Asian Journal of Chemistry Vol. 6, No. 2 (1994), 313–322

Boron(III), Aluminium(III) and Arsenic(III) Derivatives of 1-Hydroxy-2-Naphthoic and 3-Hydroxy-2-Napththoic Acids

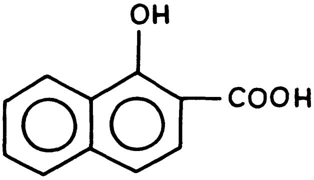
YASHMANI GUPTA, TRIPTI GANGWAR and MADHUP CHANDRA*
Department of Chemistry
DSB Campus, Kumaun University
Nainital 263 002, India

Several elemento(III) derivatives of 1-hydroxy-2-naphthoic and 3-hydroxy-2-naphthoic acids have been prepared by the interaction of boron-, aluminium- or arsenic triisopropoxide with the latter in various stoichiometric ratios *viz.* 1 : 1, 1 : 2 and 1 : 3 involving alcoholysis reactions in benzene/toluene medium. The compounds thus prepared were obtained generally as coloured solids, with some of them being hygroscopic. All these compounds have been characterized by azeotrope and elemental analyses, as well as by IR and PMR spectral measurements.

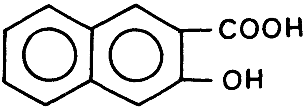
INTRODUCTION

Hydroxy-naphthoic acids containing hydroxy group (–OH) located adjacent to the carboxylic acid group (–COOH) provide a favourable geometry for stable metal chelate ring formation which prompted attention of the workers towards the investigation of their metal chelates both in solution[1-6] and in solid[7] states. In spite of considerable work having been reported on the chelating tendencies of hydroxy-naphthoic acids, practically no work appears to be on record towards the preparation of their metallo derivatives especially *via* the reactivity of the corresponding metal alkoxides, particularly in view of the fact that these hydroxy-naphthoic acids possess replaceable hydrogen(s).

As a consequence, the present work deals with the preparation of the various elemento(III) *viz.* boron, aluminium or arsenic derivatives of 1-hydroxy-2-napththoic acid (abbreviated as LH_2) [I] and 3-hydroxy-2-napththoic acid (abbreviated as $L(H_2)$ [II] employing alcoholysis reactions involving the interaction



(I)



(II)

of the corresponding elemento (III) isopropoxide with LH_2 or $L'H_2$ in appropriate stoichiometric ratios *viz.* 1 : 1, 1 : 2 and 1 : 3 in a suitable reaction medium *viz.* benzene/toluene. The amount of isopropanol liberated during the course of reaction was fractionated out azeotropically and estimated to monitor the completion of the reaction in each case. The compounds thus prepared were obtained as coloured solids and amongst them those containing isopropoxy group were found to be hygroscopic. These compounds were characterized by azeotrope and elemental analyses, as well as by IR and PMR (in several representative cases) spectral measurements.

EXPERIMENTAL

Stringent precautions were taken to exclude moisture throughout the experiments, using assemblies with interchangeable joints. The alcoholysis reactions were performed in a fractionating column (30 cm long) packed with Raschig rings and fitted to a total condensation variable take-off stillhead. Special weighing tubes and measuring pipettes with standard joints were used for the analytical sampling of the compounds. For filtration purposes, a specially designed G_4 sintered glass filtration funnel, fitted with a guard tube at the upper end and filled with fused calcium chloride, was used.

Benzene (BDH, AR), toluene (E. Merck AnalaR), isopropanol (BDH, Glaxo AnalaR) and solvent ether (E. Merck) were dried by standard procedures[8]. 1-Hydroxy-2-napththoic acid (E. Merck) and 3-hydroxy-2-naphthoic acid (Koch-Light) were used after recrystallization from 50% (v/v) aqueous ethanol. Boric acid (S. Merck, GR) was dried under vacuum, aluminium foil (E. Merck) was degreased and arsenic trichloride (Riedel) was purified by distillation at 223°C. Boron-, aluminium- and arsenic triisopropoxide were prepared by already reported methods[9–11].

Melting points were recorded on a digital m.pt. apparatus and are uncorrected. Boron(III) was estimated by Thomas method[12], aluminium(III) as aluminium oxinate[13], while arsenic(III) was first oxidized to arsenic(V) and then estimated iodometrically[14].

The IR spectra were recorded on a Perkin-Elmer Model 983 Spectrometer in the region 4000–400 cm^{-1}, using KBr pellets, while the PMR spectra were taken in DMSO-d_6 solution on a Varian EM 390, 90 MHz Spectrometer, using TMS as an internal standard.

Reaction between Boron Triisopropoxide and $L'H_2$; 1 : 1 Molar Ratio

A mixture of $B(OPr^i)_3$ (2.4697 g; 13.13 mmol) and $L'H_2$ (2.4708 g; 13.13 mmol) suspended in dry toluene (60 ml) taken in a R.B. flask was refluxed on a wax bath (125–130°), using a fractionating column. After *ca.* 10 h of reflux, isopropanol toluene azeotrope was fractionated out azeotropically and the amount of isopropanol liberated was estimated by an oxidimetric method[15, 16]. On completion of the reaction, the excess of solvent from the reaction mixture was removed under reduced pressure, when the product, $B(OPr^i)(L')$ isolated as a dark yellow solid. The product was purified by washing with solvent ether to remove unreacted $B(OPr^i)_3$ or $L'H_2$, if any, and finally dried *in vacuo*. The compound was found to be soluble in dimethylformamide and dimethylsulphoxide but insoluble in other common organic solvents like ethanol, benzene, toluene, carbon tetrachloride and chloroform etc.

Identical procedure was adopted for the preparation and purification of other derivatives. The relevant analytical details, characteristic IR frequencies and PMR data (in several representative cases) are summarized in Tables 1–3, respectively.

TABLE 1
ANALYTICAL DETAILS OF BORON(III), ALUMINIUM(III) AND ARSENIC(III) DERIVATIVES OF 1-HYDROXY-2-NAPHTHOIC AND 3-HYDROXY-2-NAPHTHOIC ACIDS

Sl. No.	Compound (molar ratio)	m.pt. (°C)	Azeotrope analysis Pr^iOH(g) found (calcd)	Elemental analysis		
				%C found (calcd)	%H found (calcd)	%M found (calcd)
1.	$B(OPr^i)(L)$	240 d	0.88	65.38	5.09	4.20
	(1 : 1) (white)		(0.91)	(65.67)	(5.11)	(4.22)
2.	$B(OPr^i)(LH)_2$	260 d	0.71	67.27	4.74	2.42
	(1 : 2) (Light yellow)		(0.73)	(67.59)	(4.76)	(2.43)
3.	$B(LH)_3$	260 d	2.08	68.89	3.69	1.88
	(1 : 3) (Light yellow)		(2.13)	(69.26)	(3.70)	(1.89)
4.	$Al(OPr^i)(L)$	280 d	1.07	61.54	4.79	9.87
	(1 : 2) (white)		(1.11)	(61.77)	(4.81)	(9.91)
5.	$Al(OPr^i)(LH)_2$	260 d	1.11	64.96	4.58	5.83
	(1 : 2) (Light brown)		(1.15)	(65.22)	(4.60)	(5.86)
6.	$Al(LH)_3$	>300	1.35	67.06	3.59	4.57
	(1 : 3) (Brown)		(1.39)	(67.35)	(3.60)	(4.59)
7.	$As(OPr^i)(L)$	190	1.06	52.27	4.07	23.50
	(1 : 1) (white)		(1.09)	(52.52)	(4.09)	(23.40)
8.	$As(OPr^i)(LH)_2$	205	0.49	58.81	4.14	14.66
	(1 : 2) (white)		(0.51)	(59.07)	(4.16)	(14.74)
9.	$B(OPr^i)(L')$	>300	1.53	65.37	5.09	4.21
	(1 : 1) (Dark yellow)		(1.57)	(65.67)	(5.11)	(4.22)
10.	$B(OPr^i)(L'H)_2$	>300	0.98	67.25	4.74	2.42
	(1 : 2) (Dark yellow)		(1.02)	(67.59)	(4.76)	(2.43)
11.	$B(L'H)_3$	>300	1.13	68.85	3.69	1.88
	(1 : 3) (Dark yellow)		(1.17)	(69.26)	(3.70)	(1.89)
12.	$Al(OPr^i)(L')$	>300	0.69	61.54	4.83	9.79
	(1 : 2) (Yellow)		(0.72)	(61.77)	(4.81)	(9.91)
13.	$Al(OPr^i)(L'H)_2$	>300	0.87	64.96	4.59	5.84
	(1 : 2) (Yellow)		(0.89)	(65.22)	(4.60)	(5.86)
14.	$Al(L'H)_3$	>300	0.80	66.99	3.59	4.57
	(1 : 3) (Yellow)		(0.82)	(67.35)	(3.60)	(4.59)
15.	$As(OPr^i)(L')$	200	0.92	52.27	4.08	23.29
	(1 : 1) (Light yellow)		(0.95)	(52.52)	(4.09)	(23.40)
16.	$As(OPr^i)(L'H)_2$	208	1.11	58.80	4.15	14.63
	(1 : 2) (Light yellow)		(1.14)	(59.07)	(4.16)	(14.74)

Abbreviations : $OPr^i = OC_3H_7$, LH_2 or $L'H_2 = C_{11}H_8O_3$ and M = B, Al or As.

TABLE 2

CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) OF 1-HYDROXY-2-NAPHTHOIC AND 3-HYDROXY-2-NAPHTHOIC ACIDS AND THEIR BORON (III), ALUMINIUM (III) AND ARSENIC (III) DERIVATIVES

S. No.	Compound	ν(OH)	ν(C–H)	ν_{as}(COO)	ν_s(COO)	Δν(COO)	C–H bending of *gem* dimethyl structure of the isopropoxy group	O–H bending	ν(C–O)	ν(M–O)
1.	LH_2	3200–2400(mb)*	—	1640(vsb)	1420(m)	—	—	1310(m)	1260(m)	—
2.	$L'H_2$	3300(mb)	3100–2780(mb)	1670(b)	1405(m)	—	—	1320(m)	1260(m), 1225(s)	—
3.	$B(OPr^i)(L)$	—	3050(w), 2860(w)	1630(vsb)	1430(w)	200	1360(msh)	—	1260(s), 1220(m)	1360(msh)
4.	$B(OPr^i)(LH)_2$	3350–3100(mb)	3060(m), 2940(w), 2860(w)	1620(vsb)	1430(mb)	190	1370(m)	1330(m), 1310(s)	1260(m), 1220(m)	1370(m)
5.	$B(LH)_3$	3300–3150(vb)	3070(m), 2940(w), 2850(m)	1620(vs)	1420(s)	200	—	1310(m)	1260(s)	1370(m)
6.	$Al(OPr^i)(L)$	—	3080(m), 2950(w), 2880(w)	1580(sb)	1415(m)	165	1365(m)	—	1270(s), 1230(m)	640(mb) 590(m)
7.	$Al(OPr^i)(LH)_2$	3500–3220(b)	3080–2920(b)	1610(vs)	1415(m)	195	1370(m)	1300(mb)	1270(s), 1210(m)	630(m), 585(m)
8.	$Al(LH)_3$	3500–3100(vb)	3060(m), 3000(m)	1610(mb)	1400(mb)	210	—	1340(w)	1250(mb)	620(s)
9.	$As(OPr^i)(L)$	—	3100–2700(mb)	1630(vsb)	1430(m)	200	1360(sh)	—	1255(m), 1200(s)	605(s), 570(s)

S. No.	Compound	ν(OH)	ν(C–H)	ν_{as}(COO)	ν_s(COO)	Δν(COO)	C–H bending of *gem* dimethyl structure of the isopropoxy group	O–H bending	ν(C–O)	ν(M–O)
10.	As(OPr^i)(LH)$_2$	3300–3100(b)	3000–2700(mb)	1630(vsb)	1430(m)	200	1370(m)	1310(s)	1260(mb), 1210(s)	605(s)
11.	B(OPr^i)(L′)	—	3060–2800(mb)	1640(vsb)	1440(m)	200	1350(sh)	—	1290(s) 1220(s)	1350(sh)
12.	B(OPr^i)(L′H$_2$)	3300(s)	3070(m) 2940(m) 2860(w)	1680(vs)	—	—	1360(s)	1290(s)	1220(s)	1360(s)
13.	B(L′H)$_3$	3300(s)	3060(m) 2940(m)	1690(vs)	—	—	—	1310(m)	1285(s) 1220(s)	1360(sh)
14.	Al(OPr^i)(L′)	—	3000(m) 2955(m) 2940(w)	1610(s)	1430(s)	200	1350(sh)	—	1235(m) 1200(s)	600(mb)
15.	Al(OPr^i)(L′H)$_2$	3300(s)	3040(m) 2960(m) 2840(m)	1620(s)	1440(s)	180	1385(s)	1310(s)	1280(s) 1210(m)	600(mb)
16.	Al(L′H)$_3$	3300(s)	3060(m) 3000(w) 2940(m)	1640(mb)	1450(mb)	190	—	1290(s)	1225(s)	610(m)
17.	As(OPr^i)(L′)	—	3040–2840(mb)	1630(sb)	1440(m)	190	1350(s)	—	1280(s) 1215(ssh)	580(w) 550(vw)
18.	As(OPr^i)(L′H)$_2$	3300(s)	3040–2840(mb)	1640(sb)	1440(s)	200	1360(sh)	1280(vs)	1220(s)	600(s)

Abbreviations: w = weak, m = medium, b = broad, mb = medium broad, vb = very broad, sb = strong broad, s = sharp, vs = very sharp, vsb = very sharp broad, sh = shoulder, msh = medium shoulder

*Overlapping of ν(OH) and ν(C–H)

TABLE 3
PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ VALUE) OF 1-HYDROXY-2-NAPHTHOIC AND 3-HYDROXY-2-NAPHTHOIC ACIDS AND THEIR SEVERAL BORON (III), ALUMINIUM (III) AND ARSENIC (III) DERIVATIVES

S. No.	Compound	–COOH and –OH protons (Hydrogen bonded)	Naphthyl ring protons	OH group proton	Gem dimethyl protons of the isopropoxy group
1.	LH_2	9.90–10.50(m)	8.60(d), 7.40–7.90(m)	—	—
2.	$L'H_2$	9.90–12.90(m)	8.58(s), 7.34–7.99(m)	—	—
3.	$B(OPr^i)(LH)_2$	—	7.12–8.33(m)	6.25(s)	1.00–1.25(d)
4.	$Al(OPr^i)(L)$	—	6.80–8.50(m)	—	1.10–1.30(d)
5.	$B(OPr^i)(L')$	—	6.95–8.20(m)	—	0.90–1.10(d)
6.	$Al(L'H)_3$	—	6.90–8.20(m)	6.20(s)	—
7.	$As(OPr^i)(L'H)_2$	—	7.00–8.10(m)	6.15(s)	0.80–0.85(d)

Abbreviations: s = singlet, d = double, m = multiple

RESULTS AND DISCUSSION

The reactions occurring between boron triisopropoxide and $L'H_2$ may be illustrated as under:

$$B(OPr^i)_3 + L'H_2 \rightarrow B(OPr^i)(L') + 2Pr^iOH \quad (1)$$

$$B(OPr^i)_3 + 2L'H_2 \rightarrow B(OPr^i)(L')_2 + 2Pr^iOH \quad (2)$$

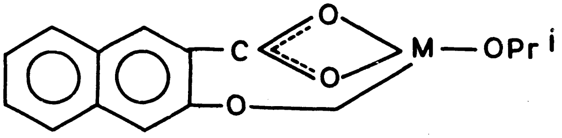
$$B(OPr^i)_3 + 3L'H_2 \rightarrow B(L'H)_3 + 3Pr^iOH \quad (3)$$

Similar reactions followed in case of other derivatives. However, 1 : 3 derivatives could not be isolated in case of arsenic even after prolonged reflux and fractionation.

Infrared Spectra

The derivative, $B(OPr^i)(L')$ displays a medium broad band in the region 3060–2800 cm^{-1} which may be assigned to ν(C–H) of the naphthyl ring and the isopropoxy group[17, 18]. The medium broad band at 3300 cm^{-1} due to ν(OH) of the hydroxy group, as noted in $L'H_2$, is found to be absent here indicating the participation of the hydroxy group in bonding with boron. A very sharp broad band at 1640 cm^{-1} occurs due to the overlapping of $\nu_{as}(COO)$ and aromatic ν(C=C). The medium bands at 1510 cm^{-1} and 1470 cm^{-1} correspond to aromatic skeletal vibrations, while a medium band at 1440 cm^{-1} may be ascribed to $\nu_s(COO)$. A shift of 35 cm^{-1} in $\nu_s(COO)$, as compared to $L'H_2$, indicates the bonding of the carboxylate oxygen with boron[19]. Further, the separation value, $\Delta\nu(COO)$ $(\nu_{as}(COO)-\nu_s(COO))$ of 200 cm^{-1} suggests the presence of a bridged or coordinated carboxylate group[20–22]. A medium band occurring at 1350 cm^{-1} with a shoulder may be assigned to the overlapping of ν(B–O) and C–H bending of the *gem* dimethyl structure of the isopropoxy group[23, 24]. The strong bands at

1290 and 1220 cm^{-1} occur due to ν(C–O) of the hydroxy group, while another at 1150 may be ascribed to ν(C–O) of the isopropoxy group. The medium bands at 1080 cm^{-1} and 1020 cm^{-1} show the aromatic C–H in-plane bending, while those at 910 cm^{-1}, 880 cm^{-1}, 850 cm^{-1}, 840 cm^{-1} and 800 cm^{-1} correspond to the aromatic C–H out-of-plane bending. The absorptions below 700 cm^{-1} occur because of the skeletal vibrations. It is thus evident that the boron atom in B(OPr^i)(L′) [III] exhibits tetra-coordination as a result of bonding with both the oxygens from the carboxylate group, as well as the oxygen from the hydroxy group, along with an isopropoxy group.



Where M= B, Al or As

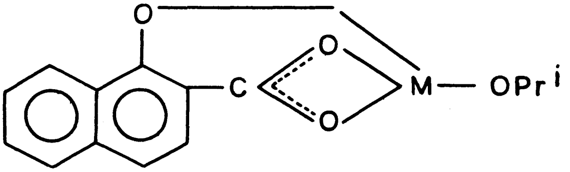
(III)

Proton Magnetic Resonance Spectra

The appearance of a multiplet between δ 6.95–8.20 in B(OPr^i)(L′) shows the presence of the naphthyl ring protons[18, 25]. A doublet in the region δ 0.90–1.10 corresponds to the *gem* dimethyl protons of the isopropoxy group[21]. The signals due to the protons of the carboxylic acid and hydroxy groups as observed in $L'H_2$ between δ 9.90–12.90 disappear here and no additonal peak is observed to occur which suggests the participation of both of these groups in bonding with boron. The signal owing to the DMSO impurity occurs at δ 2.50. Thus, the conclusions drawn here are in conformity to those inferred from the IR spectral measurements earlier.

The IR and PMR (in several representative cases) data in respect of other derivatives were interpreted similarly and the main findings are as under:

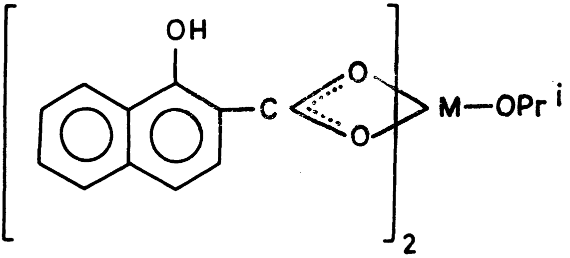
The derivatives, B(OPr^i)(L), Al(OPr^i)(L), As(OPr^i)(L) [IV] and Al(OPr^i)(L′) and As(OPr^i)(L′) [III] contain a tetra-coordinated B, Al or As atom in each case by way of similar modes of bonding as those observed in B(OPr^i)(L′).



Where M= B, Al or As

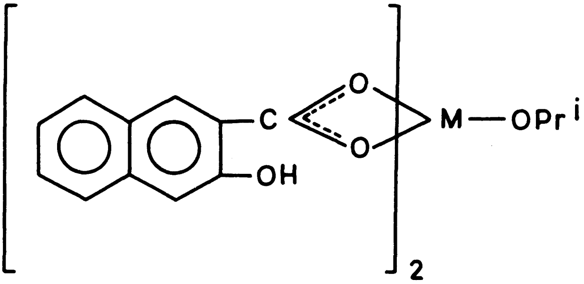
(IV)

The B, Al or As atom in $B(OPr^i)(LH)_2$, $Al(OPr^i)(LH)_2$, $As(OPr^i)(LH)_2$ [V] and $Al(OPr^i)(L'H)_2$ and $As(OPr^i)(L'H)_2$ [VI] displays penta-coordination in each case as a consequence of bonding with both the oxygens from each of the two carboxylate groups available from two moles of LH_2 or $L'H_2$, along with an isopropoxy group.



Where M = B, Al or As

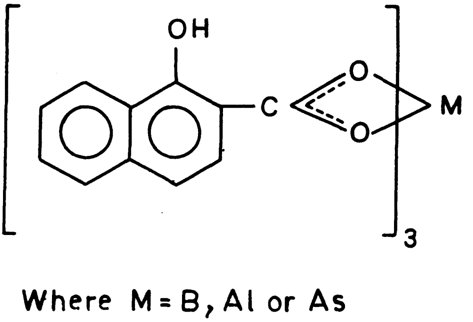
(V)



Where M = Al or As

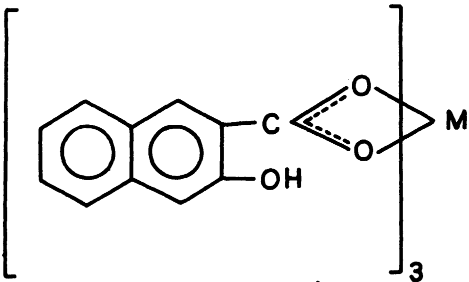
(VI)

The derivatives $B(LH)_3$, $Al(LH)_3$ [VII] and $Al(L'H)_3$ [VIII] possess a hexa-



Where M = B, Al or As

(VII)

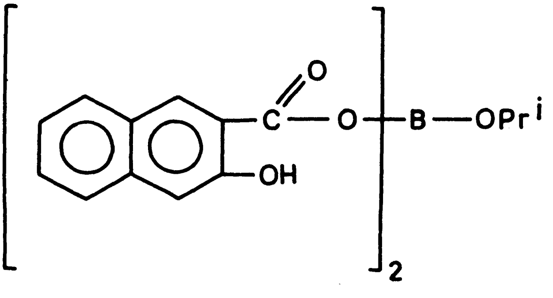


Where M = Al or As

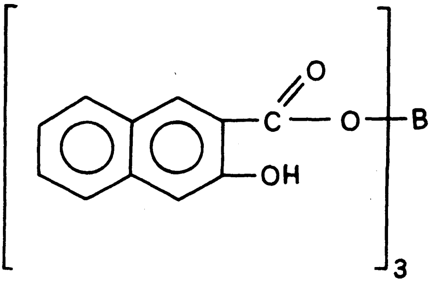
(VIII)

coordinated B or Al atom in each case as a result of bonding with both the oxygens from each of the three carboxylate groups available from three moles of LH_2 or $L'H_2$.

However, the boron atom in $B(OPr^i)(L'H)_2$ [IX] appears to be bonded with one of the oxygens from each of the two carboxylate groups available from two moles of $L'H_2$ through a normal ester type of linkage (as evidenced by a very sharp band at 1680 cm^{-1} due to $\nu(C=O)$), along with an isopropoxy group. Again, the boron atom is observed to be bonded with one of the oxygens from each of the three carboxylate groups available from three moles of $L'H_2$ through a normal ester type of linkage (as evidenced by a very strong band at 1690 cm^{-1} due to $\nu(C=O)$ in case of $B(L'H)_3$ [X] exhibiting trivalency in each case.



(IX)



(X)

REFERENCES

1. K. Dwivedi, M. Chandra and A.K. Dey, *Transition Metal Chem.*, **2**, 186 (1977).
2. P.K. Datta, M. Chandra, and A.K. Dey, *Transition Metal Chem.*, **5**, 1 (1980); *Indian J. Chem.*, **19A**, 380 (1980); *J. Indian Chem. Soc.*, **57**, 931 (1980).
3. D.P. Bhatt, D. Prakash and M. Chandra, *Chim. Acta Turcica*, **11**, 259 (1983); *Trans. Soc. Adv. Electrochem. Sci. Tech. (India)*, **22**, 253 (1987).
4. P.C. Pant, D.P. Bhatt and M. Chandra, *Trans. Soc. Adv. Electrochem. Sci. Tech. (India)*, **26**, 247 (1985); **21**, 181 (1986); *Chim. Acta Turcica*, **15**, 121 (1987).
5. D.P. Bhatt, P.C. Pant and M. Chandra, *Chim. Acta Turcica*, **14**, 23 (1986).
6. D.P. Bhatt, M. Chandra, R.M. Mehrotra and D. Prakash, *Trans. Soc. Adv. Electrochem. Sci. Tech. (India)*, **25**, 87 (1990).
7. Y.H. Deshpandey and V.R. Rao, *J. Inorg. Nucl. Chem.*, **35**, 3626 (1973).
8. A.I. Vogel, A Text Book of Practical Organic Chemistry, 4th Ed., Longmans, London (1978).
9. W. Gerrard, M.F. Lappart, and H.B. Silver, *J. Chem. Soc.*, 1647 (1967).
10. S.J. Teichner, *Compt. Rend.*, **237**, 810 (1953).
11. G. Kamai, *Uchenye Zapsili Kazan Grosudarst Univ.*, **10**, 43 (1955); *Refrat. Zur. Khim. Abstr. No.* 61605 (1956); *Chem. Abstr.*, **53**, 1205 (1959).
12. L.H. Thomas, *J. Chem. Soc.*, 820 (1946).
13. A.I. Vogel, Quantitative Inorganic Analysis, Longmans, London (1975).
14. C.L. Wilson and D.W. Wilson (Eds.), Comprehensive Analytical Chemistry, **IB**, Elsevier, New York (1960).
15. R.C. Mehrotra, *J. Indian Chem. Soc.* **31**, 904 (1954).
16. D. C. Bradley, F.M.A. Halim and W. Wardlaw, *J. Chem. Soc.*, 3450 (1950).
17. L.J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen, London (1962).
18. R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectroscopic Identification of Organic Compounds, John Wiley, New York (1981).
19. P.P. Sharma and R.C. Mehrotra, *J. Indian Chem. Soc.*, **44**, 74 (1967).
20. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley, New York (1978).
21. B. Ramchandran, A.K. Narula, P.N. Kapoor, P.K. Gupta and R.N. Kapoor, *Polyhedron*, **4**, 1007 (1985).
22. T.N. Srivastava and J.D. Singh, *Indian J. Chem.*, **26A**, 489 (1985).
23. H. Steinberg, Organoboron Chemistry, John Wiley, New York (1964).
24. S.M. Tripathi and J.P. Tandon, *Indian J. Chem.*, **16A**, 794 (1978).
25. Asahi Research Centre Co. Ltd., Tokyo (Ed.), Hand Book of Proton NMR Spectra and Data, Vols. 3 and 4, Academic Press, Japan (1985).

(*Received:* 28 December 1992 *Accepted:* 12 June 1993) AJC-649