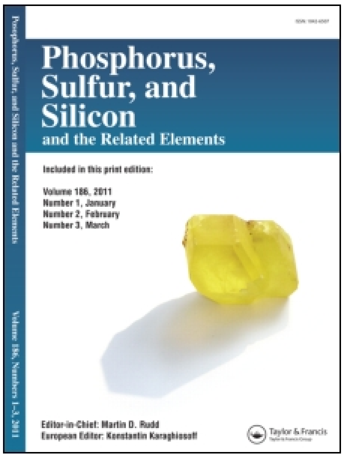

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Synthesis and Characterization of a New Class of Heteronuclear Derivatives of Arsenic(III) and Aluminium Containing Bifunctional Tridentate Schiff Base Ligands

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Synthesis and Characterization of a New Class of Heteronuclear Derivatives of Arsenic(III) and Aluminium Containing Bifunctional Tridentate Schiff Base Ligands

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A series of new heteronuclear derivatives of As(III) $R'C(NR\overline{O)CHC(R'')OA}sORNC(R')CHC(R'')OAl(OPr^i)_2$, *(2a–2e) has been synthesized by the reaction of mononuclear derivative AsLLH* $(R'C(NR\overline{O)CH(R'')OA}sORNC(R')CHC(R'')OH$ *(Ia–Ie)]* $R = (-CH_2)_2$, $R' = R'' = -CH_3$ *(Ia & 2a)*, $R = (-CH_2)_2$, $R' = -C_6H_5$, $R'' = -CH_3$ *(Ib & 2b)*, $R = (-CH_2)_3$, $R' = R'' = -CH_3$ *(Ic & 2c)*, $R = (-CH_2)_3$, $R' = -C_6H_5$, $R'' = -CH_3$ *(Id & 2d)*, $R = (-CH_2)_2$, $R' = 4\text{-}ClC_6H_4$, *and* $R'' = -CH_3$ *(Ie & 2e) with aluminium isopropoxide. All these heteronuclear derivatives have been characterised by elemental analysis and molecular weight measurements. A plausible structure for these new derivatives has been suggested on the basis of spectral (IR and NMR [*^1H, ^{13}C, *and* ^{27}Al*]) studies.*

Keywords Heteronuclear derivatives of As(III) and Al; hexacoordinated As and tetracoordinated Al; schiff base

INTRODUCTION

During the last two to three decades, the interest in heterobimetallic alkoxides has been renewed due to their use in the preparation of oxide-based ceramic materials by sol-gel and MOCVD process.[1–15,21,22] In fact, the water susceptibility of metal alkoxides and modulation of their chemical reactivity by the use of chelating ligands like carboxylates, β-diketonates, and alkoxyethoxides makes them attractive precursors for the synthesis of mixed metal oxide ceramic materials by the sol-gel technique.[1–15] Although heterometallic alkoxides of antimony[16–19] and bismuth[20] have been reported in the literature. A survey of literature reveals that no work has been reported on the heterometallic alkoxides of As-containing chelating ligands.

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We report the first series of binuclear complexes of As with Al containing chelating Schiff base ligands. All these compounds have been characterised by elemental analysis and molecular weight measurements, and their tentative structure has been proposed on the basis of IR and NMR (^1H, ^{13}C, and ^{27}Al) spectroscopic evidences.

RESULTS AND DISCUSSION

Reactions of $As(OPr^i)_3$ with bifunctional tridentate schiff base ligands LH_2 [R′C(NROH)CHC(R″)OH] $R = (-CH_2)_2$, $R' = R'' = -CH_3$ (L^1H_2), $R = (-CH_2)_2$, $R' = -C_6H_5$, $R'' = -CH_3$(L^2H_2), $R = (-CH_2)_3$, $R' = R'' = -CH_3$ (L^3H_2), $R = (-CH_2)_3$, $R' = -C_6H_5$, $R'' = -CH_3$(L^4H_2), $R = (-CH_2)_2$, $R' =$ 4-ClC_6H_4, and $R'' = -CH_3$ (L^5H_2) in a 1:2 molar ratio in refluxing benzene yielded mononuclear precursor complexes AsLLH (Ia–Ie).

$$As(OPr^i)_3 + 2LH_2 \xrightarrow[\text{reflux}]{\text{benzene}} AsLLH + 3Pr^iOH \tag{1}$$

$L = L^1 = \text{Ia}, L = L^3 = \mathbf{I}\text{c}, L = L^5 = \text{Ie}$

$L = L^2 = \text{Ib}, L = L^4 = \text{Id}$

On further treatment of these complexes with $Al(OPr^i)_3$ in an equimolar ratio in benzene affords heteronuclear derivatives (2a–2e):

$$AsLLH + Al(OPr^i)_3 \xrightarrow[\text{reflux}]{\text{benzene}} AsLLAI(OPr^i)_2 + Pr^iOH \tag{2}$$

$L = L^1 = 2a, L = L^3 = 2c, L = L^5 = 2e$

$L = L^2 = 2b, L = L^4 = 2d$

All the heteronuclear derivatives (2a–2e) are yellow-brown viscous liquids, moisture sensitive, and soluble in common organic solvents and monomeric in benzene solution.

Spectroscopic Studies

IR Spectra

A broad band due to νOH vibrational mode in mononuclear derivatives (Ia–Ie) in the range 3200–3400 cm^{-1} has been found to be absent in the spectra of heteronuclear derivatives (2a–2e) showing the deprotonation of the –OH group.

The appearance of bands in the region 420–442 cm^{-1} and 470–485 cm^{-1} in the spectra of 2a–2e may be assigned to $\nu As \leftarrow N$[32] and $\nu AS - O$,[33] respectively, with a small shift toward a lower wave number as compared to their position in the spectra of Ia–Ie. A new band observed in the region 658–680 cm^{-1} may be attributed to ν Al—O[34] in the spectra of heteronuclear derivatives (2a–2e).

The schiff base moieties of heteronuclear derivatives (2a–2e) show the following bands:

1) a band at 1610–1635 for νC=N, with a small (~15 cm^{-1}) shift toward a lower wave number as compared to that observed (1610–1620 cm^{-1}) in the corresponding mononuclear derivatives,
2) a band at 1580–1600 cm^{-1} for νC—O (CH_3CO) with a small shift (~10 cm^{-1}) toward a lower wave number as compared to mononuclear derivatives, and
3) a band in the range 1050–1085 for νC—O, due to metal-alkoxide bond.

All the datas have been summarised in Table I.

^{1}H NMR Spectra

The ^{1}H NMR spectra (Table IV) of derivatives (Ia–Ie) show the disappearance of the signal for —OH group of amino alcohol present in the spectra of ligand at 4.06–4.34 ppm. A small shift in the position of the signal for enolic hydroxy group as compared to its position in the spectra of ligand indicates that although this group is not deprotonated, it is involved in the coordination. The enolic —OH signal is found to be absent in heteronuclear derivatives (2a–2e) indicating its deprotonation.

^{1}H NMR spectra of compounds (Ia–Ie) exhibit 2 sets of signals for methine and methyl protons of the ligand moiety. This shows the presence of two different types of ligand environments in these compounds. Both

TABLE I IR Spectra of New Complexes (in cm^{-1})

Complex	νC=N	νC—O (CH_3CO)	νC—O (Metal Alkoxide)	νC—O (Alcoholic)	νC—O (Isopropoxy)	As← N	As—O	Al—O
1a	1620	1585	—	1080	—	438	460	—
2a	1625	1600	1085	—	950	443	482	663
1b	1612	1590	—	1065	—	430	470	—
2b	1615	1598	1070	—	1010	432	475	658
1c	1605	1577	—	1072	—	435	480	—
2c	1610	1580	1080	—	1008	442	485	670
1d	1622	1578	—	1045	—	428	482	—
2d	1630	1580	1050	—	1002	430	485	660
1e	1627	1596	—	1051	—	440	470	—
2e	1635	1600	1060	—	1005	442	475	680

the —OH groups of one of the ligand have been deprotonated, whereas only one —OH group (amino alcoholic) is deprotonated, and enolic-OH group remains as such in the second ligand.

In the spectra of heteronuclear derivatives (2a–2e) we still get 2 sets of methyl and methine protons signals with a small downfield shift. This is due to the fact that one ligand is chelated exclusively to Arsenic atom, whereas another ligand bridges the two metals As and Al. In the spectra of all the compounds, an Ia–Ie and 2a–2e $C\mathbf{H}_3C{=}N$ signal was observed in the region δ 1.98–2.04 ppm. However, this signal shows a small downfield shift in the spectra of 2a–2e as compared to its position in the spectra of Ia–Ie. The phenyl protons appear as a multiplet in the region δ 7.27–7.86 ppm. The signals for isopropoxy group appear as a doublet $(CH(C\mathbf{H}_3)_2)$ and as septet $(C\mathbf{H}(CH_3)_2)$ at δ 1.13–1.26 and δ 3.93–4.39 ppm, respectively. The appearance of only one set of signals indicates the presence of only one type of isopropoxy group in these compounds.

^{13}C NMR Spectra

The ^{13}C NMR spectra (Table V) of (Ia–Id) exhibit 2 sets of signals for C—O (δ 172.57–176.3 and δ 170.89–175.58) suggesting the presence of two types of CO groups in the ligands, i.e., **C**—OAs and **C**—OH, respectively. There is small downfield shift in the position of these carbon signals with the introduction of two metals in the complexes in the spectra of heteronuclear complexes (2a–2d) as compared to their position in the spectra of compounds Ia–Id.

Again the presence of 2 sets of signals for **C**H=C (Ia–Id) in the region (δ 90.01–96.98 and δ 91.95–97.77 ppm) also supports the two types of ligand environments as discussed in the ^{1}H NMR spectra section. However, some shifting is observed in the position of signals (methine carbon) of (2a–2d) as compared to the derivatives (Ia–Id) showing the coordination with different metals.

The signal for >C=N carbon in the spectra of heteronuclear derivatives (2a–2d) has been assigned in the region δ 162.99–166.97 ppm with a small downfield shift as compared to the mononuclear derivatives (Ia–Id). The downfield shift in the spectra confirms involvement of >C=N group in bonding.

The signals, one each for $\mathbf{C}H(CH_3)_2$ and $CH(\mathbf{C}H_3)_2$ carbons of isopropoxy group in the spectra of heteronuclear derivatives (2a–2d), have been assigned in the region δ 56.78–59.36 and δ 24.79–32.30 ppm, respectively. The presence of only one set of signals supports the presence of only one type of isopropoxy group.

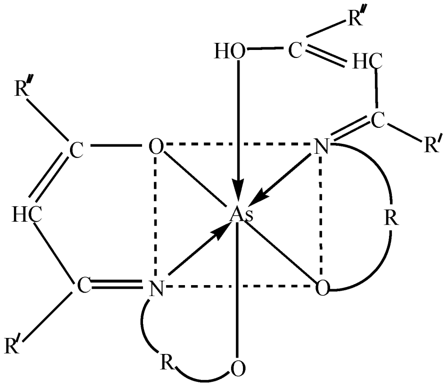

FIGURE 1 Structure for AsLLH (Ia–Ie).

^{27}Al NMR Spectra

^{27}Al NMR spectra (Table V) of compounds (2a–2d) exhibit a sharp signal in the region δ 32.42–56.61 ppm. Appearance of the signal in this range indicates the presence of the tetracoordinated Al atom (28–31) in these compounds.

In view of the bifunctional tridentate nature of the ligand, the following structure (Figure 1), in which the arsenic atom is hexacoordinated, may be proposed for the derivatives (Ia–Ie).

On the basis of spectral studies discussed so far, a structure (Figure 2) in which the Al is tetracoordinated and As is hexacoordinated may be proposed for heteronuclear derivatives (2a–2e).

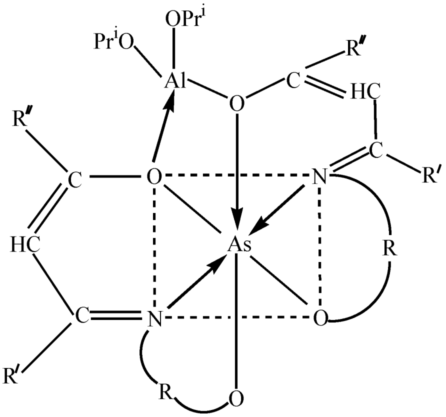

FIGURE 2 Structure for AsLLAl(OPr^i)$_2$ (2a–2e).

TABLE II Analytical and Physical Properties of the New Complexes AsLLH (1a–1e)

Compound	Empirical Formula, Color (Yield %)	R′	R	R″	Reactants, g (mmol)		Pr^i OH Found (Calcd.)	Analysis% Found (Calcd.)		Mol. Wt. Found (Calcd.)
					$As(OPr^i)_3$	LH_2		As	N	
1a	$C_{14}H_{23}AsN_2O_4$ Brown viscous liquid (93.58)	Me	Et	Me	1.44 (5.71)	1.63 (11.39)	0.98 (1.03)	19.59 (20.92)	7.41 (7.82)	337.58 (358.08)
1b	$C_{24}H_{27}AsN_2O_4$ Brown viscous liquid (92.77)	Ph	Et	Me	3.97 (15.77)	6.47 (31.53)	2.75 (2.84)	14.28 (15.54)	5.47 (5.81)	471.50 (482.22)
1c	$C_{16}H_{27}AsN_2O_4$ Brown viscous liquid (86.38)	Me	n-Pr	Me	4.59 (18.21)	5.72 (36.40)	3.18 (3.28)	18.88 (19.40)	7.05 (7.25)	374.11 (386.15)
1d	$C_{26}H_{31}AsN_2O_4$ Brown viscous liquid (95.19)	Ph	n-Pr	Me	3.48 (13.83)	6.06 (27.64)	2.37 (2.49)	13.79 (14.68)	5.08 (5.49)	499.74 (510.29)
1e	$C_{24}H_{25}AsN_2O_4Cl$ Brown viscous liquid (98.32)	4-ClPh	Et	Me	2.12 (8.40)	4.01 (16.80)	1.50 (1.51)	12.97 (13.64)	4.78 (5.10)	534.81 (549.13)

TABLE III Analytical and Physical Properties of the New Complexes AsLLAl(OPr^i)$_2$ (2a–2e)

					Reactants, g (mmol)			Analysis% Found (Calcd.)				
Compound	Empirical Formula, Color (Yield %)	R′	R	R″	AsLLH	Al(OPr^i)$_3$	Pr^i OH Found (Calcd.)	As	Al	N	OPr^i	Mol. Wt. Found (Calcd.)
2a	$C_{20}H_{36}AlAsN_2O_6$ Brown viscous liquid (97.6)	Me	Et	Me	1.82 (5.08)	1.038 (5.08)	0.29 (0.30)	13.87 (14.92)	5.15 (5.37)	5.37 (5.58)	22.18 (23.53)	493.52 (502.24)
2b	$C_{30}H_{40}AlAsN_2O_6$ Brown viscous liquid (94.5)	Ph	Et	Me	1.55 (3.21)	0.65 (3.21)	0.18 (0.19)	10.91 (11.96)	4.20 (4.31)	4.29 (4.47)	18.21 (18.87)	613.75 (626.38)
2c	$C_{22}H_{40}AlAsN_2O_6$ Brown viscous liquid (73.4)	Me	nPr	Me	1.66 (4.32)	0.88 (4.32)	0.24 (0.26)	13.17 (14.12)	4.32 (5.09)	5.01 (5.28)	21.84 (22.28)	522.82 (530.3)
2d	$C_{32}H_{44}AlAsN_2O_6$ Yellow viscous liquid (90.76)	Ph	n-Pr	Me	1.78 (3.49)	0.71 (3.49)	0.19 (0.21)	10.81 (11.45)	3.75 (4.12)	4.03 (4.28)	17.77 (18.06)	640.9 (654.44)
2e	$C_{32}H_{44}AlAsN_2O_6Cl$ Yellow, viscous liquid (98.92)	4-ClPh	Et	Me	1.45 (2.64)	0.54 (2.64)	0.13 (0.14)	10.05 (10.80)	3.11 (3.89)	3.82 (4.04)	16.01 (17.04)	669.57 (693.28)

EXPERIMENTAL

All reactions were carried out under a moisture-free environment. Solvents (E-Merck, Mumbai, Maharastra, India) have been dried by the literature method.[23] $\mathrm{Al(OPr^i)_3}$[24] and $\mathrm{As(OPr^i)_3}$[25] were prepared by the literature method. The isopropoxy group in the derivatives and isopropanol in the azeotrope **was** estimated by the reported method.[26] Nitrogen was estimated by Kjeldhal's method,[27] aluminium was estimated gravimetrically as oximate,[27] and arsenic was estimated iodometrically.[27] Molecular weights were determined cryscopically in benzene solution. ^{1}H (300 MHz), ^{13}C (75 MHz), and ^{27}Al (23.39 MHz) NMR spectra in $\mathrm{CDCl_3}$ solution were recorded on a JEOL FT AL 300 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded using TMS as internal reference and ^{27}Al using aluminium nitrate as the external reference. IR spectra have been recorded

TABLE IV ^{1}H NMR Spectra of New Complexes

1a	3.89–3.95 (t,$\mathrm{2CH_2}$-O), 3.27–3.44 (t, $\mathrm{2CH_2}$-N), 5.14 (s, –CHCO), 4.96 (s, –C**H**COH), 1.96 (s, $\mathrm{CH_3CO}$), 1.92 (s, $\mathrm{2CH_3CN}$), 1.24 (s, $\mathrm{C\mathbf{H}_3COH}$), 10.86 (s, $\mathrm{\mathbf{H}OCCH_3}$)
2a	3.81–3.91 (t, $\mathrm{2CH_2}$-O) 3.31–3.58 (t, $\mathrm{2CH_2}$-N), 5.09 (s, –CHCO), 4.97 (s, –CHCOAl), 3.93–4.33 (Septet, 2,O-C**H** $\mathrm{(CH_3)_2}$), 2.0 (s, $\mathrm{CH_3CO}$), 1.98 (s, $\mathrm{2CH_3}$,CN), 1.26 (s, $\mathrm{CH_3COAl}$), 1.13–1.23 (d, 2,O-$\mathrm{CH(C\mathbf{H}_3)_2}$)
1b	3.97–4.04 (t, $\mathrm{2CH_2}$-O), 3.44–3.53 (t, $\mathrm{2CH_2}$-N), 5.67 (s, –CHCO), 5.65 (s, –C**H**COH), 2.04 (s, $\mathrm{CH_3CO}$), 1.26 (s, $\mathrm{C\mathbf{H}_3COH}$), 11.48 (s, **H**O-C-$\mathrm{CH_3}$), 7.34–7.85 (m, $\mathrm{2C_6H_5}$)
2b	3.51–3.60 (t, $\mathrm{2CH_2}$-O), 3.33–3.47 (t, $\mathrm{2CH_2}$-N), 5.68 (s, –C**H**CO), 5.54 (s, –C**H**COAl), 3.99–4.03 (Septet, $\mathrm{2OC\mathbf{H}(CH_3)_2}$), 2.05 (s, $\mathrm{CH_3CO}$), 1.27 (s, $\mathrm{CH_3COAl}$), 1.18–1.25 (d, 2,$\mathrm{OCH(C\mathbf{H}_3)_2}$), 7.27–7.86 (m, $\mathrm{2C_6H_5}$)
1c	3.94–4.03 (t, $\mathrm{2CH_2O}$), 3.32–3.42 (t, $\mathrm{2CH_2}$-N), 3.70–3.90 (q, $\mathrm{2C\mathbf{H}_2}$-$\mathrm{CH_2}$-O), 5.17 (s,-C**H**CO), 4.95 (s, C**H**COH), 1.98 (s, $\mathrm{C\mathbf{H}_3CO}$), 1.94 (s, $\mathrm{2CH_3CN}$), 1.26 (s, $\mathrm{C\mathbf{H}_3COH}$), 10.84 (s, $\mathrm{\mathbf{H}OCCH_3}$)
2c	3.88–3.92 (t, $\mathrm{2CH_2}$-O), 3.38–3.64 (t, $\mathrm{2CH_2}$-N), 3.34–3.36 (quartet, $\mathrm{2C\mathbf{H}_2}$-$\mathrm{CH_2}$-O), 5.04 (s, –C**H**CO), 4.95 (s, –C**H**OAl), 1.98 (s, $\mathrm{C\mathbf{H}_3CO}$), 1.94 (s, $\mathrm{2C\mathbf{H}_3CN}$), 1.28 (s, $\mathrm{C\mathbf{H}_3COAl}$), 1.13–1.24 (doublet, 2, $\mathrm{OCH(C\mathbf{H}_3)_2}$), 4.01–4.39 (septet, 2, $\mathrm{OC\mathbf{H}(CH_3)_2}$)
1d	3.74–3.85 (t, $\mathrm{2CH_2}$-O), 3.57–3.63 (t, $\mathrm{2CH_2}$-N), 3.20–3.37 (quartet, 2-$\mathrm{CH_2}$-$\mathrm{CH_2O}$), 5.61 (s, –C**H**CO), 5.39 (s, –C**H**COH), 2.03 (s, $\mathrm{C\mathbf{H}_3CO}$), 1.20 (s, $\mathrm{C\mathbf{H}_3COH}$), 11.59 (s, $\mathrm{\mathbf{H}OCCH_3}$), 7.31–7.87 (m, $\mathrm{2C_6H_5}$)
2d	3.95–3.99 (t, $\mathrm{2CH_2O}$), 3.67–3.73 (t, $\mathrm{2CH_2}$-N), 3.40–3.48 (quartet, 2-$\mathrm{C\mathbf{H}_2}$-$\mathrm{CH_2O}$), 5.66 (s, –C**H**CO), 5.47 (s, –C**H**COAl), 2.11 (s, $\mathrm{C\mathbf{H}_3CO}$), 1.29 (s, $\mathrm{C\mathbf{H}_3COAl}$), 4.01–4.37 (septet, 2, $\mathrm{OC\mathbf{H}(CH_3)_2}$), 1.18–1.26 (doublet, 2, $\mathrm{OCH(C\mathbf{H}_3)_2}$)
1e	3.69–3.80 (t, $\mathrm{2CH_2}$-O), 3.48–3.50 (t, $\mathrm{2CH_2}$-N), 5.59 (s, –C**H**CO), 5.37 (s, –C**H**COH), 2.01 (s, $\mathrm{C\mathbf{H}_3CO}$), 1.23 (s, $\mathrm{C\mathbf{H}_3COH}$), 7.31–7.98 (m, 4-$\mathrm{C_6H_4Cl}$), 11.48 (s, $\mathrm{CH_3CO\mathbf{H}}$)
2e	3.76–4.02 (t, $\mathrm{2CH_2}$-O), 3.50–3.56 (t, $\mathrm{2CH_2}$-N), 5.73 (s, –C**H**CO), 5.66 (s, –CHCOAl), 2.02 (s, $\mathrm{C\mathbf{H}_3CO}$), 1.26 (s, $\mathrm{C\mathbf{H}_3}$-COAl), 7.24–7.81 (m, 4-$\mathrm{C_6H_4Cl}$), 4.04–4.41 (septet, 2, $\mathrm{OC\mathbf{H}(CH_3)_2}$), 1.07–1.24 (doublet, 2, $\mathrm{OCH(C\mathbf{H}_3)_2}$)

TABLE V ^{13}C and ^{27}Al NMR Spectra of New Complexes

	C—O	C=N	Aromatic Carbon	Alkylene Carbon	^{27}Al NMR
1a	175.98, 174.15	162.84	—	95.54 (—**C**HCO), 95.17 (—**C**HCOH), 66.20–66.63 (CH$_2$—O) 61.42–61.89 (CH$_2$-N), 28.66 (**C**H$_3$CO), 25.40–25.49 (**C**H$_3$CN), 18.86 (**C**H$_3$COH)	—
2a	177.22, 175.26	162.99	—	95.63 (—**C**HCO), 95.29 (—**C**HCOAl), 65.72–66.39 (CH$_2$—O), 62.83–64.23 (CH$_2$—N), 28.83 (**C**H$_3$CO), 25.36–26.01 (**C**H$_3$CN), 26.01, 26.24 (OCH(**C**H$_3$)$_2$), 56.78 (O**C**H(CH$_3$)$_2$), 21.48–22.10 (**C**H$_3$COAl)	39.65
1b	174.58, 173.71	165.48	126.86–130.42	96.56 (—**C**HCO), 92.45 (—**C**HCOH), 62.09 (CH$_2$—O), 61.58–61.62 (CH$_2$-N), 25.59 (**C**H$_3$CO), 19.59 (**C**H$_3$COH)	—
2b	172.36, 170.16	166.97	126.51–139.91	96.06 (—**C**HCO), 92.02 (—**C**HCOAl), 65.76–66.43 (CH$_2$—O) 64.36 (CH$_2$-N), 25.68 (**C**H$_3$CO), 19.6–22.4 (**C**H$_3$COAl), 25.35–25.68 (OCH(**C**H$_3$)$_2$), 56.93 (O**C**H(CH$_3$)$_2$)	56.61
1c	172.57, 170.89	163.07	—	97.77 (—**C**HCO), 96.98 (—**C**HCOH), 66.74–67.07 (CH$_2$—O), 65.88–66.02 (CH$_2$-N), 60.34 (**C**H$_2$-CH$_2$—O), 29.07 (**C**H$_3$CO), 26.48–27.45 (**C**H$_3$CN), 21.07–23.99 (**C**H$_3$COH)	—
2c	175.32, 173.79	163.42	—	99.67 (—**C**HCO), 95.17 (–**C**HCOAl), 65.74–66.17 (CH$_2$—O), 63.08–63.8 (CH$_2$-N), 59.36–62.80 (**C**H$_2$-CH$_2$—O), 28.77 (**C**H$_3$CO), 25.68–26.01 (**C**H$_3$CN), 21.44–21.87 (**C**H$_3$COAl), 24.79 (OCH(**C**H$_3$)$_2$), 58.95, 59.36 (O**C**H(CH$_3$)$_2$)	32.42
1d	176.3, 175.58	163.81	125.33–139.87	91.95 (—**C**HCO), 90.01 (—**C**HCOH), 63.87 (CH$_2$—O), 64.39 (CH$_2$-N), 64.03 (**C**H$_2$-CH$_2$—O), 23.48 (**C**H$_3$CO), 21.09 (**C**H$_3$COH)	—
2d	177.83, 176.04	164.20	125.45–139.55	92.87 (—**C**HCO), 90.86 (—**C**HCOAl), 65.19 (CH$_2$—O), 64.74 (CH$_2$-N), 63.27 (**C**H$_2$-CH$_2$-O), 24.66 (**C**H$_3$CO), 21.55 (**C**H$_3$COAl), 58.38 (O**C**H(CH$_3$)$_2$), 32.30 (OCH(**C**H$_3$)$_2$)	33.92

as nujol mull using KBr cells in the range of 4000–400 cm^{-1} on FTIR spectrophotometer model 8400 S Shimadzu.

Synthesis of New Heteronuclear Complexes

Preparation of As L^1L^1H(Ia)

A benzene solution (~20 mL) of As $(OPr^i)_3$ (1.44 g, 5.71 mmol) mixed with a benzene solution (~30 mL) of a bifunctional tridentate Schiff base ligand L^1H_2 (1.63 g, 11.39 mmol) was refluxed under a fractionating column. The liberated isopropanol fractionated out azeotropically in benzene. Progress of the reaction was checked by estimating isopropanol in the azeotrope. The reaction was completed in ~28 h. After the completion of the reaction, the excess solvent was removed under reduced pressure and yellow-brown compound was obtained as a viscous liquid. The analysis was found to have As, 19.59; and N, 7.41 calculated for $C_{14}N_{23}AsN_2O_4$; As, 20.92; N, 7.82. All the other derivatives (Ib–Ie) were prepared by adopting the procedure similar to Ia, and all their analytical data have been summarized in Table II.

Preparation of the Heteronuclear Derivative (2a)

The reaction mixture containing Ia (1.82 g, 5.08 mmol) and $Al(OPr^i)_3$ (1.03 g, 5.08 mmol) in benzene (50 cm^3) solution was refluxed on a fractionating column for ~10 h. Progress of the reaction was monitered by estimating the liberated isopropanol fractionated out azeotropically. After completion of reaction, the excess solvent was removed under reduced pressure to yield product (2a) as a brown viscous liquid. The analysis was found to have As, 13.87; Al, 5.15; N, 5.17; and OPr^i, 22.18 calculated for $C_{20}H_{36}AlAsN_2O_6$; As, 14.92; Al, 5.37; N, 5.58; and OPr^i, 23.53.

A similar procedure is adopted for the synthesis of all other derivatives (2b–2e), and the analytical data have been summarised in Table (III).

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