido nitrogen atoms, the possibility of the

bond breaking cannot be ruled out especially in view of the weak coordination capabilities of amido nitrogen. This has been further supported by the fact that as the steric effect of R group increase the intensity of this signal increases, because due to the steric effect the coordinating tendency of nitrogen decreases. The intensity of this signal is very low when R = C<sub>2</sub>H<sub>5</sub> as in that case due to less steric hindrance the formation of B-N bond is effective and the presence of molecule having tri-coordinated boron is very low. But as the steric hindrance increases the number of molecules having tri-coordinated boron atoms increases there by increasing the intensity of the signal.

The IR and NMR (<sup>1</sup>H and <sup>13</sup>C) spectral evidences reveal that [2-mercapto-N(alkyl) acetamidato] – 1,3,2 – benzodioxaborole exist in following two isomeric forms in which central boron atom maintain a coordination number of four.



However, the <sup>11</sup>B NMR spectra analysis reveals the presence of tri coordinated boron complex having the following structure –



along with two isomeric four coordinated complexes. The ratio of 4 to 3 coordinated boron complexes increases with the increase in the steric effect of the substituent R on the nitrogen in the ligand moiety.

This work highlights that the coordination chemistry of boron with N-alkyl-2-mercaptoacetamides is strongly governed by steric factors and ligand isomerism. The study provides clear experimental and theoretical evidence for the coexistence of multiple coordination states, enhancing the understanding of structure–property relationships in boron complexes.

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