

## PREPARATION AND CHARACTERIZATION OF SOME MIXED BORON ARYLAZO COMPLEXES

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### ABSTRACT

Some new mixed boron aryazo complexes were prepared from boric acid and arylazonaphthols in excess acetic anhydride. The analytical and spectral characterization studies of the bis (acetato) boron arylazonaphthol derivatives, (AcO)<sub>2</sub>B[OC<sub>10</sub>H<sub>6</sub>: NN(Ar)] (Ar = C<sub>6</sub>H<sub>5</sub>, o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, p-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, p-BrC<sub>6</sub>H<sub>4</sub>, p-ClC<sub>6</sub>H<sub>4</sub> and p-FC<sub>6</sub>H<sub>4</sub>) show the formation of tetra-coordinated derivatives with a bi-coordinated azo ligand and terminally coordinated acetato groups.

**Keywords:** bis (acetato) boron arylazonaphthol, tetracoordinated boron, Bi-coordinated azo ligand, terminally coordinated acetato groups.

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### INTRODUCTION

The chemistry of main group complexes with oxygen and/or nitrogen donor ligands has been actively pursued and continues to be of interest due to the diverse applicability of these compounds<sup>1-4</sup>. In the past two decades there has been a growing interest in the study of boron complexes probably due to potential utility in biomedical sciences and industry.<sup>5-6</sup>

In the present paper the preparation and physico-chemical characterization of some bis (acetato) boron arylazonaphthol derivatives as shown in figure-1, has been reported.

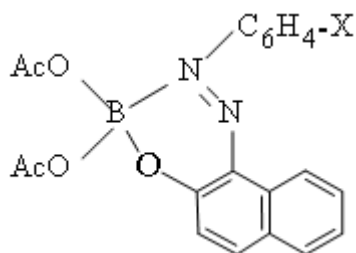


Fig.-1: Phenylazonaphthol complexes of boron  
(X = H, o-CH<sub>3</sub>, p-CH<sub>3</sub>, p-OCH<sub>3</sub>, p-Br, o-Cl, p-Cl, p-F).

Solvents were purified by distillation and solids by recrystallization using standard methods. Boron was estimated as methyl boron and acetoxy group were estimated as acetic acid by titrating against standard (N/10) sodium hydroxide solution<sup>7</sup>.

### EXPERIMENTAL

IR spectra (4000-400cm<sup>-1</sup>) were recorded in KBr on SHIMA-DZU FT-IR 8400 spectrophotometer. NMR data were collected on a JEOL FX 300 FT NMR spectrometer in CDCl<sub>3</sub>.

Arylazo naphthols were prepared by the reported methods from the diazonizimun chloride of the respective amines and 2- naphthol<sup>8,9</sup>.

Bis (acetato) boron arylazonaphthols were obtained by an equimolar reaction of boric acid with arylazo ligands in excess acetic anhydride. The procedure for the synthesis of bis (acetato) boron phenylazonaphthol,  $(\text{AcO})_2\text{B}[\text{OC}_{10}\text{H}_6\text{:NN}(\text{C}_6\text{H}_5)]$  is discussed all other derivatives were similarly prepared. A boric acid (.1.) was dissolved in 20 ml. of acetic anhydride and a calculated amount of the azo ligand (g) was added. The reaction mixture was refluxed for 8 hours and cooled to room temperature. The precipitated obtained was filtered and was purified by crystallization from benzene: n-hexane (80:20).

## RESULTS AND DISCUSSION

Arylazonaphthols exist predominately in the azohydroxy tautomeric form and behave as bifunctional monodentate ligands<sup>9,10</sup>. The mixed ligand boron derivatives were prepared by the reaction of boric acid with arylazonaphthols in excess acetic anhydride. The characterization data of the complexes is given in Table-1.

Table-1: The Characterization Data of the Complexes

S.No.	Arylazo	M.Pt. (°C)	IR (cm <sup>-1</sup> )			NMR(ppm)			<sup>11</sup> B
						<sup>1</sup> H			
			ν(N=N)	ν(B-O)	ν(C=O)	CH <sub>3</sub> (Acetate)	Ar-CH <sub>3</sub> or Ar-OCH <sub>3</sub>	Ar-H	
1.	C <sub>6</sub> H <sub>5</sub> NN	159	1545	740	1275	2.04	-	6.86-8.08	7.32
2.	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NN	147	1540	745	1280	2.01	2.33	6.82-8.07	7.33
3.	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NN	161	1535	745	1285	2.02	2.34	6.92-8.09	7.36
4.	<i>p</i> -OCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NN	167	1540	745	1295	2.02	3.62	6.85-8.00	7.33
5.	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> NN	191	1540	750	1280	2.03	-	6.84-8.01	7.40
6.	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub> NN	154	1545	750	1295	2.01	-	6.81-8.05	7.34
7.	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> NN	172	1540	740	1300	2.04	-	6.83-8.05	7.45
8.	<i>p</i> -FC <sub>6</sub> H <sub>4</sub> NN	183	1535	745	1285	2.03	-	6.78-8.06	7.41

The ir spectra of the complexes shows a medium band 1545-1540 cm<sup>-1</sup> which has been assigned to a  $\nu(\text{N}=\text{N})$  vibration and the absence of  $\nu(\text{O}-\text{H})/\nu(\text{N}-\text{H})$  vibration observed in the spectra of free ligands ~3100 cm<sup>-1</sup>. The sharp band ~1725 cm<sup>-1</sup> and medium intensity band ~1280 cm<sup>-1</sup> in the spectra of the complexes has been assigned to the  $\nu(\text{C}=\text{O})$  and  $\nu(\text{C}-\text{O})$  vibrations of the terminal acetato groups<sup>12</sup>. The medium intensity bands at ~730 cm<sup>-1</sup> has been assigned to the  $\nu(\text{B}-\text{O})$  stretching modes<sup>13</sup>.

In the ir spectra bis (acetato) boron azopyrazolones intense bands at 1310-1380 cm<sup>-1</sup> characteristic for tri-coordinated boron<sup>14</sup> are absent. The spectra are consistent with the unidentate coordination of the acetate groups and the formation of tetracoordinate complexes. The important peaks observed for the complexes are given in Table-1.

In the <sup>1</sup>H nmr spectra of the complexes aryl protons signals were observed at  $\delta$  6.8 -  $\delta$  8.10 and the N-H/O-H proton signal observed in the spectra of the free azo ligands was not observed. The absence of signal is due to the deprotonation of the ligands on coordination with boron. The -CH<sub>3</sub> proton signal of the acetate group is at  $\sim \delta$  2.04 and CH<sub>3</sub>- and -OCH<sub>3</sub> proton signals of the substituted methyl and methoxy group in the azophenyl moiety in the complexes are observed at  $\delta$  2.3-2.4 and  $\delta$  3.7 respectively<sup>12,15</sup>. The <sup>1</sup>H nmr spectra of the complexes gives evidence for the formation of tetracoordinated complexes.

In the <sup>11</sup>B NMR spectra of bis (acetato) boron azo derivatives in CDCl<sub>3</sub> with reference to BF<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O the boron signal was observed as a sharp singlet at  $\sim \delta$  1.0 and is consistent with the tetra coordination of the boron atom.<sup>16</sup>

On the basis of the analytical and spectral data for the bis (acetato) boron phenylazonaphthol phenylazonaphthol the formation of tetracoordinated complexes with the plausible structure as shown in Fig. -1 can be proposed.

## REFERENCES

1. Y.Fazaeli , M.M. Amini , E.Najafi , E. Mohajerani , M. Janghouri , A.Jalilian , S.W. Ng ,*J. Fluoresc.* **22**, 1263(2012).
2. M.A.Girasolo , L.Canfora ,P.Sabatino , D.Schillaci, E.Foresti , S.Rubino , G.Ruisi , G.Stocco , *J. Inorg. Biochem.* **106** , 156 (2012).
3. Panayiotis V. Ioannou, *Monatsh Chem*, **143**, **1349** (2012).
4. Peter B. Hitchcock , Michael F. Lappert , Gang Li and Andrey V. Protchenko , *Chem. Commun.*, **4**, 428 (2009).
5. A. D'Aléo , D.Gachet , V. Heresanu , M. Giorgi , F. Fages , *Chemistry.*, **18** , 12764 (2012).
6. A. D'Aléo, F. Fages, *Photochem Photobiol Sci.*, **20**, 500 (2013).
7. L.H. Thomas, *J. Chem. Soc.*, 820 (1946).
8. A. Buraway, A. G. Salem and A. R. Thompson, *J. Chem. Soc.*, 4793(1952).
9. K. J. Morgan, *J. Chem. Soc.*, 2151(1961).
10. A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 1443(1953).
11. Nathaniel W. Alcock, Valerie M. Tracy, Thomas C. Waddington, *J. Chem. Soc. (Dalton)*, **21**, 2243(1976).
12. P. N. Gates and E. F. Mooney, *J. Inorg. Nucl. Chem.*, **30**, 839 (1968).
13. N. B. Colthup, L. H. Daly and S. F. Wiberby, *Introduction to infrared and Raman Spectroscopy*, 2nd Ed., Academic Press, London p.335 (1975) .
14. R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Wiley, New York (1981).
15. H. Noeth, B. Wrack Meyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Springer-Verlag, Berlin (1978).

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