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Mono- and heterodi-nuclear complexes of aluminium: synthesis, characterization and antifungal activity

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Some new types of mononuclear derivatives, AlL(1–4)L(1–4)H (1a–1d) of aluminium were synthesized by the reaction of $Al(OPr^i)_3$ and LH_2 [XC(NYOH)CHC(R)OH], X = CH_3, Y = $(CH_2)_2$, R = CH_3($L1H_2$); X = C_6H_5, Y = $(CH_2)_2$, R = CH_3($L2H_2$); X = CH_3, Y = $(CH_2)_3$, R = CH_3($L3H_2$); X = C_6H_5, Y = $(CH_2)_3$, R = CH_3($L4H_2$) in 1:2 molar ratio in refluxing benzene. Reactions of AlL(1–4)L(1–4)H with hexamethyldisilazane in 2:1 molar ratio yielded some new ligand bridged heterodinuclear derivatives AlL(1–4)L(1–4)$SiMe_3$ (2a–2d). All these newly synthesized derivatives were characterized by elemental analysis and molecular weight measurements. Tentative structures were proposed on the basis of IR and NMR spectra (^1H, ^{13}C,^{27}Al and ^{29}Si) and FAB-mass studies. Schiff base ligands and their mono- and heterodi-nuclear derivatives with aluminium have been screened for fungicidal activities. These compounds showed significant antifungal activity against *Aspergillus niger* and *A. flavus*. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: heterodinuclear compounds; pentacoordinated aluminium; tetracoordinated silicon; multinuclear NMR; FAB mass spectrometry

INTRODUCTION

During the last three or four decades, there have been considerable developments in the chemistry of metallic and organometallic complexes of Schiff bases and β-ketoamines.[1–5] During the past 15 years, there has been increasing interest in the heterometallic chemistry of group 13 metals.[6–8] Apart from their structural diversity, these complexes also assume importance due to their biological, agricultural and industrial applications. Aluminium compounds exhibit biological activities.[9–11]

Although the most common coordination numbers of aluminium are 4 and 6,[12–14] a number of compounds of aluminium with coordination number 5 are also known.[15–22] However, heterometal complexes of aluminium are limited in number.[23–27]

In this paper, we report the synthesis and characterization of some new Schiff base derivatives of aluminium which have been used for the synthesis of a new series of heterodinuclear compounds with organosilicon. The aluminium atom is pentacoordinated in the compounds of both series. A comparative study of the antifungal activity of the ligands and the corresponding mono- and heteronuclear derivatives of aluminium is also reported in this paper.

EXPERIMENTAL

Rigorous precautions were taken to exclude moisture throughout the course of these investigations. Solvents were dehydrated following a literature method.[28] The ligands were prepared as described previously.[29] Aluminium isopropoxide was prepared using a literature method.[30] Hexamethyl disilazane was distilled prior to use. Isopropyl alcohol in the azeotrope was determined oxidimetrically[31] and aluminium was determined as the oxinate.[32] Nitrogen was estimated using Kjeldhal's method.[32] Molecular weights were determined cryscopically in benzene solution. ^1H (300 MHz), ^{13}C (75.4 MHz), ^{27}Al (23.92 MHz) and ^{29}Si (17.55 MHz) NMR spectra in $CDCl_3$ solution were recorded on a Jeol FT Al 300 spectrometer. ^1H and ^{13}C NMR spectra were recorded using TMS as internal reference, ^{27}Al NMR spectra using $Al(NO_3)_3$ and ^{29}Si NMR spectra using Me_3SiCl as external references.

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Table 1. Analytical and physical properties of the new complexes AlLLH (**1a–1d**)

Compound	R	X	Y	Reactants, g (mmol) $Al(OPr^i)_3$	Reactants, g (mmol) LH_2	Pr^iOH found (calcd.)	Empirical formula, colour, physical state (yield %), melting point (°C)	Analysis, % found (calcd) Al	N	C	H	Molecular found weight (calcd)
1a	Me	Me	$(CH_2)_2$	3.32 (1.62)	4.66 (3.25)	2.91 (2.93)	$C_{14}H_{23}AlN_2O_4$ Creamy yellow, solid (98.2) 86	8.72 (8.70)	8.99 (9.03)	54.17 (54.21)	7.34 (7.42)	320.17 (310.14)
1b	Me	Ph	$(CH_2)_2$	2.73 (1.33)	5.49 (2.67)	2.40 (2.41)	$C_{24}H_{27}AlN_2O_4$ Light yellow, solid (90.70) 80	6.19 (6.21)	6.47 (6.45)	66.02 (66.33)	6.12 (6.22)	440.57 (434.28)
1c	Me	Me	$(CH_2)_3$	3.77 (1.84)	5.80 (3.69)	3.31 (3.32)	$C_{16}H_{27}AlN_2O_4$ Brown viscous, solid (98.87)	8.00 (7.98)	8.25 (8.28)	56.75 (56.81)	8.04 (7.98)	350.78 (338.21)
1d	Me	Ph	$(CH_2)_3$	2.76 (1.35)	5.93 (2.70)	2.43 (2.44)	$C_{26}H_{31}AlN_2O_4$ Dark yellow, solid (94.79) 92	5.86 (5.83)	6.01 (6.06)	67.41 (67.54)	6.62 (6.70)	475.81 (462.35)

Table 2. Analytical and physical properties of the new complexes $AlLLSiMe_3$ (**2a–2d**)

Compound	R	X	Y	Reactants, g (mmol) AlLLH	Reactants, g (mmol) Me_6Si_2NH	Empirical formula, colour, physical state (yield, %), melting point (°C)	Analysis, % found (calcd) Al	N	C	H	Molecular weight found (calcd)
2a	Me	Me	$(CH_2)_2$	1.08 (0.35)	0.28 (0.17)	$C_{17}H_{31}AlSiN_2O_4$ Brown, solid (99.25) 100	7.00 (7.06)	7.29 (7.33)	53.29 (53.40)	8.04 (8.11)	395.75 (382.33)
2b	Me	Ph	$(CH_2)_2$	1.62 (0.37)	0.30 (0.18)	$C_{27}H_{35}$, $AlSiN_2O_4$ Dark yellow, solid (97.35) 98	5.35 (5.33)	5.50 (5.53)	63.97 (64.02)	6.79 (6.91)	508.01 (506.47)
2c	Me	Me	$(CH_2)_3$	1.37 (0.40)	0.33 (0.20)	$C_{19}H_{35}AlSiN_2O_4$ Brown, viscous solid (93.37)	6.60 (6.57)	6.81 (6.82)	55.54 (55.60)	8.48 (8.53)	425.18 (410.39)
2d	Me	Ph	$(CH_2)_3$	1.47 (0.32)	0.26 (0.16)	$C_{29}H_{39}AlSiN_2O_4$ Light yellow, solid (96.79) 93	5.00 (5.05)	5.26 (5.24)	65.21 (65.16)	7.23 (7.29)	550.87 (534.53)

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IR spectra were recorded as nujol mull using KBr cells in the range 4000–400 cm^{-1} on an FTIR spectrophotometer model 8400S Shimadzu. The FAB-mass spectra were recorded on a Micromass Quattro II triple quadrupole mass spectrometer. Elemental analyses (C and H) were carried out on a Perkin Elmer-2400 C, H, N analyser.

As the synthetic procedures for the preparation of each member of a particular series are the same, the preparative details of only one compound of each series is given and the analytical and preparative details of the rest of the compounds are summarized in Tables 1 and 2.

Synthesis of AlL1L1H (1a)

A benzene solution (50 cm^3) containing $Al(OPr^i)_3$ (3.32 g, 1.62 mmol) and a Schiff base ligand $L1H_2$ (4.66 g, 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 of the reaction, the excess solvent was removed under reduced pressure to yield a cream-coloured solid. The compound was purified by dissolving the compound in dry benzene and then *n*-hexane was added until turbidity in the solution appeared. The solution was heated to obtain a clear solution. The solution was stored at −5 °C overnight. A cream-coloured compound separated out. The solvent was decanted off and the compound was dried under reduced pressure. The analysis of **1a** was found to have Al 8.72, N 8.99, C 54.17, H 7.34; calculated for $C_{14}N_{23}AlN_2O_4$, Al 8.70, N 9.03, C 54.21, H 7.42%.

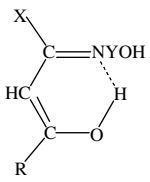
Synthesis of AlL1L1SiMe$_3$ (2a)

A mixture of **1a** (1.08 g, 0.35 mmol) and hexamethyldisilazane (0.28 g, 0.17 mmol) in benzene was refluxed (for 13 h), until the evolution of ammonia ceased. After the completion of the reaction, the solvent was removed under reduced pressure, yielding a brown solid. The compound was recrystallized from a benzene/*n*-hexane mixture. The analysis of $AlL1L1SiMe_3$ was found to have Al 7.00, N 7.29, C 53.29, H 8.04; calculated for $C_{17}H_{31}AlSiN_2O_4$, Al 7.06, N 7.33, C 53.40, H 8.11%.

Antifungal activity

The agar diffusion method was used to observe the antifungal activity of the complexes. In this method, 0.1 ml inoculum of the test organism was spread uniformly on the surface of the agar medium (potato, dextrose, agar medium) in a Petri plate using a spreader. The 10 and 30% solutions of the complexes were prepared respectively by dissolving 0.1 and 0.3 g of complex in 1 ml methanol. Sterilized Whatman filter paper discs of 6 mm diameter were dipped into the solution and then placed on the surface of the agar. The plates were incubated at 28 °C for 24 h. During incubation, the complex diffused from the filter paper into the medium. The activity of the complexes was assessed by measuring the diameter of the inhibited zone in millimetres. The results were compared against those of the control, which was screened simultaneously.

L = L1: **1a**, L = L2: **1b**, L = L3: **1c**, L = L4: **1d**.



$L1H_2$ [Y = $(CH_2)_2$, R = X = CH_3]
$L2H_2$ [Y = $(CH_2)_2$, R = CH_3, X = C_6H_5]
$L3H_2$ [Y = $(CH_2)_3$, R = X = CH_3]
$L4H_2$ [Y = $(CH_2)_3$, R = CH_3, X = C_6H_5]

Figure 1. Bifunctional tridentate Schiff bases.

RESULTS AND DISCUSSION

The reactions of $Al(OPr^i)_3$ with Schiff bases LH_2 [XC(NYOH)CHC(R)OH] (Fig. 1), in 1 : 2 molar ratio in refluxing benzene under anhydrous conditions are facile and 3 mol of Pr^iOH are readily fractionated off azeotropically with benzene.

$$Al(OPr^i)_3 + 2LH_2 \xrightarrow[\text{reflux}]{\text{benzene}} AlL(1-4)L(1-4)H + 3Pr^iOH \quad (1)$$

L = L1 : **1a**, L = L2 : **1b**, L = L3 : **1c**, L = L4 : **1d**.

After the removal of the excess of solvent, the complexes AlL(1–4)L(1–4)H (**1a–1d**) have been obtained as creamy yellow to brown solids. The reaction of AlL(1–4)L(1–4)H with $(Me_3Si)_2NH$ in 2 : 1 molar ratio in refluxing benzene yielded the heterobinuclear derivatives (**2a–2d**).

$$2AlL(1-4)L(1-4)H + (Me_3Si)_2NH \xrightarrow[\text{reflux}]{\text{benzene}} 2AlL(1-4)L(1-4)SiMe_3 + NH_3 \uparrow \quad (2)$$

L = L1 : **2a**, L = L2 : **2b**, L = L3 : **2c**, L = L4 : **2d**.

All these heterodinuclear derivatives are yellow-brown solids having sharp melting points. They are less moisture sensitive, soluble in common organic solvents and monomeric in benzene solution.

Spectroscopic studies

IR spectra

A broad absorption band observed in the spectra of **1a–1d** at 3200–3600 cm^{-1}, due to νOH, is found to be absent in the spectra of the heterodinuclear derivatives **2a–2d**, which is due to the deprotonation of the OH group owing to the reaction with hexamethyldisilazane. This is supported by a small shift in the position of the C–O bond (observed at 1560–1585 cm^{-1} in the spectra **2a–2d** as compared with its position in **1a–1d**). This indicates the attachment of the Me_3Si group to C–O. The

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Table 3. ^{1}H, ^{13}C, ^{27}Al and ^{29}Si NMR spectra of new complexes (**1a–1d** and **2a–2d**)

Compound	^{1}H NMR	C–O	C=N	Aromatic region	^{13}C NMR	^{27}Al	^{29}Si
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**H**$_3$COH), 10.74 (s, CH_3CO**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 (**C**H_3CO), 28.0 (**C**H_3CN), 19.04 (**C**H_3COH),	14.19	—
2a	3.60–3.89 (t, 2CH_2O), 3.25–3.54 (t, 2CH_2N), 5.61 (s, CHCO), 5.49 (s, CHCOSi), 2.01 (s, CH_3CO), 1.95 (s, 2CH_3CN), 1.88 (s, CH_3COSi), 0.09–0.1 (broad, $OSi(CH_3)_3$)	195.01, 194.94	163.79, 163.69	—	95.74 (**C**HCO), 95.68 (**C**HCOSi), 61.63 (CH_2O), 60.57 (CH_2N), 28.69 (**C**H_3CO), 27.57 (**C**H_3CN), 19.11 (**C**H_3COSi), 2.47 ($OSi(CH_3)_3$)	33.89	21.57
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**H**$_3$COH), 7.22–7.86 (m, 2C_6H_5), 11.47 (s, CH_3CO**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 (**C**H_3CO), 19.40 (**C**H_3COH)	14.19	—
2b	3.72–3.81 (t, 2CH_2O), 3.45–3.49 (t, 2CH_2N), 5.69 (s, CHCO), 5.67 (s, C**H**COSi), 2.09 (s, CH_3CO), 2.01 (s, CH_3COSi), 0.08–0.1 (broad, $OSi(CH_3)_3$), 7.25–7.87 (m, 2C_6H_5)	189.51, 188.11	165.79, 165.35	128.35–140.71	93.75 (**C**HCO), 92.71 (**C**HCOSi), 59.71 (CH_2O), 59.60 (CH_2N), 32.66 (**C**H_3CO), 20.01 (**C**H_3COSi), 2.46 ($OSi(CH_3)_3$)	39.63	20.18
1c	3.82–4.0 (t, 2CH_2O), 3.52–3.70 (m, 2C**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**H**$_3$COH), 10.76 (s, CH_3CO**H**)	194.55, 194.42	163.22, 163.15	—	100.0 (**C**HCO), 94.98 (**C**HCOH), 64.08 (CH_2O), 62.3 (**C**H_2CH_2O), 59.18 (CH_2N), 29.69 (**C**H_3CO), 28.75 (**C**H_3CN), 18.78 (**C**H_3COH)	14.44	—
2c	3.64–3.74 (t, 2CH_2O), 3.39–3.53 (m, 2C**H**$_2CH_2O$), 3.33–3.37 (t, 2CH_2N), 4.98 (s, CHCO), 4.96 (s, CHCOSi), 1.99 (s, CH_3CO), 1.94 (s, 2CH_3CN), 1.81 (s, CH_3COSi), 0.09–0.2 (broad, $OSi(CH_3)_3$)	194.67, 194.61	163.62, 163.36	—	95.17 (**C**HCO), 95.12 (**C**HCOSi), 63.95 (CH_2O), 62.11 (**C**H_2CH_2O), 59.14 (CH_2N), 28.72 (**C**H_3CO), 28.68 (**C**H_3CN) 18.79 (**C**H_3COSi), 2.44 ($OSi(CH_3)_3$)	35.64	22.71
1d	3.53–3.72 (t, 2CH_2O), 3.42–3.51 (m, 2C**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**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 (**C**H_2CH_2O), 59.30 (CH_2N), 32.88 (**C**H_3CO), 19.33 (**C**H_3COH)	15.05	—
2d	3.51–3.80 (t, 2CH_2O), 3.39–3.48 (m, 2C**H**$_2CH_2O$), 3.26–3.37 (t, 2CH_2N), 5.71 (s, CHCO), 5.63 (s, CHCOSi), 7.28–7.89 (m, 2C_6H_5), 2.11 (s, CH_3CO), 1.91 (s, CH_3COSi), 0.08–0.2 (broad, $OSi(CH_3)_3$)	188.01, 187.91	165.55, 165.41	126.45–140.51	92.21 (**C**HCO), 92.01 (**C**HCOSi), 62.18 (CH_2O), 61.97 (**C**H_2CH_2O), 59.35 (CH_2N), 32.01 (**C**H_3CO), 19.35 (**C**H_3COSi), 2.48 ($OSi(CH_3)_3$)	34.81	22.86

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formation of an Si–O bond[33] is supported by the appearance of a new band in the region 865–875 cm^{-1}.

A medium intensity band is observed for **2a–2d** in the region 1615–1625 cm^{-1} for ν(C═N) with a small (~15 cm^{-1}) shift towards lower wave numbers compared with that observed (1610–1620 cm^{-1}) in the spectra of **1a–1d**. Some other important absorption bands have been observed at 1245 ± 10 cm^{-1}, ν(Si–Me) deformation band; at 670 ± 8 cm^{-1}, ν(Al–O); and 520 ± 5 cm^{-1}, ν(Al ← N).

^{1}H NMR spectra

In the spectra (Table 3) of the compounds **1a–1d**, the absence of a –OH (aminol) signal at δ 4.06–4.34 ppm (present in the spectra of H_2L) indicates the deprotonation of the –OH group of the aminol. The enolic –OH group appeared at δ 10.76–11.47 ppm in the spectra of **1a–1d**. There was no significant shift in the position of the –OH resonance as compared with its position in the spectra of H_2L. This indicates that this group is not involved in the bonding. This signal disappeared in the spectra of **2a–2d**, indicating its deprotonation.

The spectra of **1a–1d** exhibited two sets of signals for the methyl and methine protons. This suggests the two different types of ligand environments in **1a–1d**, i.e. both –OH groups of one of the ligands have been deprotonated: one –OH enolic group remains in the second ligand and only the aminol OH group is deprotonated.

Two sets of signals have been observed for the methine and methyl protons, even in the spectra of **2a–2d**. This may be explained in the light of the presence of two types of ligands, even in the compounds **2a–2d**. One ligand chelates with aluminium whereas the second ligand acts as a bridge between aluminium and silicon atoms. These signals show slight downfield shifts in the spectra of **2a–2d** as compared with their positions in **1a–1d** because of the bonding of the second ligand with two metals in the compounds **2a–2d**. Me_3Si protons appear as a singlet at 0.08–0.2 ppm in the spectra of **2a– 2d**.

^{13}C NMR spectra

The ^{13}C NMR spectra (Table 3) of **1a–1d** exhibit two sets of signals for C–O (δ 187.45–194.79 and δ 187.40–194.57) suggesting the presence of two type of C–O groups in the compound, i.e. C–O–Al and C–OH, respectively. These signals appear with a small downfield shift in the spectra of **2a–2d** due to the introduction of two different metals in the complexes, i.e. C–O–Al and C–O–Si. The presence of two sets of signals for **C**H═C of **1a–1d** also supports the two types of ligand environment, as discussed with regards to the ^{1}H NMR spectra. However, some shifting in the position of the **C**H═C signals observed in the spectra of **2a–2d** suggests the coordination of the ligand with two different metals.

The signal for C═N in the spectra of **2a–2d** was observed in the region δ 163.36–163.79 ppm with a small shift as compared with its position in the spectra of **1a–1d**. The shifts may be due to the presence of two metals in these compounds. The signals for OSi(**C**H_3)$_3$ in the spectra of **2a–2d** were observed in the region δ 2.44–2.48 ppm.

^{29}Si NMR spectra

^{29}Si NMR signals in the spectra (Table 3) of compounds **2a–2d** were observed in range δ 20.18–22.86 ppm. The appearance of the signal in this range indicates the presence of a tetracoordinated Si atom[34,35] in these compounds.

^{27}Al NMR spectra

The presence of a sharp signal in the ^{27}Al NMR spectra (Table 3) of these compounds in the region δ 14.19–39.63 ppm for the derivatives **1a–1d** and **2a–2d** supports the pentacoordination around aluminium[19,36–38] in the compounds of both the series.

FAB-mass spectra

The FAB-mass spectrum of one of the heterodinuclear compound (**2b**) was recorded, which shows the monomeric nature of this compound. The mass spectral fragmentation pattern of compound **2b** is summarized in Table 4.

In view of the bifunctional tridentate nature of the ligand and the ^{27}Al and ^{29}Si NMR spectral data, the following

Table 4. Mode of fragmentation for $C_6H_5C(CHC\overline{OCH_3)N(CH_2)_2OAl}O(CH_2)_2NC(CHC(CH_3)OSi(CH_3)_3C_6H_5$

Complex	*m/e*
$C_6H_5C(CHC\overline{OCH_3)N(CH_2)_2OAl}O(CH_2)_2NC(CHC(CH_3)O)C_6H_5$	508
$C_6H_5C(CHC\overline{OCH_3)N(CH_2)_2OAl}O(CH_2)_2NC(CH(CH_2))C_6H_5$	433
$C_6H_5C(CHC\overline{OCH_3)N(CH_2)_2OAl}O(CH_2)_2NC(CH)C_6H_5$	406
$C_6H_5C(CHC\overline{OCH_3)N(CH_2)_2OAl}O(CH_2)_2NC$	391
$C_6H_5C(CHC\overline{OCH_3)N(CH_2)_2OAl}O$	289
$C_6H_5C(CHCOCH_3)N(CH_2)_2O$	205
$C_6H_5C(CHCOCH_3)N(CH_2)_2$	189
$C_6H_5C(CHCOCH_3)N$	161
C_6H_5CN	105

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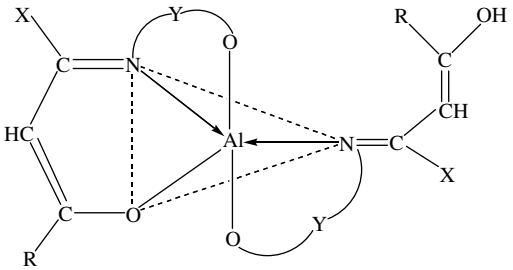
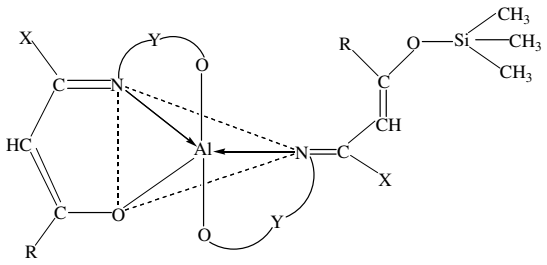


1a, X = CH_3, Y = $(CH_2)_2$, R = CH_3
1b, X = C_6H_5, Y = $(CH_2)_2$, R = CH_3
1c, X = CH_3, Y = $(CH_2)_3$, R = CH_3
1d, X = C_6H_5, Y = $(CH_2)_3$, R = CH_3

Figure 2. Structure for AlL(1–4)L(1–4)H (**1a**–**1d**).



2a, X = CH_3, Y = $(CH_2)_2$, R = CH_3
2b, X = C_6H_5, Y = $(CH_2)_2$, R = CH_3
2c, X = CH_3, Y = $(CH_2)_3$, R = CH_3
2d, X = C_6H_5, Y = $(CH_2)_3$, R = CH_3

Figure 3. Structure for AlL(1–4)L(1–4)SiMe3 (**2a**–**2d**).

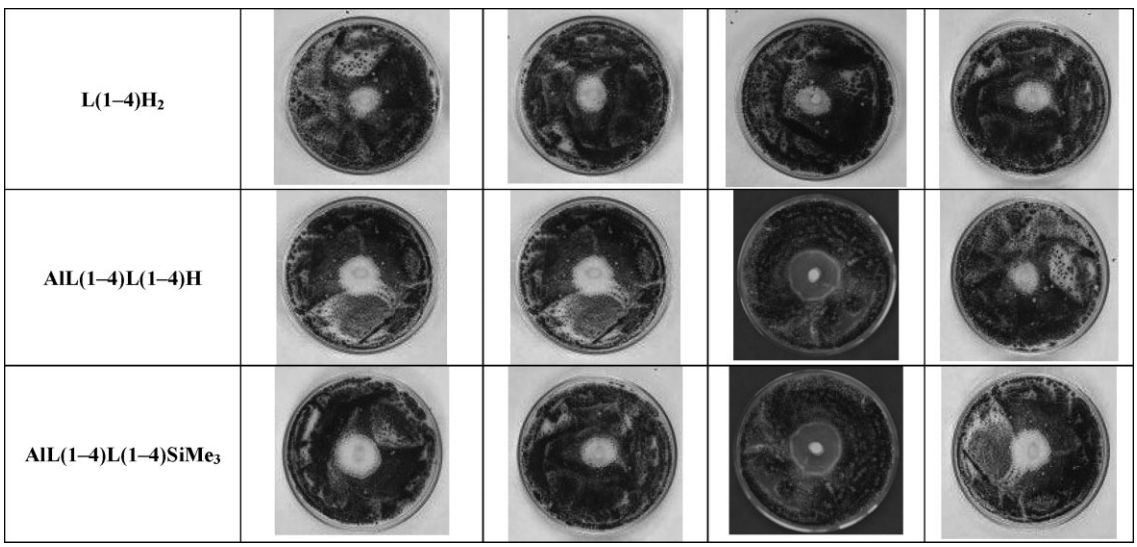


Figure 4. Photographs of the antifungal activity of the ligands and their metal complexes against *Aspergillus niger*.

structures may be suggested for **1a**–**1d** (Fig. 2) and for **2a**–**2d** (Fig. 3), in which Al is pentacoordinated and Si tetracoordinated.

Biological activity

The ligands and their respective metal derivatives were tested against *A. niger* and *A. flavus* to examine their growth inhibitory potential towards the fungi (Fig. 4). The results indicate that the order of the activity of these derivatives is **2a**–**2d** > **1a**–**1d** > $L1H_2$–$L4H_2$. This is summarized in Table 5.

A possible explanation of the toxicity increase may be considered in the light of Tweedy's chelation theory.[39] These results indicate that metal derivatives show more inhibitory effect than do the parent ligands. The increase in antifungal activity of the metal chelates may be due to the effect

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Table 5. Antifungal studies of the ligands and their mononuclear and heterodinuclear complexes

Compound	Concentration (%)	Zone size in mm	
		A. niger	*A. flavus*
$L1H_2$	10	8	5
	30	10	10
$L2H_2$	10	7	6
	30	11	8
$L3H_2$	10	6	5
	30	9	9
$L4H_2$	10	7	7
	30	10	9
AlL1L1H	10	10	6
	30	15	12
AlL2L2H	10	9	7
	30	13	8
AlL3L3H	10	7	6
	30	15	10
AlL4L4H	10	8	8
	30	12	11
$AlL1L1SiMe_3$	10	11	6
	30	16	14
$AlL2L2SiMe_3$	10	10	8
	30	12	10
$AlL3L3SiMe_3$	10	12	9
	30	15	13
$AlL4L4SiMe_3$	10	9	8
	30	13	14

of the metal ion on the normal cell process. This can be explained by the chelation theory. According to this theory, the chelation reduces the polarity of the metal ion and enhances the lipophilic character of the central metal atom which subsequently favours its permeation through the lipid layers of the cell membrane. Since the aluminium complexes inhibit the growth of microorganisms, it is assumed that the production of ATP and enzymes is being affected by the microorganism as they are unable to utilize food for themselves or intake of nutrient decreases and consequently growth diminishes.

The inhibition growth of the fungi was also found to be dependent on the concentration of the compound: at lower concentration, the activity of the organisms will be slowed down and the organisms may be able to grow at a slow rate, while at higher concentration, more enzymes will become inhibited, leading to a quicker death of the organism. As currently viewed, all the fungicides are metabolic inhibitors, that is, they block some vital metabolic processes.

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