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SYNTHESIS AND CHARACTERIZATION OF SOME UNIQUE HETEROCYCLIC DERIVATIVES CONTAINING ALUMINIUM ATOMS IN FOUR- AND SIX-COORDINATION STATES—I. BIS(ACETYLACETONATO) ALUMINIUM(III)-DI-μ-ISOPROPOXO-GLYCOLATO ALUMINIUM

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Abstract—Some mixed ligand complexes of aluminium of the type $[(acac)_2Al(\mu\text{-}OPr^i)_2\overline{Al(O\text{-}G\text{-}O)}]_n$ have been prepared by the reactions of $[Al(OPr^i)_2(acac)]_2$ and glycols (HO—G—OH) in 1 : 1 molar ratio in refluxing benzene (where acac = $CH_3COCHCOCH_3$; G = $(CH_2)_2$, $CH_2CH(CH_3)$, $C(CH_3)_2CH_2CH(CH_3)$, $CH_2CH(C_2H_5)CH(C_2H_7)$, $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$; $n = 1$ or 2). These are soluble in common organic solvents and show tetranuclear behaviour in chloroform except $[(acac)_2\overline{Al(\mu\text{-}OPr^i)_2Al\{OC(CH_3)_2CH_2CH(CH_3)O\}}]$, which is dinuclear. These derivatives have been characterized by elemental analysis, IR, ^1H, ^{13}C and ^{27}Al NMR spectral studies. Two types of aluminium sites, tetrahedral and octahedral, are present in the ^{27}Al NMR spectra of all these novel heterocyclic derivatives.

In view of the electron-deficient nature, alkoxides[1] and allied β-diketonate[2] derivatives of aluminium show varying degree of association, depending upon the nature (steric bulk and chelating characteristics) of the ligands.

The mixed ligand complexes of aluminium have received rather less attention.[3] Complexes of the type $[Al(OR)_2(acac)]_n$ (acac = $CH_3COCH COCH_3$; $n = 1$ for R = $SiPh_3$; $n = 2$ for R = $SiMe_3$, Pr^i, Bu^t; $n = 3$ for R = Pr^i) showed interesting structural features.[3–5]

An interesting feature of these derivatives appears to be that they prefer alkoxy bridged complexes of the type $[(acac)_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ with both octahedral and tetrahedral aluminium atoms, rather than a symmetric structure of the type $[(Pr^iO)(acac)Al(\mu\text{-}OPr^i)_2Al(acac)(OPr^i)]$ in which both the aluminium atoms are pentacoordinate. In view of this interesting behaviour with β-diketonate ligands, it was considered interesting to see how such derivatives react with bifunctional weaker chelating ligands like glycols. In this paper we report the reactivity of the dimeric complex,[5] $[(acac)_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$, with a variety of glycols.

RESULTS AND DISCUSSION

Reactions of $[Al(OPr^i)_2(acac)]_2$ with glycols in 1 : 1 molar ratio in refluxing benzene occur as follows:

$$[Al(OPr^i)_2(acac)]_2 + n(HO\text{—}G\text{—}OH) \xrightarrow{\text{Benzene}} [(acac)_2Al(\mu\text{-}OPr^i)_2\overline{Al(O\text{—}G\text{—}O)}]_n + 2nPr^iOH$$

[where acac = $CH_3COCHCOCH_3$; G = $(CH_2)_2$, $CH_2CH(CH_3)$, $C(CH_3)_2CH_2CH(CH_3)$, $CH_2CH(C_2H_5)CH(C_3H_7)$; $n = 1$ or 2].

The above reaction is quite facile and the liberated isopropanol was estimated in the benzene–isopropanol azeotrope collected.

Reactions of $[Al(OPr^i)_2(acac)]_2$ with glycols

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Table 1. IR data of $[(acac)_2Al(\mu\text{-}OPr^i)_2Al(O—G—O)]_n$(cm^{-1})

S. No.	Product $[(acac)_2Al(\mu\text{-}OPr^i)_2Al(O—G—O)]_n$	Acetylacetonato moiety $\nu(C\cdots O)$	Acetylacetonato moiety $\nu(C\cdots C)$	Isopropoxy group $\nu(C—O)$	Glycolato group $\nu(C—O)$	$\eta(Al—O—Al)$
1	$G = (CH_2)_2$	1575	1500	1075	1005	745
2	$G = CH_2CH(CH_3)$	1575	1500	1070	1005	750
3	$G = C(CH_3)_2CH_2CH(CH_3)$	1575	1505	1075	1000	745
4	$G = CH_2CH(C_2H_5)CH(C_3H_7)$	1575	1500	1070	1005	745
5	$G = (CH_2)_4$	1570	1495	1075	1005	750
6	$G = (CH_2)_5$	1570	1495	1070	1005	740
7	$G = (CH_2)_6$	1570	1500	1070	1005	750

(HO—G—OH) in 1 : 2 molar ratio led to uncharacterized products. It appears that the substitution of two terminal isopropoxy groups is quite facile and further substitution becomes increasingly slow, resulting in an incomplete removal of the fourth isopropoxy group even after prolonged refluxing (~5–6 h) conditions.

All the above derivatives $[(acac)_2Al(\mu\text{-}OPr^i)_2Al(O—G—O)]_n$ are highly soluble in benzene and common organic solvents, except those with ethylene glycol (partially insoluble) and hexamethylene glycol (insoluble). The derivative with 2-methyl-2,4-pentanediol was found to be dinuclear in chloroform, while all other derivatives with 1,2-propanediol, 1,4-butanediol, 1,5-pentanediol and 2-ethyl-1,3 hexanediol were found to be tetranuclear. The factors responsible for the dinuclear nature of $[(acac)_2Al(\mu\text{-}OPr^i)_1Al\{OC(CH_3)_2CH_2CH(CH_3)O\}]$ are not quite clear. It may be mentioned that out of a number of glycols studied, derivatives of metals[1] (e.g. Si, Sn, Ti, Zr, Nb, Fe etc.) with 2-methyl-2,4-pentanediol alone are soluble in organic solvents, which has again been explained in general terms in the lower state of association exhibited by the derivatives of this particular glycol.

IR spectra

Disappearance of a broad signal due to $\nu(O—H)$ in the spectra of these complexes indicates formation of an Al—O bond through deprotonation of glycol and acetylacetone ligands. Bands of medium intensity observed in the region 1000–1005 and 1070–1075 cm^{-1} may be assigned to $\nu(C—O)$ stretching vibrations of the glycol moiety and isopropoxy groups, respectively. Strong bands in the regions 1570–1575 and 1495–1505 cm^{-1} may be assigned to $\nu(C\cdots O)$ and $\nu(C\cdots C)$ stretching vibrations of the acetylacetonate moiety, respectively. The positions of these bands suggest a bidentate chelating nature of the acetylacetonate ligand. The $\nu(Al—O—Al)$ vibrations were observed[6] in their characteristic region 745–750 cm^{-1}. Important IR data are summarized in Table 1.

^{1}H *NMR spectra*

Characteristic signals in the ^{1}H NMR spectra of these derivatives are summarized in Table 2. The absence of —OH signals in these derivatives confirmed the deprotonation of the acetylacetone and glycol moieties. The downfield shifts of protons on the carbon atom attached to oxygen of the glycol moieties indicate its bonding to the aluminium atom. Signals at 1.94 and 5.48–5.54 ppm may be assigned to the methyl and methine protons of the acetylacetonate moiety, respectively. Similarly a doublet at 1.16 ppm and a multiplet at 4.01 ppm may be assigned to the methyl and methine protons of the isopropoxy group.

^{13}C *NMR spectra*

^{13}C NMR chemical shifts of these compounds are summarized in Table 3. ^{13}C NMR spectral data show the presence of the expected number of signals corresponding to the number of chemically different types of carbon atoms present in these compounds. Signals at 24.70–26.22, 100.71–101.03 and 190.20–192.53 ppm are assigned to methyl, methine and carboxyl carbons of the acetylacetonate moiety, respectively. Characteristic chemical shift values of the isopropoxy group observed at 25.57–26.54 and 62.90–63.66 ppm have been assigned to methyl and methine carbons, respectively. All these derivatives show downfield shifts of $—OCH_2$ and —OCH in the regions 58.46–65.42 and 68.60–69.74 ppm, respectively, indicating bonding of glycol moieties to the aluminium atom.

Table 2. ^{1}H NMR Chemical shifts (δ, ppm) of $[(acac)_2Al(\mu\text{-}OPr^i)_2\overline{Al(O—G—O)}]_n$[a]

S. No.	Product $[(acac)_2Al(\mu\text{-}OPr^i)_2\overline{Al(O—G—O)}]_n$	Acetylacetonato moiety —CH<	Acetylacetonato moiety —CH$_3$	Isopropoxy group —OCH<	Isopropoxy group —CH$_3$	Glycolato moiety —OCH$_2$	Glycolato moiety —OCH<	Other protons
1	G = $(CH_2)_2$	5.48,s (2H)	1.94,s (12H)	4.01,m (2H)	1.16,d (12H)	3.42,b (4H)	—	—
2	G = $CH_2CH(CH_3)$	5.54,s (2H)	1.94,s (12H)	4.01,m (2H)	1.16,d (12H)	3.57,b (2H)	4.01,m (1H)	0.98,b (3H)
3	G = $C(CH_3)_2CH_2CH(CH_3)$	5.51,s (2H)	1.94,s (12H)	4.01,m (2H)	1.16,d (12H)	—	3.94–4.53,b (1H)	1.67,b (2H) 1.34,b (3H) 1.00–1.80,b (6H)
4	G = $CH_2CH(C_2H_5)CH(C_3H_7)$	5.51,s (2H)	1.94,s (12H)	4.01,m (2H)	1.16,d (12H)	3.35,b (2H)	3.73,m (1H)	1.16–1.37,b (6H) 0.53–0.97,b (6H)
5	G = $(CH_2)_4$	5.48,s (2H)	1.94,s (12H)	4.01,m (2H)	1.16,d (12H)	3.57,b (4H)	—	1.43,m (4H)
6	G = $(CH_2)_5$	5.54,s (2H)	1.94,s (12H)	4.01,m (2H)	1.16,d (12H)	3.65,b (4H)	—	1.47,m (6H)
7	G = $(CH_2)_6$	5.54,s (2H)	1.94,s (12H)	4.01,m (2H)	1.16,d (12H)	3.62,b (4H)	—	1.43,m (8H)

[a] s = singlet, d = doublet, m = multiplet, b = broad.

Table 3. ^{13}C NMR chemical shifts (δ, ppm) of $[(acac)_2Al(\mu\text{-}OPr^i)_2\overline{Al—G—G—O)}]_n$

S. No.	Product $[(acac)_2Al(\mu\text{-}OPr^i)_2\overline{Al(O—G—O)}]_n$	Acetylacetonato moiety >C=O	Acetylacetonato moiety —CH<	Acetylacetonato moiety —CH$_3$	Isopropoxy group —OCH<	Isopropoxy group —CH$_3$	Glycolato moiety —OCH$_2$	Glycolato moiety —OCH<	Other carbons
1	G = $(CH_2)_2$	191.13	101.03	25.62	63.49	26.54	62.24	—	—
2	G = $CH_2CH(CH_3)$	191.03	101.03	24.70	63.60	25.57	65.42	68.60	24.60
3	G = $C(CH_3)_2CH_2CH(CH_3)$	192.53	100.71	26.17	62.91	26.44	—	69.74	26.60, 26.33, 25.89, 51.13, 73.46
4	G = $CH_2CH(C_2H_5)CH(C_3H_7)$	192.16	100.82	25.75	63.44	26.22	63.30	66.26	12.80, 13.00, 20.30, 22.21, 22.86
5	G = $(CH_2)_4$	191.18	101.03	25.51	63.66	26.54	60.53	—	26.27
6	G = $(CH_2)_5$	190.2	100.74	26.22	62.90	26.54	58.46	—	26.54

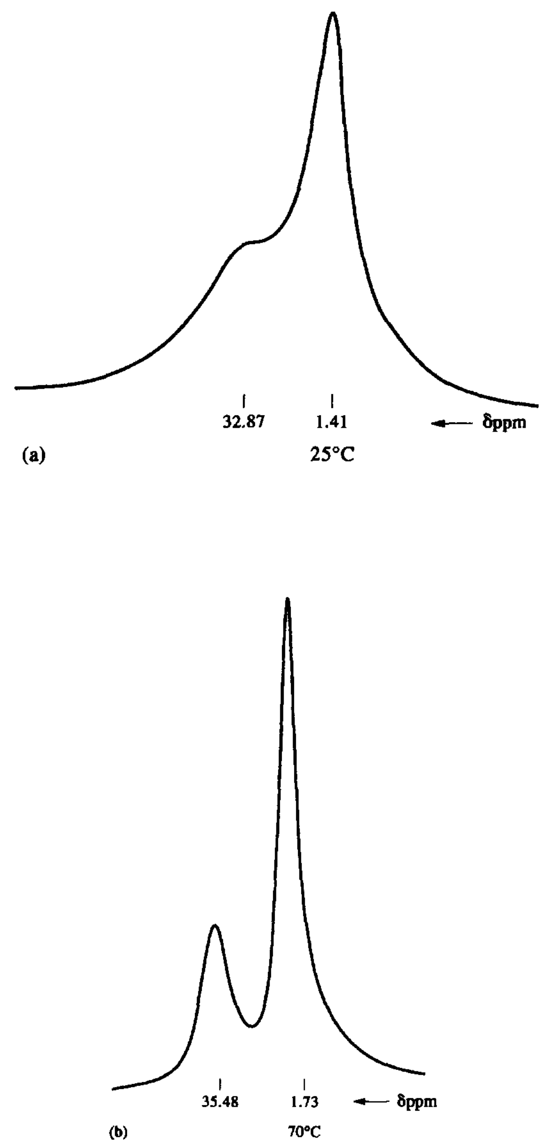

Fig. 1. ^{27}Al NMR spectrum of $[(acac)_2Al(\mu\text{-}OPr^i)_2Al\{OC(CH_3)_2CH_2CH(CH_3)O\}]$.

^{27}Al *NMR spectra*

Variable temperature ^{27}Al NMR spectra appear to be an important tool in differentiating tetrahedral and octahedral aluminium sites. The ^{27}Al NMR spectrum of $[(acac)_2Al(\mu\text{-}OPr^i)_2Al\{OC(CH_3)_2CH_2(CH_3)O\}]$ at 25°C exhibits a broad signal in the region -30 to 72 ppm. It consists of a sharp signal at 1.41 ppm and hump at 32.87 ppm (Fig. 1a). However, at elevated temperature (70°C) two distinct peaks, a sharp and intense peak at 1.73 ppm and a peak of relatively lesser intensity at 35.48 ppm, were observed (Fig. 1b), which indicate two types of aluminium sites, octahedral and tetrahedral respectively. The ^{27}Al NMR spectra of all the other compounds recorded at 25°C generally show broad signals. It is interesting that the complex $[(acac)_2Al(\mu\text{-}OPr^i)_2Al\{OCH_2CH(C_2H_5)CH(C_3H_7)O\}$ exhibits sharp signals at 1.72 and 33.44 ppm due to hexa- and tetra-coordinated aluminium sites, respectively, even at room temperature (Table 4).

Although in the absence of an X-ray crystal structure of at least one of the representative complexes, it is quite difficult to comment on the molecular structure, the above results suggest that the mixed ligand compounds of the type $[(acac)_2Al(\mu\text{-}OPr^i)_2Al(O{-}G{-}O)]_2$ and $[(acac)_2Al(\mu\text{-}OPr^i)_2Al(O{-}G{-}O)]$ have structures of the types shown in Fig. 2a and b, respectively.

EXPERIMENTAL

Moisture was carefully excluded throughout experimental manipulation. Aluminium isopropoxide was prepared as described by Mehrotra.[7]

Table 4. ^{27}Al NMR shifts (δ, ppm) of $[(acac)_2Al(\mu\text{-}OPr^i)_2Al(O{-}G{-}O)]_n$[a]

S. No.	G in product	Temp. (°C)	Shift, δ	Assignment
1	$CH_2CH(CH_3)$	25	+0.16 (s)	Octahedral
			+46.6 (b)	Tetrahedral
2	$C(CH_3)_2CH_2CH(CH_3)$	25	+1.4 (s)	Octahedral
			+32.8 (b)	Tetrahedral
		70	+1.7 (s)	Octahedral
			+35.5 (s)	Tetrahedral
3	$CH_2CH(C_2H_5)CH(C_3H_7)$	25	+1.7 (s)	Octahedral
			+33.4 (b)	Tetrahedral
4	$(CH_2)_4$	25	−45 to +57	Octahedral and tetrahedral
5	$(CH_2)_5$	25	−90 to +107	Octahedral and tetrahedral

[a] s = sharp, b = blunt.

Table 5. Physical and analytical data of $[(acac)_2Al(\mu\text{-}OPr^i)_2\overline{Al(O{-}G{-}O)}]_2$

S. No.	Reactants (g) $[Al(OPr^i)_2(acac)]_2$	Reactants (g) HO—G—OH	Molar ratio	Pr^iOH (g) found (calc.)	*n*-Membered heterocyclic ring	Yield	Found (calc.), %	Physical state and colour	Analysis, found (calc.), % Al	Analysis, found (calc.), % OPr^i	Mol. wt. (g) found (calc.)
1		G = $(CH_2)_2$	1 : 1	0.85	5	3.03	100	Pale yellow	12.7	26.8	—
	3.44	0.45		(0.85)		(3.03)		solid	(12.5)	(27.5)	
2		G = $CH_2CH(CH_3)$	1 : 1	0.99	5	3.64	100	Pale yellow	12.2	26.2	889
	4.01	0.63		(0.99)		(3.65)		solid	(12.4)	(26.6)	(444)
3		G = $C(CH_3)_2CH_2CH(CH_3)$	1 : 1	1.09	6	4.40	100	Pale yellow	11.0	24.1	479
	4.45	1.09		(1.09)		(4.43)		solid	(11.1)	(24.3)	(486)
4		G = $CH_2CH(C_2H_5)CH(C_3H_7)$	1 : 1	1.40	6	5.83	97	Pale yellow	10.4	22.3	1005
	3.44	0.45		(1.41)		(6.02)		solid	(10.5)	(23.0)	(514)
5		G = $(CH_2)_4$	1 : 1	1.11	7	4.32	100	Pale yellow	11.9	25.6	907
	4.61	0.86		(1.31)		(4.33)		solid	(11.8)	(25.8)	(458)
6		G = $(CH_2)_5$	1 : 1	1.59	8	6.29	98	Pale yellow	11.7	24.7	926
	6.64	1.42		(1.63)		(6.42)		solid	(11.4)	(25.0)	(472)
7		G = $(CH_2)_6$	1 : 1	1.06	9	4.15	95	Pale yellow	11.4	24.0	—
	4.38	1.06		(1.08)		(4.36)		solid	(11.1)	(24.3)	—

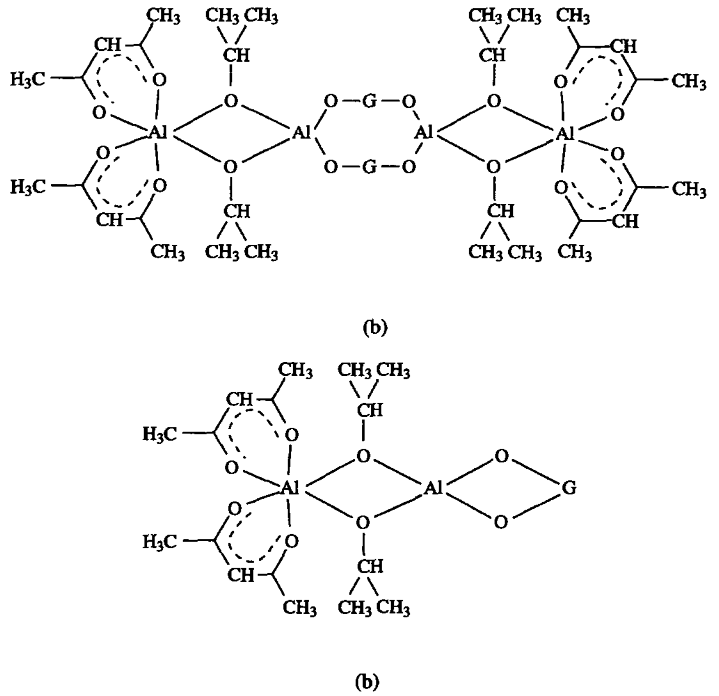

Fig. 2. (a) Structure of $[(acac)_2Al(\mu\text{-}OPr^i)_2Al(O—G—O)]_2$. (b) Structure of $[(acac)_2Al(\mu\text{-}OPr^i)_2Al(O—G—O)]$, where G = $C(CH_3)_2CH_2CH(CH_3)$.

All glycols and acetylacetone were distilled before use. Solvents were dried by reported methods.[8]

Aluminium was estimated gravimetrically as the oxinate. Isopropanol was estimated by chromate oxidimetric methods.[9] Isopropoxy groups in the products were estimated by hydrolysing them and collecting the liberated isopropanol azeotropically with benzene.

IR spectra were recorded as Nujol mulls using KBr and CsI plates in the range 4000–200 cm^{-1} on a Perkin–Elmer spectrophotometer model 577. ^1H NMR spectra were recorded using TMS as an internal reference, while ^{13}C and ^{27}Al NMR spectra were recorded in benzene solution using D_2O locks. Molecular weight measurements were carried on a Knauer Vapour Pressure Osmometer in chloroform at 45°C.

$[Al(OPr^i)_2(acac)]_2$ was prepared by a slightly modified reported method.[5] It is a colourless liquid obtained by 1 : 1 reaction of $Al(OPr^i)_3$ and acetylacetone in refluxing benzene for ~2 h. The completion of reaction was checked by estimating the isopropanol liberated azeotropically with benzene. Found: Al, 11.0; OPr^i, 48.2. Requires Al, 11.0; OPr^i, 48.4%.

Reactions of $[Al(OPr^i)_2(acac)]_2$ with glycols were carried out using the same general procedures; therefore, only one representative reaction is described in detail and the data have been summarized in Table 5.

Reaction of $[Al(OPr^i)_2(acac)]_2$ *with* $HOCH_2CH(CH_3)OH$

To a benzene solution (~60 cm^3) of $[Al(OPr^i)_2(acac)]_2$ (4.0094 g, 8.21 mmol), 1,2-propanediol (0.6270 g, 8.24 mmol) was added dropwise. The contents were refluxed for about 2–3 h. Completion of the reaction was checked by estimating the isopropanol collected azeotropically with benzene. A pale yellow solid was obtained in good yield, after the removal of the excess solvent under reduced pressure.

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