SHORT PAPER

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Reactions of bis(N-phenylsalicylidene iminato)aluminium-di-μ-isopropoxo-di-isopropoxo aluminium(III) with glycols†

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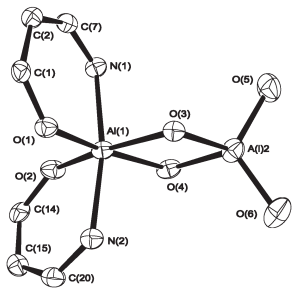
Reactions of bis(N-phenylsalicylidene iminato)aluminium-di-μ-isopropoxo-di-isopropoxo aluminium(III), $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2$ with glycols in 1:1 molar ratio in refluxing anhydrous benzene yielded binuclear complexes of the type, $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(O\text{-}G\text{-}O)$ [where G = $(CH_2)_2$, $CH_2CH(CH_3)$, $CH_2CH(C_2H_5)$, $CH(CH_3)CH(CH_3)$, $(CH_2)_5$, $C(CH_3)_2CH_2CH(CH_3)$, $(CH_2)_6$],respectively. All these binuclear complexes have been characterised by elemental analysis, molecular weight measurements and spectroscopic(IR and NMR) studies.

Keywords: bis(N-phenylsalicylidene iminato)aluminium-di-μ-isopropoxo-di-isopropoxo-aluminium(III), glycolate, N-phenylsalicylidene iminate

Recently we have reported[1] the crystal structure of a unique heterocyclic derivative, $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2$**(I)** containing aluminium(III) atoms in six- and four- coordination states:



(I)

In order to examine the stability of the basic unit,[2] some replacement reactions of terminal alkoxy groups by a number of glycols have been carried out. We now report the results of these studies.

Results and discussion

Reactions of $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2$ with a number of glycols in 1:1 molar ratio in refluxing anhydrous benzene solution yielded the desired products as indicated below:

$$[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2 + HO\text{-}G\text{-}OH \longrightarrow [C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2\overline{Al(O\text{-}G\text{-}O)} + 2Pr^iOH$$

where G = $(CH_2)_2$, $CH_2CH(CH_3)$, $CH_2CH(C_2H_5)$, $CH(CH_3)$ $CH(CH_3)$, $(CH_2)_5$, $C(CH_3)_2CH_2CH(CH_3)$, $(CH_2)_6$.

All these reactions are quite facile and are quantitative. The liberated isopropanol could be removed readily in 4h as an azeotrope. The completion of the reaction was checked by estimating the liberated isopropanol present in the azeotrope. All these products are yellow foamy solids, hygroscopic in nature and are soluble in common organic solvents(benzene, chloroform, carbontetrachloride *etc.*), except those with ethylene glycol(partially soluble) and hexamethylene glycol(insoluble). Molecular weight measurements indicate the binuclear nature of these complexes in refluxing benzene (Table 1).

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

FAB mass spectra: The FAB mass spectrum of one of the representative derivative,

$$[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(O\text{-}CH_2(CH_2)_3CH_2\text{-}O)$$

indicates binuclear nature of the compound.[1]

IR spectra: The relevent IR spectral data for these new heterocyclic derivatives have been summarised in Table 2. A medium intensity band at 3300 cm^{-1} in the free ligand due to ν(OH) is absent in the IR spectra of these complexes, indicating deprotonation of the -OH groups of glycols and the formation of Al-O bond. This is further supported by the appearance of a new band in the region 655–700 cm^{-1} assigned to ν(Al-O).[3,4] A strong band is observed in the free Schiff's base, N-phenylsalicylidene imine, at 1625 cm^{-1}, characterstic of the azomethine(>C=N) group.[5] Coordination of N-Phenylsalicylidene imine to aluminium through the azomethine nitrogen atom is expected to reduce the electron density in the azomethine link and lower the (>C=N) absorption frequency. In the spectra of all the new complexes, the band due to ν(C=N) appears at lower wave number, 1610–1620 cm^{-1}, indicating coordination of the azomethine nitrogen to the aluminium atom.[6] This is further supported by the appearance of a new band at 610–640 cm^{-1} assigned to ν(Al-N)[3]. The absorption frequency of the glycolate ν C-O is observed[7] at 1000–1005 cm^{-1}. The Al-O-Al vibrations[8,9] are observed in the region 750–765 cm^{-1}.

^{1}H NMR spectra: Characterstic signals in the ^{1}H NMR spectra of all these derivatives are summarised in Table 3. The hydroxy group resonance present in the glycols is absent in the ^{1}H NMR spectra of all these complexes, indicating the deprotonation of the OH group and formation of Al–O bond. The presence of doublet for azomethine proton signal of the N-phenylsalicylidene imine group in the spectra of all these complexes, indicates the nonequivalent nature of the azomethine protons.[1] These signals appeared downfield as compared to the free Schiff's base,suggesting deshielding of the azomethine protons due to coordination to aluminium through the azomethine nitrogen.[1] A doublet observed at δ1.10–1.20 ppm and multiplet at δ3.92–4.02 ppm may be assigned to the methyl and methine protons of the isopropoxy groups.[10] The downfield shifts of protons on the carbon atom attached to oxygen of the glycol moieties indicate the bonding of oxygen to the aluminium atom.[7]

^{13}C NMR spectra: The ^{13}C NMR chemical shifts of these compounds are summarised in Table 4. The azomethine carbon signals are deshielded. Appearance of two signals at δ160.0–161.1 ppm and δ161.4–162.6 ppm indicates

Table 1 Synthetic and analytical data of $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2\overline{Al(O\text{-}G\text{-}O)}$

S.No.	Reactants(g) a. $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2$ b. HO-G-OH	Molar ratio	Pr^iOH(g) found (calcd.)	% Yield	% OPr^i	% Al	M.Wt. found (calcd.)
1	a. 2.26g b. $(CH_3)_2C(OH)CH_2$-$CH(CH_3)OH$ 0.39g	1:1	0.35 (0.38)	99	16.9 (17.3)	7.85 (7.93)	663 (680.58)
2	a. 2.70g b. $HO(CH_2)_6OH$ 0.48g	1:1	0.45 (0.47)	97	17.0 (17.4)	7.74 (7.93)	–
3	a. 3.90g b. $HO(CH_2)_2OH$ 0.36g	1:1	0.65 (0.68)	97.7	18.0 (18.9)	8.58 (8.64)	608 (624.58)
4	a. 2.22g b. $HOCH_2CH(CH_3)OH$ 0.24g	1:1	0.35 (0.39)	96.5	18.1 (18.4)	7.81 (7.91)	624 (638.58)
5	a. 2.31g b. $HO(CH_2)_5OH$ 0.35g	1:1	0.40 (0.40)	97.7	17.1 (17.7)	8.10 (8.10)	688 (666.58)
6	a. 3.56g b. $HOCH_2CH(C_2H_5)OH$ 0.48g	1:1	0.61 (0.62)	96.5	17.9 (18.1)	8.15 (8.27)	603 (652.58)
7	a. 2.50g b. $HOCH(CH_3)CH(CH_3)$-OH 0.33g	1:1	0.43 (0.44)	98.8	18.0 (18.1)	8.12 (8.27)	646 (652.58)

Table 2 IR spectra(cm^{-1}) for $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2\overline{Al(O\text{-}G\text{-}O)}$

S.No.	Compound	N-phenylsalicylidene imenato moiety ν C=C	ν C=N	Isopropoxy group ν C-O	Glycolate group ν C-O	ν Al-N	ν Al-O	ν Al-O-Al
1	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPr^i)_2Al[OC(CH_3)_2CH_2CHCH_3O]$	1480s	1620s	1075m	1005m	620w	675w	750w
2	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPr^i)_2Al[OCH_2(CH_2)_4CH_2O]$	1470s	1620s	1070m	1005m	625w	695w	750w
3	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPr^i)_2Al[O(CH_2)_2O]$	1475s	1610s	1075m	1005m	610w	695w	750w
4	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPr^i)_2Al[OCH(CH_3)CH_2O]$	1470s	1610s	1070m	1000m	615w	675w	750w
5	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPr^i)_2Al[OCH_2(CH_2)_3CH_2O]$	1480s	1610s	1075m	1005m	620w	700w	750w
6	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPr^i)_2Al[OCH(C_2H_5)CH_2O]$	1475s	1610s	1070m	1000m	640w	695w	765w
7	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPr^i)_2Al[OCH(CH_3)CH(CH_3)O]$	1475s	1610s	1075m	1000m	610w	655w	750w

Table 3 ^1H NMR Spectra(δ ppm) for $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2\overline{Al(O\text{-}G\text{-}O)}$

S.No.	Compound	N-phenylsalicylidene imenato moiety CH=N	Aromatic protons	Isopropoxy moiety CH3	OCH	Glycolate moiety OCH_2	OCH	Other protons
1	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPri)_2Al[OC(CH_3)_2CH_2CHCH_3O]$	8.55,d(2H) (2H)	6.47–7.35,m (18H)	1.11,d (12H)	3.96,m (2H)	–	4.10–4.34,b (1H)	1.43,b;(2H) 1.34,b(3H); 1.13,b(6H)
2	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPri)_2Al[OCH_2(CH_2)_4CH_2O]$	8.62,d(2H) (18H)	6.96–7.41,m	1.19,d (12H)	4.02,m (2H)	3.62,b (4H)	–	1.43,m (8H)
3	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPri)_2Al[O(CH_2)_2O]$	8.64,d (2H)	6.78–7.51,m (18H)	1.16,d (12H)	4.01,m (2H)	3.42,b (4H)	–	–
4	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPri)_2Al[OCH(CH_3)CH_2O]$	8.62,d (2H)	6.86–7.45,m (18H)	1.16,d (12H)	3.93,m (2H)	3.62,b (2H)	4.41,m (1H)	1.55,b (3H)
5	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPri)_2Al[OCH_2(CH_2)_3CH_2O]$	8.63,d (2H)	6.94–7.43,m (18H)	1.20,d (12H)	4.00,m (2H)	3.64,b (4H)	–	1.54,m(6H)
6	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(\mu\text{-}OPri)_2Al[OCH(C_2H_5)CH_2O]$	8.54,d (2H)	6.44–7.88,m (18H)	1.10,d (12H)	3.92,m (2H)	3.62,b (2H)	3.96,b (1H)	1.12,b(3H); 1.18,b(2H)
7	$[\{C_6H_4O\{CH{=}N(C_6H_5)\}\}]_2Al$-$(m\text{-}OPri)_2Al[OCH(CH_3)CH(CH_3)O]$	8.63,d (2H)	6.94–7.45,m (18H)	1.13,d (12H)	4.01,m (2H)	–	4.41–4.43,m (2H)	1.25,b (6H)

Table 4 ^{13}C NMR Spectra for $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(O\text{-}G\text{-}O)$

S.No.	Compound	N-phenylsalicylidene imenato moiety		Isopropoxy moiety		Glycolate moiety		
		CH=N	Aromatic carbons	CH_3	OCH	OCH_2	OCH	Other carbons
1.	$[\{C_6H_4O\{CH=N(C_6H_5)\}\}]_2Al$ - $(\mu\text{-}OPr^i)_2Al[OC(CH_3)_2CH_2CHCH_3O]$	160.1, 161.6	114.7,116.9, 118.2,122.6, 125.8,127.1, 128.4,133.1, 134.7,147.5	25.8	63.4	-	69.7	25.8,26.6, 26.6,51.1, 73.4
2.	$[\{C_6H_4O\{CH=N(C_6H_5)\}\}]_2Al$ - $(\mu\text{-}OPr^i)_2Al[O(CH_2)_2O]$	160.0, 161.5	115.1,117.2, 119.7,123.0, 126.4,128.5, 129.3,134,1, 135.9,148.0	26.0	63.4	62.2	-	-
3.	$[\{C_6H_4O\{CH=N(C_6H_5)\}\}]_2Al$ - $(\mu\text{-}OPr^i)_2Al[OCH(CH_3)CH_2O]$	160.1, 161.4	114.6,116.4, 118.0,122.9, 125.0,127.6, 128.1,133.9, 134.9,147.3	25.2	64.5	65.4	68.6	24.6
4.	$[\{C_6H_4O\{CH=N(C_6H_5)\}\}]_2Al$ - $(\mu\text{-}OPr^i)_2Al[OCH_2(CH_2)_3CH_2O]$	161.1, 162.0	115.3,117.7, 119.8,121.2, 124.7,128.3, 129.0,133.9, 135.2,149.1	25.9	64.0	58.4	-	26.5
5.	$[\{C_6H_4O\{CH=N(C_6H_5)\}\}]_2Al$ - $(\mu\text{-}OPr^i)_2Al[OCH(C_2H_5)CH_2O]$	160.2, 161.6	114.8,116.2, 118.1,122.6, 125.8,127.8, 128.3,133.0, 134.7,149.4	24.3	63.3	65.0	67.8	26.8,28.5
6.	$[\{C_6H_4O\{CH=N(C_6H_5)\}\}]_2Al$ - $(\mu\text{-}OPr^i)_2Al[OCH(CH_3)CH(CH_3)O]$	161.0, 162.6	115.7,117.8, 119.1,121.0, 125.7,128.0, 129.3,133.0, 135.6,148.4	25.2	64.2	-	68.9	29.6

nonequivalent nature of the azomethine carbon signals[1] as well as coordination through the azomethine nitrogen to the aluminium. The aromatic carbon signals of the N-phenylsalicylidene iminato moiety appear in the range δ114.6–149.4 ppm. Characterstic chemical shift values of the isopropoxy groups observed at δ24.3–26.0 ppm and δ63.3–64.5 ppm for methyl and methine carbons, respectively.[1,2,11]. All these derivatives show downfield shifts of $–OCH_2$ and –OCH carbon signals.These appear in the regions δ58.4–65.4 ppm and δ67.8–69.7 ppm, respectively, indicating bonding of oxygen of the glycol moieties to the aluminium atom.[7]

^{27}Al NMR spectra: ^{27}Al NMR spectra of two representative derivatives $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al[OC(CH_3)_2CH_2CHCH_3O]$ and $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al[OCH(C_2H_5)CH_2O]$ were recorded at 25°, 50° and 70°C in benzene d_6. Two broad signals at δ9.3, 9.9 ppm and δ 60.1, 51.9 ppm, were observed at 25°C.On increasing the temperature these become relatively sharp at 70°C, indicating hexa- and tetra- coordination around aluminium(III) atoms in these heterocyclic derivatives.[1] The spectra of the complex, $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al[OCH(C_2H_5)CH_2O]$, is shown in Fig. 1.

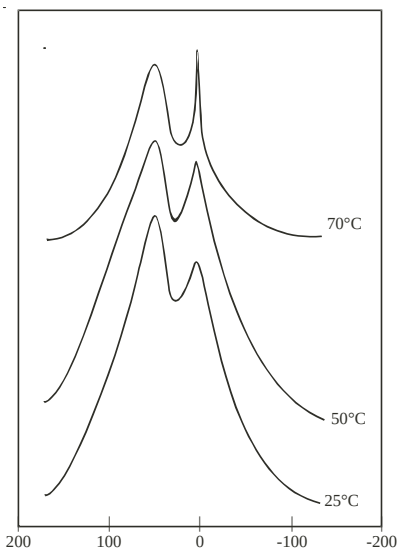

Fig.1 ^{27}Al NMR of $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al[OCH(C_2H_5)CH_2O]$ at 25°, 50° and 70°C.

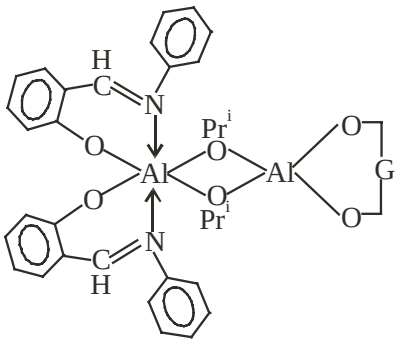

Fig.2 Proposed structure of $[C_6H_4O\{CH=N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(O\text{-}G\text{-}O)$, where G = $(CH_2)_2$, $CH_2CH(CH_3)$, $CH_2CH(C_2H_5)$, $CH(CH_3)CH(CH_3)$, $(CH_2)_5$, $C(CH_3)_2CH_2CH(CH_3)$, $(CH_2)_6$.

The above studies suggest the retentation of the basic unit of the precursor **(I)** in all the above derivatives as shown in Fig. 2.

Experimental

Moisture was carefully excluded throughout the experimental manipulations. Solvents were purified and dried according to the published procedures.[12] Glycols were distilled prior to use. The Schiff's base, N-phenylsalicylidene imine was prepared according to the reported methods.[13] Aluminium[12] was estimated gravimetrically as the oxinate.Isopropanol was estimated by chromate oxidimetric method.[12,14]

Infrared spectra were recorded as Nujol mulls on a Nicolet Magna 550 spectrophotometer in the range 4000–400cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol FX 90 Q spectrometer using TMS as an internal reference in $CDCl_3$ and $CHCl_3$, respectively. Molecular weight measurements were carried out by elevation in boiling point method using Beckmann's Thermometer (Einstellthermometer n-Beckmann, Labortherm-N, Skalenwart, 0.01K, made in GDR) fitted in glass assembly (supplied by JSGW, India)in anhydrous benzene under anhydrous conditions. The instrument was calibrated using samples of known molecular weights like naphthalene/benzophenone/benzil in anhydrous benzene($M = 1000\ K_b \times w/W \times \Delta T_b$, where M = molecular weight, w = weight of solute in g, K_b = molar elevation constant, W = weight of the solvent in g, ΔT_b = elevation in boiling point). FAB mass spectra was recorded on a Jeol SX 102/DA-6000 mass spectrometer/data system using argon/xenon(6KV,10mA) as the FAB gas and *m*-nitrobenzyl alcohol as the matrix.

Synthesis of $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al[OCH_2CH(CH_3)O]$*:* To a benzene solution (40ml) of $[C_6H_4O\{CH{=}N(C_6H_5)\}]_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2$(2.22g), 1,2-Propandiol (0.24g) dissolved in benzene(20ml) was added.The contents were refluxed on fractionating column for about 4 h. Completion of the reaction was checked by estimating the isopropanol collected azeotropically with benzene. After removing the volatile fractions under reduced pressure, a pale yellow foamy solid was obtained which was recrystallised from dichloromethan and n-hexane mixture (6:1), yield 96.5%.

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