Synthesis and Characterization of Mixed Ligand Homo- and Hetero-metallic Compounds of Gallium

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ABSTRACT

Four new type of heteronuclear derivatives of gallium have been synthesized by equimolar reactions of mononuclear derivatives: Ga(L)(LH) (**1a**) (LH_2 = $HOC_6H_4C(CH_3)$=$NCH_2CH(CH_3)OH$) and $Ga(L^1)(L^2)(OGOH)$ (**1c**)(L^1H = $(CH_3)_2CHCH_2N$=CHC_6H_4OH), L^2H = $HOC(CH_3)$=$CHC(CH_3)$=NCH_2CH_3, and HOGOH = $HOC(CH_3)_2CH_2CH(CH_3)OH$), with isopropoxides of aluminium and boron. All these derivatives have been characterized by elemental analysis, molecular weight measurements and spectral [IR, NMR (^1H ^{13}C, ^{11}B and ^{27}Al)] studies, and plausible structures have been suggested for them.

INTRODUCTION

The Schiff base ligands have played an important role in the development of interesting transition metal coordination chemistry /1,2/. During the past few years there have been considerable development in the chemistry of homometal complexes derived from bifunctional tetradentate (N_2O_2) Schiff bases of main group elements /3-8/. Surprisingly, heterometal complexes of main group elements containing Schiff base ligands are limited in number /7,8/. Furthermore, a survey of the literature reveals that only a few studies have been carried on the bifunctional tetradentate Schiff base complexes of gallium /7,8/. However, heteronuclear complexes of gallium based on monofuntional bidentate and bifunctional tridentate Schiff bases appear not to have been reported so far.

In view of the above, in this paper we report synthesis and spectroscopic characterization of heterobinuclear derivatives of gallium containing aluminium or boron derived from Schiff bases (Fig. 1.)

MATERIALS AND METHODS

Solvents were dried by standard methods /9/. Schiff bases /10/ were prepared by equimolar condensation of 2-hydroxyacetophenone, salicylaldehyde or acetophenone with appropriate amines/10/ in benzene under refluxing conditions using Dean stark trap to remove the liberated water.

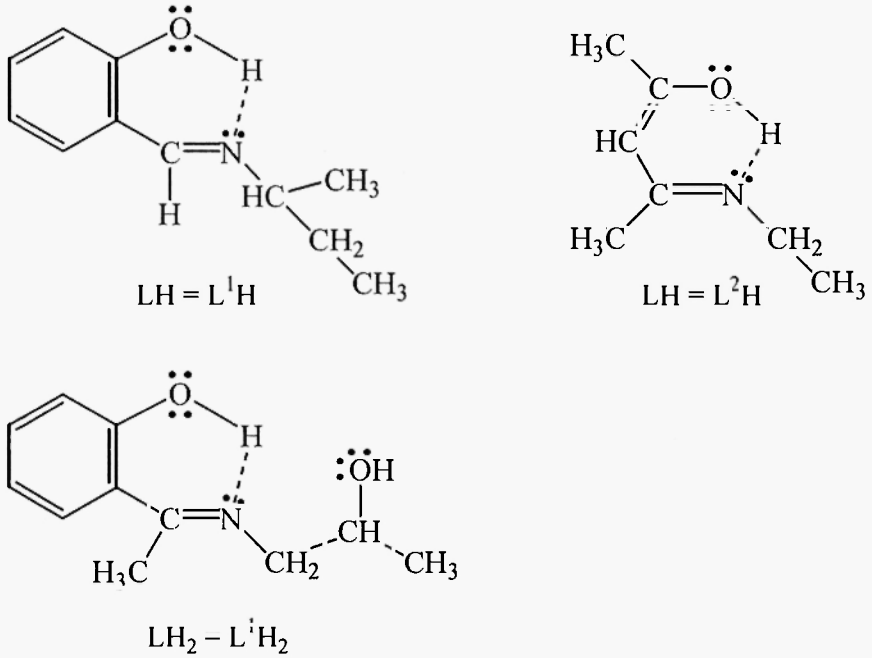


Fig. 1: Schiff base ligands

Isopropoxides of aluminum, boron and gallium were prepared by the literature methods /11/. Isopropyl alcohol in the azeotrope was determined oxidimetrically /12/ using 1N $K_2Cr_2O_7$ solution in 12.5 % H_2SO_4. Boron aluminium and gallium were determined by the methyl borate and oxinate methods /13/ respectively. Nitrogen was determined by the Kjeldahl method /13/. ^1H (300/90 MHz), ^{13}C (300 MHz), ^{27}Al (23.39 MHz) and ^{11}B (28.29 MHz) NMR spectra in $CDCl_3$ solution were recorded on a Bruker DPX 300 MHz or JEOL FX 90 Q spectrometer. IR spectra were recorded as Nujol mull on a Nicolet magna 550 spectrophometer, using KBr Optics, Molecular weights were determined ebullioscopically in benzene solutions using a Gallenkamp ebulliometer.

Preparation of homometallic gallium complexes

(a) Ga(L)(LH) (1a)

The benzene (50 cm^3) solution containing $Ga(OPr^i)_3$ (1.05 g, 4.28 mmol) and a Schiff base (L^1H_2) (1.65 g, 8.56 mmol) was refluxed for 26h, during which time the liberated isopropyl alcohol was continuously fractionated out azeotropically and determined periodically to monitor the progess and completion of the reaction. When the reaction was completed, the reaction mixture was allowed to cool to room temperature and the volatile components were removed under reduced pressure to obtain yellow solid (1.93 g, 99.4 %) , Recrystallization from 1 : 2 mixture of benzene and n-hexane at 0 °C afforded the analytically pure product in a 87 % yield.

Table 1

Analytical, and melting point data of precursor complexes

Compound	Empirical formula of the complex colour and state Yield (%)	M.P. (°C)	Pr^iOH (g) found (Calc.)	% Analysis found (Calc.)	
				Ga	N
(**1a**)	$C_{22}H_{27}N_2O_4Ga$ Light yellow solid 87	145-145.5	0.76 (0.77)	15.20 (15.38)	6.01 (6.17)
(**1b**)	$C_{21}H_{34}N_2O_3Ga$ Brownish yellow viscous liquid 85	-	0.24 (0.25)	16.02 (16.16)	6.32 (6.49)
(**1c**)	$C_{24}H_{40}N_2O_4Ga$ Brownish yellow viscous liquid 92	-	0.23 (0.23)	14.2 (14.24)	5.62 (5.72)

(b) $Ga(L^1)(L^2)(OPr^i)$ (1b)

The reaction mixture containing 1:1:1 molar amounts of $Ga(OPr^i)_3$ (0.52 g, 2.11 mmol) and the Schiff base (L^1H) (0.26 g, 2.11 mmol) and L^2H (0.37 g, 2.11 mmol) in benzene was refluxed for 20h. Isopropyl alcohol liberated during this reaction was continuously fractionated periodically and estimated (by the oxidimetric method) to monitor the progress and completion of the reaction. When the azeotrope showed the presence of a negligible amount of isopropyl alcohol, the reaction was stopped and the excess of solvents was removed under reduced pressure to afford a brown viscous compound (99.5 %). The compound was purified from a 1 : 2 mixture of benzene and n-hexane at 0 °C to give the analytically pure viscous compound in a 85 % yield.

A similar procedure was also used for the synthesis of (**1c**), which has been prepared by adding hexylene glycol (0.45 g, 3.78 mmol) in to benzene solution of (**1b**) (1.67 g, 3.89 mmol) in 1 : 1 molar ratio. The reaction mixture was refluxed for ~ 8h. Isopropyl alcohol liberated during this reaction was continuously fractionated and estimated (by the oxidimetric method).

Preparation of heteronuclear complexes (2a) and (2c)

Preparation of (2a)

The yellow coloured reaction mixture containing $B(OPr^i)_3$ (0.20 g, 1.08 mmol) and Ga(L)(LH) (0.49 g, 1.08 mmol), in benzene (50 cm^3) was refluxed for ~ 12h, during which time the liberated isopropyl alcohol was collected and determined oxidimetrically. After completion of the reaction, the volatile components from the reaction mixture were removed under reduced pressure to afford a yellow solid compound. The

compound was recrystallized from a 1 : 2 mixture of benzene and n-hexane at 0 °C to give the analytically pure compound in 89 % yield.

A procedure similar to that of (**2a**) was adopted to prepare analytically pure complex (**2b**) from appropriate reactants and their amounts actually used in are shown in square brackets :

(**2b**) : $Al(OPr^i)_3$ [0.22 g, 1.08 mmol] and Ga(L)(LH) [0.48 g, 1.07 mmol].

Table 2

Analytical, and melting point data of heteronuclear gallium complexes

Compound	Empirical formula of the complex colour and state Yield (%)	M.P. (°C)	Pr^iOH (g) found (Calc.)	% Analysis found (Calc.)		
				Ga	N	Al/B
(**2a**)	$C_{28}H_{40}N_2O_6Ga.B$ Light yellow solid 89	240-240.5	0.06 (0.06)	11.56 (11.99)	4.72 (4.81)	1.79 (1.86)
(**2b**)	$C_{28}H_{40}N_2O_6Ga.Al$ Light yellow solid 93	230-230.5	0.06 (0.06)	11.48 (11.67)	4.56 (4.68)	4.39 (4.51)
(**2c**)	$C_{30}H_{54}N_2O_6Ga.B$ Brownish yellow viscous liquid 98.6	-	0.10 (0.11)	11.16 (11.25)	4.28 (4.52)	1.68 (1.74)
(**2d**)	$C_{30}H_{54}N_2O_6Ga.Al$ Brownish yellow solid 95	280-280.5	0.14 (0.14)	10.89 (10.97)	4.36 (4.4)	4.19 (4.24)

Preparation of (2c)

$B(OPr^i)_3$ (0.33 g, 1.77 mmol) was added to a benzene solution (~ 40 ml) of $Ga(L^1)(L^2)(OGOH)$ (0.86 g, 1.76 mmol) and refluxed on a fractionating column for ~ 4h. The isopropyl alcohol formed in the reaction was fractionated out azeotropically with benzene. Progress as well as the completion of the reaction was checked by the estimation of the isopropanol in the azeotrope by oxidimetry /12/. After stripping off the solvents under reduced pressure, a brown-viscous compound was obtained in a quantitative yield 0.71 g, (98.6 %) which was purified from a mixture of benzene and n-hexane at 0 °C.

A procedure similar to that of (**2c**) was adopted to prepare following analytically pure complexes from appropriate reactant and their amounts actually used in square brackets:

(**2d**) $Al(OPr^i)_3$ [0.48 g, 2.35 mmol] and $Ga(L^1)(L^2)(OGOH)$ [1.15g, 2.34 mmol]

RESULTS AND DISCUSSION

Reaction of $Ga(OPr^i)_3$ in 1 : 2 molar ratio with $HOCH(CH_3)CH_2N{=}C(CH_3)C_6H_4OH$ (LH_2) in benzene solution yields homoleptic homonuclear gallium derivative

$$Ga(OPr^i)_3 + 2\ LH_2 \xrightarrow[\text{Reflux}]{\text{Benzene}} \underset{\textbf{(1a)}}{Ga(L)(LH)} + 3\ Pr^iOH \qquad (1)$$

Reaction of $Ga(OPr^i)_3$ with $CH(CH_3)_2CH_2N{=}CHC_6H_4OH$ (L^1H) and $HOC(CH_3){=}CHC(CH_3){=}NCH_2CH_3$($L^2H$) in 1 : 1 : 1 molar ratio in benzene solution affords heteroleptic homonuclear complex

$$Ga(OPr^i)_3 + L^1H + L^2H \xrightarrow[\text{Reflux}]{\text{Benzene}} \underset{\textbf{(1b)}}{Ga(L^1)(L^2)(OPr^i)} + Pr^iOH \qquad (2)$$

Reaction of **(1b)** in 1 : 1 molar ratio with hexylene glycol in benzene solution yields precursor gallium derivative (equation 3)

$$Ga(L^1)(L^2)(OPr^i) + HOGOH \xrightarrow[\text{Reflux}]{\text{Benzene}} \underset{\textbf{(1c)}}{Ga(L^1)(L^2)(OGOH)} + Pr^iOH \qquad (3)$$

(where HOGOH = $HOC(CH_3)_2CH_2(CH_3)CHOH$)

Complexes **(1a)** and **(1c)** on reaction with $B(OPr^i)_3$ or $Al(OPr^i)_3$ afford novel heteronuclear derivatives:

$$\textbf{(1a)} + M(OPr^i)_n \xrightarrow[\text{Reflux}]{\text{Benzene}} Ga(L)_2M(OPr^i)_{n-1} + Pr^iOH \qquad (4)$$

(2a) : M = B and n = 3; **(2b)** : M = Al and n = 3 .

$$\textbf{(1c)} + M(OPr^i)_n \xrightarrow[\text{Reflux}]{\text{Benzene}} Ga(L^1)(L^2)(OGO)M(OPr^i)_{n-1} + Pr^iOH \qquad (5)$$

(2c) : M = B and n = 3 ; **(2d)** : M = Al and n = 3.

The new heteronuclear derivatives **(2a)**-**(2d)** (Table 2) are less moisture-sensitive compared to the parent metal alkoxides. All these brown viscous, monomeric compounds are soluble in common organic solvents (such as benzene and chloroform).

Spectroscopic studies

Infrared spectra

Broad absorption bands due to νOH vibrational mode in the homometallic derivatives (**1a**) and (**1c**), which contain one hydroxy group in the range 3200-3400 cm^{-1}, are found to be absent in the spectra of heteronuclear derivatives (**2a**)–(**2d**). The spectrum of homometallic derivative (**1a**) exhibits two absorptions at 1630.3 and 1638 cm^{-1} due to νC=N mode. The presence of these two bands is due to the presence of coordinated and free ligand. However, two absorbtion bands observed at 1633 and 1649 cm^{-1} in derivatives (**1b**)-(**1C**) may be due to the presence of two different ligands. The azomethine group nitrogen on coordination shows a shift (~ 8 cm^{-1}) to lower frequency. The C-O (phenolate) stretching frequency for (**2a**)–(**2d**) appears at 1235 cm^{-1}, showing higher frequency shift of ~10 cm^{-1} with respect to that observed in the corresponding precursor derivatives. The appearance of new weak bands in the regions ~ 600-680 cm^{-1} and 433-466 cm^{-1} in the spectra of (**1a**)-(**1c**) may be attributed to νGa-O and νGa←N modes respectively. In heteronuclear derivatives (**2a**)–(**2d**) additional bands observed at 650-700 and 1288 cm^{-1} are assigned to νAl-O and νB-O respectively.

^{1}H NMR spectra

The ^{1}H NMR spectra (Table 3) of (**1a**) and (**1c**) exhibit a broad signal for the residual hydroxy group in the region δ 4.02-4.33 ppm. The broadening of this signal may be due to the involvement of this group in hydrogen bonding. Singlet for hydroxyl group in compound (**1c**) appears at δ 4.91 ppm. The spectrum of (**1a**) shows two sets of signals for alkylene protons of the $NCH_2CH(CH_3)O$ group, which is interpretable in terms of the presence of both coordinated and uncoordinated oxygen of the alcoholic OH groups (Fig. 2). The spectra of heteronuclear derivatives (**2a**) and (**2b**) also exhibit two sets of signals for alkylene group protons which support the bonding of the group $CH_2CH(CH_3)O$ to two different metals (Fig. 3).

The spectrum of compound (**1b**) shows two signals at δ 1.77, 2.02 ppm for non-equivalent methyl protons, whereas methine protons appear as a broad signal centered at 5.07 ppm. The signals of isopropyl group in (**1b**) appear as a septet at 2.85-3.61 and a doublet at 1.01-1.20 ppm, due to methine and gem-dimethyl proton respectively. Various alkylene protons of amino group in the derivative (**1b**) appear in the range δ 0.66-3.61 ppm with expected multiplicity (Table 3). The signals due to glycolate moiety also appear in the range δ 1.64-4.15 ppm with expected multiplicity. Heteronuclear derivatives (**2a**), (**2b**), (**2c**) and (**2d**) exhibit signals for isopropoxy group at δ 3.93-4.37 ppm as a septet and a doublet at δ 0.71-1.02 ppm, due to methine and gem-dimethyl protons. The alkylene protons of amino group in heteronuclear derivatives (**2c** and **2d**) are observed at δ 0.79-4.97 ppm. The observed singlet for azeomethine proton in (**2c**) and (**2d**) in the region 8.21, 8.24 exhibits a small 0.13 ppm downfield shift compared to those observed in the homounclear analogues (**1b** and **1c**). The aromatic ring protons appear as multiplets in the region δ 6.49–7.65 ppm.

^{13}C NMR spectra

The ^{13}C NMR spectrum (**1a**) exhibits two sets of signals for each of the C-O (174.57, 172.64) and CH=N (165.34, 167.00) groups, which is consistent with the presence of axial and equatorial Ga-O and Ga-N bonds

Table 3.

NMR (^{1}H, ^{11}B, ^{27}Al) data for homo- and hetero-nuclear derivatives of gallium.

Compound	^{1}H	^{11}B	^{27}Al
Ga(L)(LH) (**1a**)	0.71-0.79*, 1.06-1.18 (d, CH_3-CH); 1.25*, 1.33 (s, CH_3C=N); 2.04-2.23* (d, CH-CH_2); 2.35-2.50 (d, CH-CH_2); 3.42-3.68 (sextet, CH_3-CH-CH_2); 4.02-4.33 (s, CH_3CH-OH); 6.49-7.65 (m, $2C_6H_4$)	-	-
$Ga(L^1)(L^2)(OPr^i)$ (**1b**)	0.66-0.95 (t, CH_3-CH_2CH, CH_3CH_2N); 1.01-1.20 (d, $CH(CH_3)_2$); 1.25-1.36 (d, CH_3-CHN); 1.77-2.02 (s, H_3C-C=N, CH_3-C-O) 2.18-2.40 (Quintet $CH(CH_2)$ CH_3, q NCH_2CH_3); 2.85-3.61 (Sextet $CH(CH_3)CH_2$, Septet $CH(CH_3)_2$); 5.07 (s, CH=$C(CH_3)$); 6.46-7.41 (m, C_6H_4), 8.08 (s, C=N)	-	-
$Ga(L^1)(L^2)$OGOH (**1c**)	0.79-1.04 (t, CH_3-CH_2CH, CH_3-CH_2-N); 1.07-1.36 (s, CH_3-C=N, CH_3C=CH, $C(CH_3)_2$); 1.42-1.55 (d, CH_3-CH-N); 1.64-1.77 (d, CH_3 CH-O); 1.83-2.02 (q NCH_2CH_3, quentet $CHCH_2CH_3$, d $CH_2CH(CH_3)$); 2.91-3.39 (sextet, $OCH(CH_3)CH_2$, $NCH(CH_3)CH_2$ 4.91 (s, CH-OH); 5.42 (s, CH=$C(CH_3)$); 6.78-7.41 (m, C_6H_4); 8.14 (s, CH=N)	-	-
$Ga(L)_2B(OPr^i)_2$ (**2a**)	0.71-1.02 (d, $CH(CH_3)_2$); 1.03*, 1.39 (d, CH_3-CH); 2.14*, 2.29 (s, CH_3-C=N); 2.36-2.93* (d, CH_2-$CH(CH_3)$); 3.11-4.26 (sextet $CH(CH_3)CH_2$, septet $CH(CH_3)_2$); 6.49-7.65 (m, 2 C_6H_4)	3.39	
$Ga(L)_2Al(OPr^i)_2$ (**2b**)	1.11-1.26 (d, $CH(CH_3)_2$); 2.09*, 2.43 (s, CH_3C=N); 2.28*, 2.56 (d, CH_3-CH); 3.40-3.60 (d, CH_2-CH); 3.9-4.1 (septet, $CH(CH_3)_2$); 4.12-4.24 (sextet, $CH(CH_3)CH_2$); 6.69-7.68 (m, $2C_6H_4$)	-	44
$Ga(L^1)(L^2)$OGOB$(OPr^i)_2$ (**2c**)	0.79-1.01 (t, CH_3-CH_2-CH, CH_3-CH_2-N); 1.07-1.39 (s, CH_3-C=N, CH_3-C-O, $C(CH_3)_2$); 1.52-1.68 (d, CH_3-CH-N, CH_3-CH-O, $CH_2CH(CH_3)$); 1.74-1.83 (d, $CH(CH_3)_2$); 1.90-2.21 (q NCH_2-CH_3, quintet $CHCH_2CH_3$); 2.97-3.48 (sextet $OCH(CH_3)CH_2$, $NCH(CH_3)CH_2$)); 3.96-4.43 (septet, $CH(CH_3)_2$); 4.97 (s, CH=$C(CH_3)$); 6.65-7.51 (m, C_6H_4); 8.21 (s, HC=N)	3.89	-
$Ga(L^1)(L^2)$OGOAl$(OPr^i)_2$ (**2d**)	0.72-1.01 (t, CH_3CH_2CH, CH_3-CH_2-N); 1.07-1.39 (s, CH_3-C=N, CH_3-CO, $C(CH_3)_2$); 1.87-2.09 (d, CH_3-CH-N, CH_3-CH-CH_2, $CH_2CH(CH_3)$, $CH(CH_3)_2$); 2.25-2.50 (q NCH_2CH_3, quintet $CHCH_2CH_3$) 3.13-3.51 (sextet $OCH(CH_3)CH_2$, $NCH(CH_3)CH_2$) 3.93-4.37 (septet, $CH(CH_3)_2$), 5.04 (s, CH=$C(CH_3)$); 6.59-7.67 (m, C_6H_4); 8.24 (s, HC=N)	-	46

• Uncoordinated or attached to different metal atoms. S = singlet, d = doublet, m = multiplet, t = triplet, q = quartet.

(Fig. 2). The presence of two sets of signals for alkylene carbons is more likely due to the presence of both a coordinated (through oxygen) and uncoordinated $CH_2CH(CH_3)O$ group. In (**2a**) and (**2b**) again two sets signals for CH=N and C-O carbons have been observed. The appearance of two sets of signals for alkylene carbons is explainable in terms of the structure shown in Figure 3, in which the alkoxide oxygen of $CH_2CH(CH_3)O$ groups is bonded to two different metals. The signals for isopropyl group carbons appear at 66.25, (**C**HMe_2) and 24.94, (CH**M**e_2).

Table 4

^{13}C NMR data (δ, ppm) for homo and heteronuclear derivatives of gallium

Compound	C-O	CH=N	Other aromatic carbon	Chemical shift δ ppm
Ga(L)(LH) (**1a**)	174.57, 172.64	165.34 167.00	114.30-136.16	18.7 (**C**H_3-CH-OH); 19.48 (**C**H_3-CH-OGa); 21.68* 22.63 (**C**H_3-C=N); 57.11-57.41* (**C**H_2-CH(CH_3OH); 58.47 (**C**H_2-CH(CH_3)OGa); 64.28 (**C**H(CH_3)OH); 65.84 (**C**H(CH_3)OGa)
$Ga(L)_2B(OPr^i)_2$ (**2a**)	173.29 173.91	165.25 166.73	114.05-135.14	17.77 (**C**H_3CH-OGa); 18.49 (**C**H_3-CH-OB); 19.16*, 20.16 (**C**H_3-C=N); 22.04-22.34, (CH(**C**$H_3)_2$) 56.73, 57.88 (CH_3(CH)**C**H_2) 64.85 ($CH_3)_2$**C**HO)
$Ga(L)_2Al(OPr^i)_2$ (**2b**)	174.50 172.50	165.00 163.48	116.31-136.11	14.30 (**C**H_3CH-OGa); 15.89 (**C**H_3-CH-OAl); 18.2,* 21.00 (**C**H_3-C=N); 22.5-23.5, (**C**H($CH_3)_2$); 56.33, 58.92 (CH_3(CH)**C**H_2); 66.52 (($CH_3)_2$**C**HO),

*Uncoordinated or attached to different metal atoms.

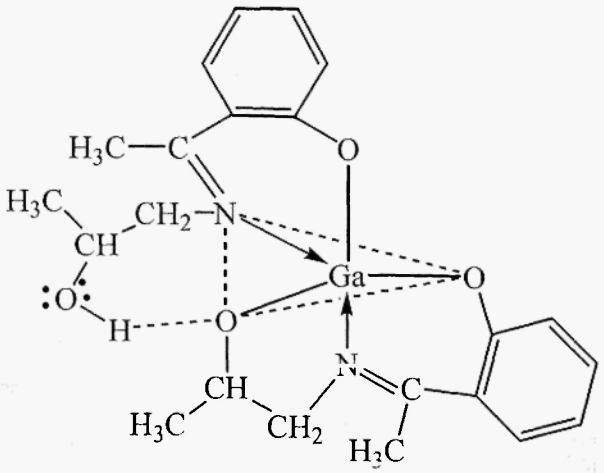


Fig. 2: Suggested structure for the homometallic derivative (**1a**)

^{27}Al NMR spectra

The heterometallic derivatives (**2b**) (Fig. 3) and (**2d**) (Fig. 5) show ^{27}Al NMR signals at δ 44 and 46 ppm respectively, which is consistent with the tetrahedral geometry for aluminum/14-17/.

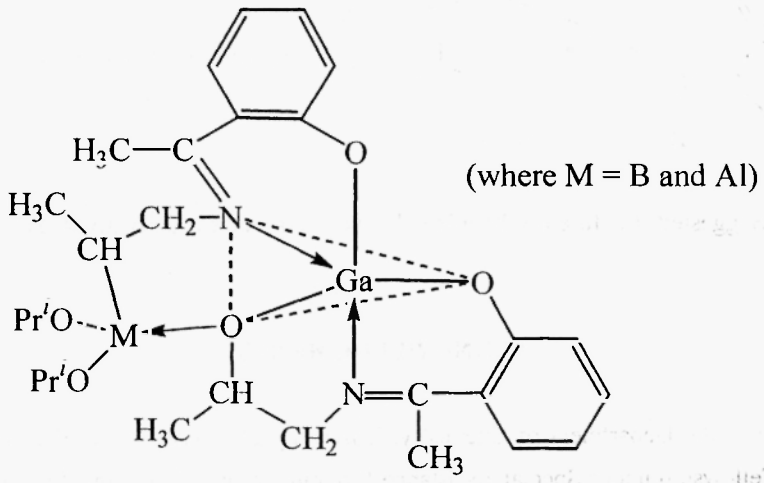


Fig. 3: Suggested structure for the heterometallic derivatives (**2a**) and (**2b**)

^{11}B NMR spectra

The appearance of sharp signals at δ 3.39 and δ 3.89 respectively for derivatives (**2a**) (Fig. 3) and (**2C**) (Fig. 5) supports the presence of tetracoordinated/18/ boron complexes.

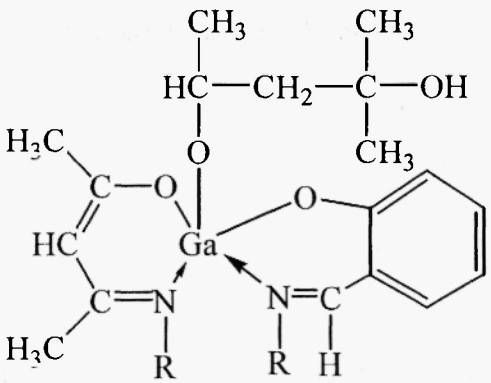
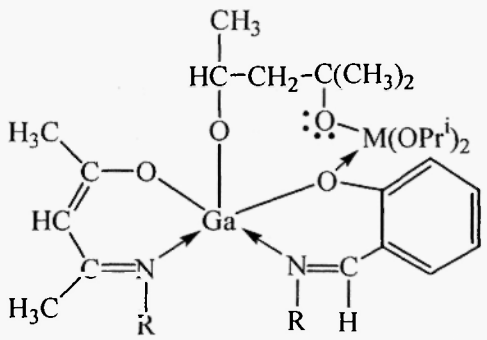


Fig. 4: Suggested structure of the mixed ligand homometallic derivative (**1c**)



(where M = B and Al)

Fig. 5: Suggested structure for the mixed ligand heteronuclear derivatives (**2c**) and (**2d**)

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