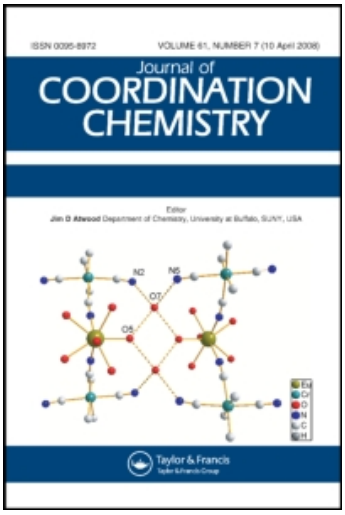

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Homo- and hetero-dinuclear derivatives of aluminium containing Schiff-base ligands: synthesis, characterization and antibacterial activity of mononuclear derivative of aluminium

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Homo- and hetero-dinuclear derivatives of aluminium containing Schiff-base ligands: synthesis, characterization and antibacterial activity of mononuclear derivative of aluminium

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Reactions of $Al(OPr^i)_3$ with $LH_2 = [R'C(NYOH)CHC(R)OH]$ R=R′=CH_3, Y = $(CH_2)_2$ (L^1H_2); R = CH_3, R′ = C_6H_5, Y = $(CH_2)_2$ (L^2H_2); R = R′ = CH_3, Y = $(CH_2)_3$ (L^3H_2); R = CH_3, R′ = C_6H_5, Y = $(CH_2)_3$ (L^4H_2), in 1 : 2 molar ratio give mononuclear derivatives of aluminium AlLLH (**1a**–**1d**). Equimolar reactions of AlLLH with $M(OPr^i)_3$ (M = Al and B) yield homo- and hetero-dinuclear derivatives $AlLLM(OPr^i)_2$ (M=Al=**2a**–**2d** M=B=**3a**–**3d**). Reaction of **2a** with L^1H_2 affords $AlL^1L^1AlL^1$ (**4**). All these derivatives have been characterized by elemental analysis, molecular weight measurements and plausible structures have been suggested on the basis of IR, NMR [^1H, ^{13}C, ^{27}Al and ^{11}B] spectral data and FAB-mass studies of **2b** and **3b**. Schiff base L^1H_2 and its mononuclear derivative with aluminium (AlL^1L^1H) have been screened for their antibacterial activity against *Escherischia coli* and *Bacillus subtilis*.

Keywords: Schiff-base ligand; Penta and tetracoordinated aluminium; Tetracoordinate boron; 11B and 27Al NMR studies

1. Introduction

Alkoxo bridged unsymmetrical homodinuclear compounds of aluminium with four- and six-coordinate aluminium has been reported in the literature [1–11]. In addition, symmetrical homodinuclear aluminium compounds containing five-coordinate aluminium have also been reported [12, 13], though the number is very small. Homodinuclear compounds of aluminium containing five- and four-coordinate aluminium are scanty [14, 15].

We report in this article the synthesis and characterization of asymmetric homodinuclear compounds of aluminium containing five- and four-coordinate Al. In addition, one-ligand bridged homodinuclear compounds of aluminium containing five-coordinate aluminium are also reported. The work is extended to synthesis and characterization of heterodinuclear compounds of aluminium with boron. The pronounced biological activity of aluminium compounds [16, 17] led us to investigate the antibacterial activity of L^1H_2 and the corresponding mononuclear derivative of

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aluminium (AlL^1L^1H) against *E. coli* and *B. subtilis*. Attempts have been made to compare the antibacterial activity of ligand with aluminium compound.

2. Experimental

All experimental operations have been carried out under moisture-free conditions. Solvents (E. Merck) were dried by literature methods [18]. AlLLH (**1a**–**1d**) were prepared by the reported method [16]. Aluminium [19] and boron [20] isopropoxides were prepared by literature methods. Ligands were synthesized by condensation of appropriate aminoalcohols and β-diketones in 1 : 1 molar ratio [21]. Aluminium was estimated by the oxinate method [22] and boron as methyl borate [22]. Isopropanol in the azeotrope and isopropoxy in the complexes were estimated by an oxidimetric method [23]. The ^1H (300 MHz), ^{13}C (75.4 MHz), ^{27}Al (23.79 MHz) and ^{11}B (96.3 MHz) NMR in $CDCl_3$ solution were recorded on a JEOL FT Al 300 spectrometer. ^1H and ^{13}C NMR spectra have been recorded using TMS as an internal reference, ^{27}Al NMR using $Al(NO_3)_3$ and ^{11}B NMR using $B(OMe)_3$ as external references. IR spectra were recorded as nujol mulls using KBr plates in the range 4000–400 cm^{-1} on an FTIR spectrophotometer model 8400 s Shimadzu. The FAB-mass spectra were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. Elemental analyses (C, H and N) were carried out on a Perkin Elmer 2400 C, H, N analyzer.

Since a similar synthetic procedure has been adopted for the preparation of all the compounds, for the sake of brevity, the synthesis of only one compound is discussed in detail and the synthetic and analytical data of other compounds have been summarized in table 1.

2.1. *Synthesis of AlL^1L^1H (1a)*

A benzene solution (50 cm^3) containing $Al(OPr^i)_3$ (3.32 gm, 1.62 mmol) and a Schiff-base ligand L^1H_2 (4.66 gm, 3.25 mmol) was refluxed on a fractionating column. The liberated isopropanol was continuously fractionated out azeotropically and determined periodically to monitor the progress as well as completion of the reaction. After completion the excess solvent was removed under reduced pressure to yield a cream-colored solid. The compound was purified by dissolving in dry benzene and then n-hexane was added until turbidity in the solution just appeared. The solution was heated to get a clear solution. The solution was stored at $-5^\circ C$ overnight and the cream compound separated out. The solvent was decanted off and the compound was dried under reduced pressure. Anal. Calcd for $C_{14}N_{23}AlN_2O_4$ (%): Al, 8.70; N, 9.03; C, 54.21; H, 7.42. Found: Al, 8.72; N, 8.99; C, 54.17; H, 7.34.

2.2. *Synthesis of $AlLLAl(OPr^i)_2$ (2a)*

A benzene solution (~50 mL) containing **1a** (1.24 gm, 4.0 mmol) and $Al(OPr^i)_3$ (0.82 gm, 4.0 mmol) was refluxed with continuous removal of Pr^iOH azeotropically with benzene until the distillate showed negligible isopropanol. After completion the excess solvent was removed under reduced pressure to yield a yellow

Table 1. Synthetic and analytical data of **2a**–**2d** and **3a**–**3d**.

	Reactants (gm mol)				Analysis % found (Calcd)						
Compound	AlLLH	$Al(OPr^i)_3$/ $B(OPr^i)_3$	Pr^iOH found (Calcd)	Empirical formula, Color, Yield (%), Melting point (°C)	Al	B	OPr^i	C	H	N	Mol. wt. found (Calcd)
2a	1.24 (4.0)	0.82 (4.0)	0.23 (0.24)	$C_{20}H_{36}Al_2N_2O_6$, yellow solid, (99.54), 92	11.12 (11.88)	–	25.11 (26.01)	52.79 (52.83)	7.84 (7.92)	5.77 (6.17)	475.1 (454.29)
2b	0.90 (2.07)	0.42 (2.07)	0.12 (0.13)	$C_{30}H_{40}Al_2N_2O_6$, cream yellow solid, (84.16), 85	8.87 (9.33)	–	6.85 (6.91)	62.27 (62.24)	6.85 (6.91)	5.21 (4.84)	580.0 (578.43)
2c	1.12 (3.30)	0.67 (3.30)	0.19 (0.20)	$C_{22}H_{40}Al_2N_2O_6$, yellowish-brown viscous liquid (99.61)	12.15 (11.19)	–	25.1 (24.5)	54.70 (54.73)	8.18 (8.29)	6.57 (5.81)	454.11 (482.36)
2d	1.14 (2.47)	0.51 (2.49)	0.14 (0.15)	$C_{32}H_{44}Al_2N_2O_6$, dark yellow solid, (96.0), 98	9.71 (8.89)	–	20.2 (19.48)	63.22 (63.31)	7.19 (7.25)	4.02 (4.62)	632.57 (606.5)
3a	1.15 (3.71)	0.70 (3.72)	0.21 (0.22)	$C_{20}H_{36}AlBN_2O_6$, yellow solid, (98.77), 88	6.38 (6.16)	2.41 (2.47)	26.81 (26.97)	54.80 (54.78)	8.15 (8.22)	6.27 (6.39)	455.58 (438.12)
3b	0.92 (2.12)	0.40 (2.12)	0.11 (0.12)	$C_{30}H_{40}AlBN_2O_6$, dark yellow, (83.65), 98	4.68 (4.80)	1.80 (1.92)	20.87 (21.02)	63.88 (64.03)	7.02 (7.11)	4.84 (4.98)	578.11 (562.26)
3c	1.11 (3.28)	0.62 (3.29)	0.18 (0.19)	$C_{22}H_{40}AlBN_2O_6$, dark yellow viscous liquid, (96.73)	5.57 (5.79)	2.45 (2.32)	25.48 (25.35)	56.70 (56.63)	8.45 (8.58)	5.94 (6.01)	438.51 (466.18)
3d	1.41 (3.04)	0.57 (3.03)	0.18 (0.18)	$C_{32}H_{44}AlBN_2O_6$, brown solid, (97.22), 95	4.48 (4.57)	2.01 (1.83)	19.18 (20.02)	64.87 (65.04)	7.38 (7.45)	4.60 (4.74)	571.18 (590.32)

solid (yield: 1.81, 99.54%). The compound was recrystallized in dichloromethane and n-hexane mixture. Anal. Calcd for $C_{20}H_{36}Al_2N_2O_6$ (%): Al, 11.88; N, 6.17; OPr^i, 26.01; C, 52.83; H, 7.92. Found: Al, 11.12; N, 5.77; OPr^i, 25.11; C, 52.79; H, 7.84.

2.3. *Synthesis of $AlL^1L^1B(OPr^i)_2$ (3a)*

A benzene solution (~50 mL) containing AlL^1L^1H (1.15 gm, 3.71 mmol) and $B(OPr^i)_3$ (0.70 gm, 3.72 mmol) was refluxed with continuous removal of Pr^iOH azeotropically until the distillate showed negligible presence of isopropanol. After completion excess solvent was removed under reduced pressure to yield a yellow solid (yield: 1.61 gm, 98.77%), which was recrystallized from dichloromethane and n-hexane mixture. Anal. Calcd for $C_{20}H_{36}AlBN_2O_6$: Al, 6.16; B, 2.41; N, 6.39; OPr^i, 26.97; C, 54.78; H, 8.22. Found: Al, 6.38; B, 2.41; N, 6.27; OPr^i, 26.81; C, 54.80; H, 8.15.

2.4. *Synthesis of $AlL^1L^1AlL^1$ (4)*

After addition of L^1H_2 (0.28 gm, 1.95 mmol) to a benzene solution (~50 mL) of **2a** (0.89 gm, 1.95 mmol), the resulting solution was refluxed under a fractionating column with continuous removal of isopropanol, which was determined periodically. After completion the excess solvent was removed under reduced pressure giving a yellow solid (yield: 0.92 gm, 97.87%). The compound was purified by recrystallization from benzene and n-hexane mixture. Anal. Calcd for $C_{21}H_{33}Al_2N_3O_6$ (%): Al, 11.30; N, 8.80; C, 59.81; H, 6.91. Found: Al, 11.03; N, 8.67; C, 52.70; H, 6.84.

2.5. *Alternate method of synthesis of $AlL^1L^1AlL^1$ (4)*

A benzene solution (~20 mL) of $Al(OPr^i)_3$ (1.06 gm, 5.19 mmol) mixed with a benzene solution (~30 mL) of a bifunctional, tridentate Schiff-base ligand L^1H_2 (1.11 gm, 7.79 mmol) was refluxed under a fractionating column. The liberated isopropanol fractionated out azeotropically in benzene. The progress of reaction was checked by estimating isopropanol in the azeotrope. The reaction was completed in ~28 h. After completion excess solvent was removed under reduced pressure and a yellow solid was obtained (yield: 1.19 gm, 96%). The compound was purified by recrystallization from benzene and n-hexane mixture. Anal. Calcd for $C_{21}H_{33}Al_2N_3O_6$ (%): Al, 11.30; N, 8.80; C, 59.81; H, 6.91. Found: Al, 11.54; N, 8.62; C, 58.47; H, 7.01.

2.6. *Antibacterial activity (paper disc method)*

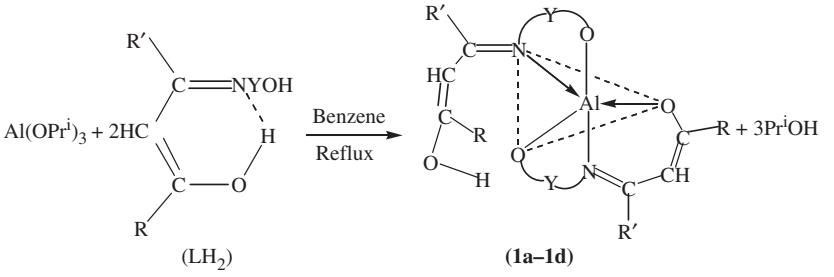
In this method sterilized nutrient agar medium and Whatman no. 1 paper disc (6 mm in diameter) were used. The agar medium was poured into petriplates and after solidification the bacterial suspension was spread uniformly on the medium. Test samples were prepared in 10 and 20% concentration by adding 0.1 and 0.2 gm compounds in 1 mL of methanol. Paper discs were dipped in this sample for half an hour and after that the discs were placed on seeded plates (Petri plate with nutrient agar and bacterial suspension spread on it). The Petri plates having these discs incubated

at a suitable temperature ($28 \pm 2^{\circ}C$) for 48–72 h, after which the inhibition zone around each disc was measured.

Table 6 shows the inhibition zones in diameter. The readings were the mean value of three replicates.

3. Results and discussion

AlLLH (**1a**–**1d**) has been synthesized by reactions of $Al(OPr^i)_3$ with LH_2 in 1 : 2 molar ratio as reported earlier [16].



(1)

$LH_2 = [R'C(NYOH)CHC(R)OH]$. $R = R' = CH_3$, $Y = (CH_2)_2(L^1H_2)$**1a**.

$R = CH_3, R' = C_6H_5, Y = (CH_2)_2(L^2H_2)$**1b**; $R = R' = CH_3$, $Y = (CH_2)_3(L^3H_2)$**1c**.

$R = CH_3, R' = C_6H_5, Y = (CH_2)_3(L^4H_2)$**1d**.

$L = L^1 =$ **1a**; $L = L^2 =$ **1b**; $L = L^3 =$ **1c**; $L = L^4 =$ **1d**.

Interaction of AlLLH (**1a**–**1d**) with $M(OPr^i)_3$ (M = B and Al) in 1 : 1 molar ratio in benzene gave homo- and hetero-dinuclear derivatives $AlLM(OPr^i)_2$.

$$\underset{(\mathbf{1a-1d})}{AlLLH} + M(OPr^i)_3 \xrightarrow[\text{reflux}]{\text{Benzene}} \underset{(\mathbf{2a-2d})\text{ and }(\mathbf{3a-3d})}{AlLLM(OPr^i)_2} + Pr^iOH \tag{2}$$

L=L^1 = **2a** and **3a**; L=L^2 = **2b** and **3b**; L=L^3 = **2c** and **3c**; L=L^4 = **2d** and **3d**.

Reaction of **2a** with L^1H_2 in 1 : 1 molar ratio gives $AlL^1L^1AlL^1$.

$$\underset{(\mathbf{2a})}{AlL^1L^1Al(OPr^i)_2} + L^1H_2 \xrightarrow[\text{reflux}]{\text{Benzene}} \underset{(\mathbf{4})}{AlL^1L^1AlL^1_2} + 2Pr^iOH \tag{3}$$

$AlL^1L^1AlL^1$ has also been prepared by reaction of $Al(OPr^i)_3$ and L^1H_2 in a 2 : 3 molar ratio in refluxing benzene.

Benzene

$$2Al(OPr^i)_3 + 3L^1H_2 \xrightarrow[\text{reflux}]{\text{Benzene}} \underset{(\mathbf{4})}{AlL^1L^1AlL^1_2} + 6Pr^iOH \tag{4}$$

All these derivatives are yellow-brown solids except **2c** and **3c** which are brown viscous liquids, soluble in common organic solvents and monomeric in freezing benzene solution.

4. Spectral studies

4.1. *IR spectra*

A broad band due to νOH in the spectra of **1a**–**1d** in the range 3200–3400 cm^{-1} is absent in the spectra of **2a**–**2d** and **3a**–**3d**, showing deprotonation of the –OH group and formation of Al–O and B–O bonds, which is supported by the appearance of new bands in the region 660–680 cm^{-1} and 1280–1295 cm^{-1} for νAl–O [8, 24] and νB–O [25], respectively.

Bands present in the region 660–680, 704–712 and 465–480 cm^{-1} in the spectra of **1a**–**1d** may be assigned to νAl–O, νAl ← O and νAl ← N [26, 27], respectively. These bands have a small shift (±10 cm^{-1}) in the spectra of **2a**–**2d**, **3a**–**3d** and **4** as compared to **1a**–**1d**. The band observed in the region 600–615 cm^{-1} in the spectra of **3a**–**3d** has been assigned to νB ← O [28].

A band at 1575–1592 cm^{-1} for νC–O of the ligand for **2a**–**2d**, **3a**–**3d** and **4** show significant shift to lower wave number as compared to its position in the spectra of **1a**–**1d** due to coordination of this group with two metal atoms.

A new band in the region 990–1020 cm^{-1} in the spectra of **2a**–**2d** and **3a**–**3d** may be attributed to νC–O of isopropoxy group, which is found to be absent in the spectra of **4**.

4.2. *^{1}H NMR spectra*

The ^{1}H NMR spectra of **1a**–**1d** show the disappearance of the –OH signal of amino alcohol present in the spectra of ligand at δ 3.77–4.34 ppm. The enolic –OH group in the spectra of **1a**–**1d** (table 2) does not shift from its position in free ligand, indicating that this group is not involved in coordination. The enolic –OH signal is absent in the spectra of **2a**–**2d** and **3a**–**3d**, indicating its deprotonation.

^{1}H NMR spectra of **2a**–**2d** and **3a**–**3d** have two sets of signals for methyl and methine protons showing two different ligand environments in these compounds. This may be explained as both –OH groups of the ligand are deprotonated in one ligand and are attached to one metal only, whereas two –OH groups of the second ligand have been deprotonated by two different metals. One set of signals appeared as a doublet ($OCH(C\mathbf{H_3})_2$) and septet ($OC\mathbf{H}(CH_3)_2$) at δ 1.10–1.38 and 3.83–4.10 ppm, respectively, in the spectra of **2a**–**2d** and **3a**–**3d** for isopropoxy, indicating the presence of one isopropoxy group. These signals are absent in the spectra of **4**.

4.3. *^{13}C NMR spectra*

The ^{13}C NMR spectra of **1a**–**1d** have two sets of signals for C–O (δ 187.45–194.79 and 187.40–194.57) suggesting two types of CO group in the ligand, i.e. C–OAl and C–OH, respectively. A very small shift in the position of these carbon signals with the introduction of another metal/metalloid atom exists in the spectra of homodinuclear and heterodinuclear complexes **2a**–**2d** and **3a**–**3d** as compared to their position in the spectra of **1a**–**1d** [16]. Two ligand environments have been confirmed by two sets of signals for **C**H=C in the spectra of **2a**–**2d** and **3a**–**3d**.

Table 2. ^{1}H, ^{13}C, ^{27}Al NMR spectra of ligands and **1a**–**1d**.

Compound	^{1}H NMR	C–O	C=N	Aromatic region	^{13}C NMR	^{27}Al
$L^{1}H_2$	3.72–3.78 (t, CH_2O), 3.39–3.44 (t, CH_2N), 4.99 (s, CHCO), 2.20 (s, CH_3CO), 2.06 (s, $CH_3C{=}N$),3.70 (s, $CH_2O\mathbf{H}$), 10.88 (s, $CH_3CO\mathbf{H}$)	193.84	163.48	–	95.09 (**C**HCO), 60.78 (CH_2O), 60.11 (CH_2N), 27.89 ($\mathbf{C}H_3CO$), 27.41 ($\mathbf{C}H_3C{=}N$)	14.19
$L^{2}H_2$	3.68–3.75 (t, CH_2O), 3.38–3.45 (t, CH_2N), 5.07 (s, CHCO), 2.04 (s, CH_3CO), 7.2–7.79 (m, C_6H_5) 4.09 (s, $CH_2O\mathbf{H}$), 11.42 (s, $CH_3CO\mathbf{H}$)	186.81	164.29	128.4–140.40	91.89 (**C**HCO), 59.11 (CH_2O), 59.01 (CH_2N), 27.94 ($\mathbf{C}H_3CO$)	14.19
$L^{3}H_2$	3.71–3.89 (t, CH_2O), 3.50 – 3.77 (m, $CH_2C\mathbf{H}_2O$) 3.21–3.35 (t, CH_2N), 5.0 (s, CHCO), 2.10 (s, CH_3CO), 2.03 (s, $CH_3C{=}N$),3.81 (s, $CH_2O\mathbf{H}$), 10.71 (s, $CH_3CO\mathbf{H}$)	194.17	163.07	–	98.71 (**C**HCO), 62.98 (CH_2O), 61.75 ($CH_2\mathbf{C}H_2O$), 61.01 (CH_2N), 30.89 ($\mathbf{C}H_3CO$), 27.91 ($\mathbf{C}H_3C{=}N$)	14.44
$L^{4}H_2$	3.50–3.69 (t, CH_2O), 3.38–3.48 (m, $CH_2C\mathbf{H}_2O$), 3.31–3.25 (t, CH_2N), 5.18 (s, CHCO), 2.09 (s, CH_3CO), 7.25–7.80 (m, C_6H_5), 4.34 (s, $CH_2O\mathbf{H}$), 11.40 (s, $CH_3CO\mathbf{H}$)	187.01	164.91	126.45–140.45	91.78 (**C**HCO), 61.45 (CH_2O), 61.25 ($CH_2\mathbf{C}H_2O$), 59.04 (CH_2N), 30.87 ($\mathbf{C}H_3CO$)	15.05
1a	3.51–3.82 (t, $2CH_2O$), 3.25–3.50 (t, $2CH_2N$), 5.06 (s, CHCO), 4.96 (s, C**H**COH), 1.97 (s, CH_3CO), 1.93 (s, $2CH_3CN$), 1.87 (s, C$\mathbf{H}_3$COH), 10.74 (s, $CH_3CO\mathbf{H}$)	194.79, 194.57	163.51, 163.49	–	95.61 (**C**HCO), 95.58 (**C**HCOH), 61.59 (CH_2O), 61.01 (CH_2N), 28.07 ($\mathbf{C}H_3CO$), 28.0 ($\mathbf{C}H_3CN$), 19.04 ($\mathbf{C}H_3COH$)	14.19
1b	3.76–3.80 (t, $2CH_2O$), 3.43–3.53 (t, $2CH_2N$), 5.69 (s, CHCO), 5.66 (s, C**H**COH), 2.08 (s, CH_3CO), 1.92 (s, C$\mathbf{H}_3$COH), 7.22–7.86 (m, $2C_6H_5$), 11.47 (s, $CH_3CO\mathbf{H}$)	187.45, 187.40	165.28, 165.26	128.4–140.40	92.26 (**C**HCO), 92.11 (**C**HCOH), 59.60 (CH_2O), 59.50 (CH_2N), 32.52 ($\mathbf{C}H_3CO$), 19.40 ($\mathbf{C}H_3COH$)	14.19
1c	3.82–4.0 (t, $2CH_2O$), 3.52–3.70 (m, $2C\mathbf{H}_2CH_2O$), 3.26–3.39 (t, $2CH_2N$), 5.05 (s, CHCO), 5.0 (s, C**H**COH), 2.14 (s, CH_3CO), 2.07 (s, $2CH_3CN$), 1.93 (s, C$\mathbf{H}_3$COH), 10.76 (s, $CH_3CO\mathbf{H}$)	194.55, 194.42	163.22, 163.15	–	100.0 (**C**HCO), 94.98 (**C**HCOH), 64.08 (CH_2O), 62.3 ($\mathbf{C}H_2CH_2O$), 59.18 (CH_2N), 29.69 ($\mathbf{C}H_3CO$), 28.75 ($\mathbf{C}H_3CN$), 18.78 ($\mathbf{C}H_3COH$)	14.44
1d	3.53–3.72 (t, $2CH_2O$), 3.42–3.51 (m, $2C\mathbf{H}_2CH_2O$), 3.36–3.40 (t, $2CH_2N$), 5.63 (s, CHCO), 5.62 (s, C**H**COH), 7.25–7.86 (m, $2C_6H_5$), 2.15 (s, CH_3CO), 1.93 (s, C$\mathbf{H}_3$COH), 11.42 (s, CH_3COH)	187.95, 187.40	165.47, 165.31	126.45–140.45	92.15 (**C**HCO), 91.98 (**C**HCOH) 62.17 (CH_2O), 61.95 ($\mathbf{C}H_2CH_2O$), 59.30 (CH_2N), 32.88 ($\mathbf{C}H_3CO$), 19.33 ($\mathbf{C}H_3COH$)	15.05

The signals for >C=N in the spectra of **2a**–**2d** and **3a**–**3d** has been assigned in the region δ 163.01–165.98 and 162.40–165.84 ppm with small shifts compared to **1a**–**1d**.

The signals for ($OCH(CH_3)_2$) and ($OCH(\mathbf{C}H_3)_2$) carbons of isopropoxy group in the spectra of homo- and hetero-dinuclear derivatives **2a**–**2d** and **3a**–**3d** have been observed in the region δ 60.12–62.06 and 24.74–29.61 ppm, respectively, and are not observed in the spectra of **4**.

4.4. *^{27}Al NMR spectra*

^{27}Al NMR spectra of these compounds have been recorded in $CDCl_3$ solution with reference to $Al(NO_3)_3$.

The ^{27}Al NMR spectra of **3a**–**3d** (table 3) have a sharp signal at δ 11.97–14.90 ppm assigned to five-coordinate aluminium [29, 30, 36, 37] and the spectra of **2a**–**2d** exhibit two signals at δ 12.94–14.19 ppm and δ 38.63–50.60 ppm, respectively, attributed to the presence of five- [29, 30, 36, 37] and four-coordinate [9, 31, 38] aluminium, respectively. In the spectra of **4** two signals are observed at δ 9.70 and 10.11 ppm suggesting two five-coordinate aluminiums [29, 30, 36, 37].

4.5. *^{11}B NMR spectra*

^{11}B NMR spectra of **3a**–**3d** (table 3) exhibit a sharp signal at δ −16.12 – (−18.54) ppm; ^{11}B signals in this region show the presence of four-coordinate boron [32–34].

4.6. *FAB-mass spectra*

FAB-mass spectra of **2b** and **3b** have been recorded showing their monomeric nature. The mass spectral fragmentation pattern of **2b** and **3b** are summarized in supplementary information.

The five-coordinate Al and four-coordinate Al (or B) and two different types of ligand environments are shown in figure 1 with one aluminium atom attached with two ligands and the aminol and azomethine group of both ligands attached to the central metal atom. Enolic CO group of one ligand is attached to only one metal after replacement of enolic –OH proton. To this metal atom two isopropoxy groups are attached as terminal groups. The fourth coordination position is occupied by aminol oxygen as indicated by the shift in position of CH_2O in ^{1}H and ^{13}C NMR spectra.

For **4** presence of five-coordinate Al and two types of ligand environment, the structure in figure 2 is proposed for these derivatives. The difference in chemical shift is due to one Al with AlO_3N_2 environment while the other Al has AlO_4N environment.

The bridging ligand is different from the remaining two ligands.

4.7. *Antibacterial activity*

Antibacterial activity of L^1H_2 and its mononuclear derivative (AlL^1L^1H) have been carried out against *E. coli* and *B. subtilis* by using the paper disc method.

Table 3. ^{1}H, ^{13}C, ^{27}Al and ^{11}B NMR spectral data for **2a**–**2d**, **3a**–**3d** and **4**.

Compound	^{1}H NMR	^{13}C NMR				^{27}Al	^{11}B
		C–O	C=N	Aromatic region	Alkylene region		
2a	3.98–4.0 (t, $2CH_2O$), 3.26–3.38 (t, $2CH_2N$), 5.07 (s, CHCO), 4.96 (s, CHCOAl), 1.96 (s, CH_3CO), 1.94 (s, $2CH_3C{=}N$), 1.90 (s, CH_3COAl), 4.02–4.06 (septet, $2OC\mathbf{H}(CH_3)_2$), 1.13–1.27 (d, 2OCH $(C\mathbf{H}_3)_2$)	173.75, 171.44	163.01, 162.40	–	99.79 (**C**HCO), 95.12 (**C**HCOAl), 62.26 (CH_2O), 61.76 (CH_2N), 60.12 ($O\mathbf{C}H(CH_3)_2$), 27.64 ($\mathbf{C}H_3CO$), 25.07 ($\mathbf{C}H_3C{=}N$), 24.98 ($OCH(\mathbf{C}H_3)_2$), 21.14 ($\mathbf{C}H_3COAl$)	12.94, 38.63	–
2b	3.76–3.78 (t, $2CH_2O$), 3.27–3.45 (t, $2CH_2N$), 5.66 (s, CHCO), 5.49 (s, CHCOAl), 2.01 (s, CH_3CO), 1.92 (s, CH_3COAl), 3.99–4.03 (septet, $2OC\mathbf{H}(CH_3)_2$), 1.18–1.20 (d, $2OCH(C\mathbf{H}_3)_2$), 7.27–7.91 (m, $2C_6H_5$)	193.97, 193.84	163.37, 163.18	128.11–130.57	95.61 (**C**HCO), 95.54 (**C**HCOAl), 62.81 (CH_2O), 62.41 (CH_2N), 29.47 ($\mathbf{C}H_3CO$), 61.11 ($O\mathbf{C}H(CH_3)_2$), 26.14 ($OCH(\mathbf{C}H_3)_2$), 25.79 ($\mathbf{C}H_3COAl$)	14.19, 41.87	–
2c	3.87–3.93 (t, $2CH_2O$), 3.51–3.58 (m, $2C\mathbf{H}_2CH_2O$), 3.46–3.49 (t, $2CH_2N$), 5.01 (s, CHCO), 4.97 (s, CHCOAl), 2.17 (s, CH_3CO), 2.10 (s, $2CH_3C{=}N$), 1.95 (s, CH_3OAl), 3.94–4.10 (septet, $2OC\mathbf{H}(CH_3)_2$), 1.10–1.25 (d, $2OCH(C\mathbf{H}_3)_2$)	195.45, 195.26	164.23, 163.77	–	96.36 (**C**HCO), 96.16 (**C**HCOAl), 67.01 (CH_2O), 62.69 ($\mathbf{C}H_2CH_2O$), 62.51 (CH_2N), 61.65 ($O\mathbf{C}H(CH_3)_2$), 29.46 ($\mathbf{C}H_3CO$), 29.35 ($\mathbf{C}H_3C{=}N$), 26.23 ($OCH(\mathbf{C}H_3)_2$), 26.00 ($\mathbf{C}H_3COAl$)	12.94, 50.60	–
2d	3.81–3.99 (t, $2CH_2O$), 3.45–3.51 (m, $2C\mathbf{H}_2CH_2O$), 3.37–3.41 (t, $2CH_2N$), 5.79 (s, CHCO), 5.68 (s, CHCOAl), 2.16 (s, CH_3CO), 2.04 (s, CH_3COAl), 7.19–7.93 (m, $2C_6H_5$), 4.01–4.03 (septet, $2OC\mathbf{H}(CH_3)_2$), 1.13–1.31 (d, $2OCH(C\mathbf{H}_3)_2$)	187.86, 187.76	165.98, 165.84	127.33–130.88	92.49 (**C**HCO), 92.31 (**C**HCOAl), 67.01 ($\mathbf{C}H_2O$), 62.69 ($\mathbf{C}H_2CH_2O$), 62.04 (CH_2N), 61.65 ($O\mathbf{C}H(CH_3)_2$, 29.46, ($\mathbf{C}H_3CO$), 26.32 ($OCH(\mathbf{C}H_3)_2$), 26.23 ($\mathbf{C}H_3COAl$)	14.19, 39.13	–

(*Continued*)

Table 3. Continued.

Compound	^{1}H NMR	^{13}C NMR				^{27}Al	^{11}B
		C–O	C=N	Aromatic region	Alkylene region		
3a	3.55–3.81 (t, 2C**H**$_2$O), 3.32–3.39 (t, 2C**H**$_2$N), 5.34 (s, C**H**CO), 4.97 (s, C**H**COB), 2.14 (s, C**H**$_3$CO), 2.06 (s, 2C**H**$_3$C=N), 1.97 (s, C**H**$_3$COB), 3.81–3.86 (septet, 2OC**H**(CH$_3$)$_2$), 1.11–1.22 (d, OCH(C**H**$_3$)$_2$)	194.99, 194.09	163.58, 162.79	–	95.71 (**C**HCO), 95.26 (**C**HCOB), 65.26 (CH$_2$O), 64.31 (CH$_2$N), 61.69 (O**C**H(CH$_3$)$_2$), 28.78 (**C**H$_3$CO), 25.35 (**C**H$_3$C=N), 24.74 (OCH(**C**H$_3$)$_2$), 21.82 (**C**H$_3$COB)	13.19	−18.54
3b	3.74–3.91 (t, 2C**H**$_2$O), 3.29–3.47 (t, 2C**H**$_2$N), 5.71 (s, C**H**CO), 5.69 (s, C**H**COB), 2.08 (s, C**H**$_3$CO), 1.88 (s, C**H**$_3$COB), 4.02–4.04 (septet, 2OC**H**(CH$_3$)$_2$), 1.19–1.21 (d, 2OCH(C**H**$_3$)$_2$, 7.27–7.90 (m, 2C$_6$H$_5$)	189.11, 188.75	165.21, 164.08	126.34–140.61	98.31 (**C**HCO), 95.61 (**C**HCOB), 64.33 (CH$_2$O), 63.67 (CH$_2$N), 61.35 (O**C**H(CH$_3$)$_2$), 32.42 (**C**H$_3$CO), 29.61 (OCH(**C**H$_3$)$_2$), 24.99 (**C**H$_3$COB)	11.97	−16.21
3c	3.70–3.98 (t, 2C**H**$_2$CH$_2$O), 3.52–3.68 (m, 2 **C**H$_2$CH$_2$O), 3.33–3.39 (t, 2C**H**$_2$N), 5.05 (s, C**H**CO), 4.99 (s, C**H**COB), 2.07 (s, C**H**$_3$CO), 2.03 (s, 2C**H**$_3$C=N), 1.98 (s, C**H**$_3$COB), 4.0–4.02 (septet, 2OC**H**(CH$_3$)$_2$), 1.15–1.38 (d, 2OCH(C**H**$_3$)$_2$)	194.43, 193.09	164.71, 163.87	–	97.68 (**C**HCO), 97.31 (**C**HCOB), 66.13 (CH$_2$O), 64.66 (**C**H$_2$CH$_2$O), 62.66 (CH$_2$N), 62.06 (O**C**H(CH$_3$)$_2$), 27.66 (**C**H$_3$CO), 27.19 (**C**H$_3$C=N), 25.18 (OCH(**C**H$_3$)$_2$), 23.91 (**C**H$_3$COB)	14.90	−15.74
3d	3.75–3.99 (t, 2C**H**$_2$CH$_2$O), 3.61–3.69 (m, 2C**H**$_2$CH$_2$O), 3.45–3.51 (t, 2C**H**$_2$N), 5.76 (s, C**H**CO), 5.68 (s, C**H**COB), 2.08 (s, C**H**$_3$CO), 1.98 (s, C**H**$_3$COB), 4.01–4.03 (septet, 2OC**H**(CH$_3$)$_2$), 1.14–1.21(d, 2OCH(C**H**$_3$)$_2$), 7.24–7.93(m, 2C$_6$H$_5$)	192.89, 192.57	165.21, 165.08	126.36–130.36	92.03(**C**HCO), 91.70 (**C**HCOB), 64.34 (CH$_2$O), 64.12 (**C**H$_2$CH$_2$O), 63.79 (CH$_2$N), 61.44 (O**C**H(CH$_3$)$_2$), 28.69 (**C**H$_3$CO), 24.81 (**C**H$_3$COB), 25.70 (OCH(**C**H$_3$)$_2$)	12.71	−15.50
4	3.74–3.75 (t, 3C**H**$_2$O), 3.40–3.42 (t, 3C**H**$_2$N), 5.0 (C**H**CO), 4.77 (C**H**COAl), 2.0 (s, 3C**H**$_3$CO), 1.96–2.0 (s, 3C**H**$_3$CO), 1.91–1.94 (s, 3C**H**$_3$CN)	194.85	164.06	–	99.03 (**C**HCO), 97.93 (**C**HCO), 95.62 (**C**HCO), 61.54 (CH$_2$O), 58.80 (CH$_2$N), 28.70 (**C**H$_3$CO), 26.25 (**C**H$_3$C=N)	10.11, 9.70	–

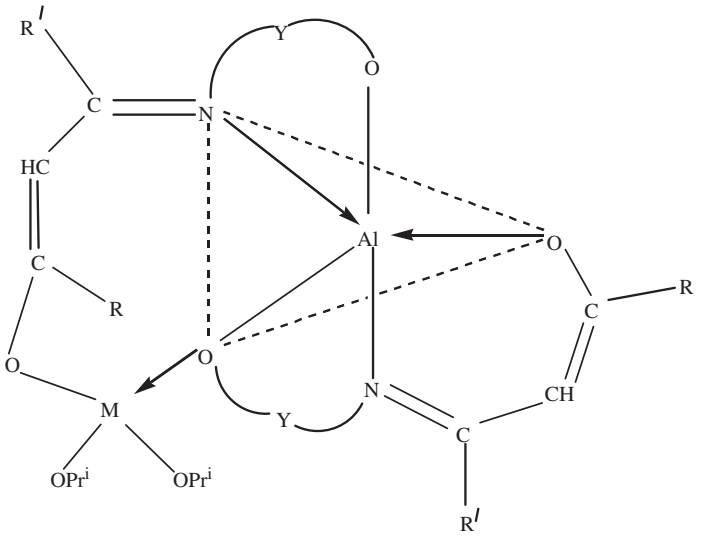


Figure 1. Proposed structure for **2a**–**2d** and **3a**–**3d** M = Al (**2a**–**2d**), B (**3a**–**3d**).

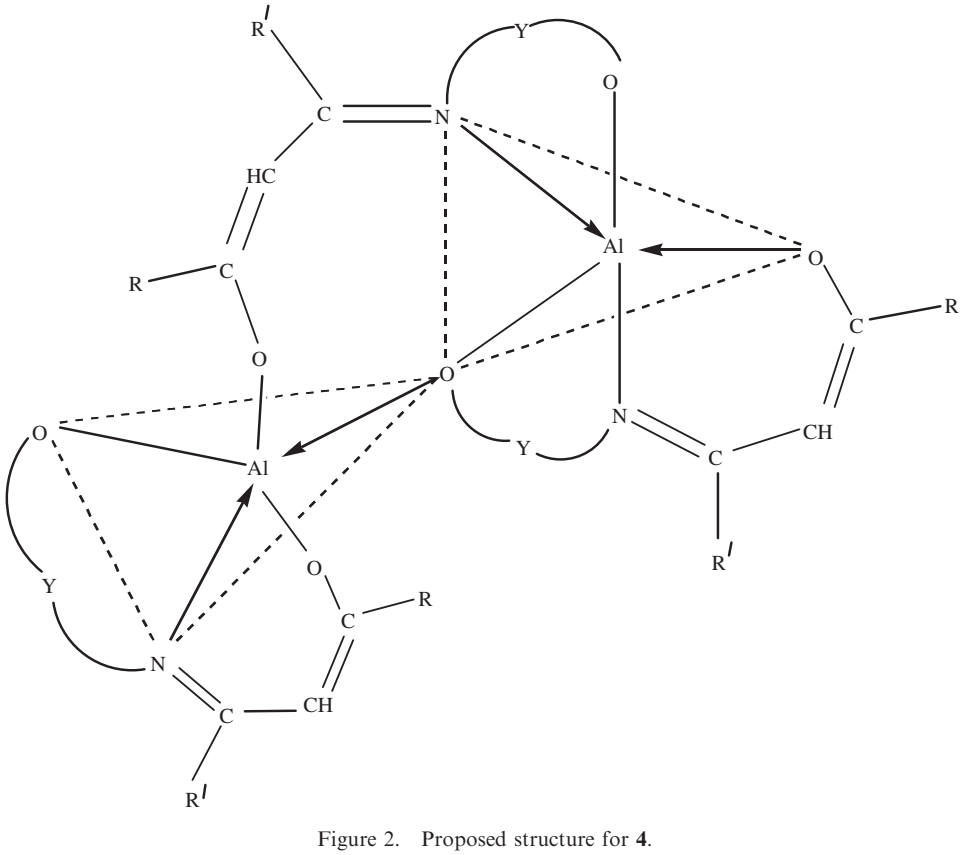


Figure 2. Proposed structure for **4**.

Table 4. Inhibition zone after 2–3 days in diameter.

Compound	Conc. (%)	Inhibition zone (mm)	
		E. coli	*B. subtilis*
L^1H_2	10	11	10
	20	19	20
AlL^1L^1H	10	15	18
	20	21	25

The antibacterial activity data indicates that gram +ve bacteria *B. subtilis* is more susceptible to the tested compounds than gram −ve bacteria *E. coli*, perhaps because gram –ve bacteria have an outer membrane which has hydrophilic polysaccharide chains as a barrier to hydrophobic test compound.

The results (table 4) indicate that the metal chelate has higher activity than the free ligand. This increased activity of the metal chelate can be explained on the basis of Overton's concept and Tweedy's [35] chelation theory. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favors passage of only lipid soluble material due to liposolubility, which is an important factor that controls antibacterial activity. On chelation, the polarity of the metal ions is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with a donor group. Further, it increases the delocalization of π-electrons over the whole chelate ring and enhances the penetration of the complexes into lipid membranes and blocks metal binding sites on the enzymes of the microorganism.

Inhibition of the bacteria was also dependent on the concentration of the complex.

Supplementary data

1H NMR spectra of L1H2, 1a, 2a, 3a, and 4 (2 : 3 complex) is provided. Table A. FAB-mass fragmentation mode of and Table B. FAB-mass fragmentation mode of

$C_6H_5C(NCH_2)_2O)CHC(CH_3)OAlO(CH_2)_2\overline{NC(C_6H_5)CHC(CH_3)}OB\ (OCH(CH_3)_2)_2$ (3b) is also

is also

$C_6H_5C(NCH_2)_2O)CHC(CH_3)OAlO\overline{(CH_2)_2NC(C_6H_5)CHC(CH_3)}OAl(OCH(CH_3)_2)_2$ (2b) and

provided.

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