Synthesis and Structural Elucidation of Some Novel Penta-Coordinated Mono-Di-Ethylaluminium(III) Complexes with Internally Functionalized Oximes

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ABSTRACT

Reactions of triethylaluminium etherate adduct ($\text{Et}_3\text{Al} \cdot \text{Et}_2\text{O}$) with internally functionalized oximes $\{\text{Ar}(\text{R})\text{C}=\text{NOH}\}$ in 1:1 and 1:2 molar ratios in diethyl ether yielded mono- and di-ethylaluminium(III) complexes of the types $\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{R})\text{Ar}\}$ and $\text{EtAl}\{\text{ON}=\text{C}(\text{R})\text{Ar}\}_2$ (where $\text{R} = \text{CH}_3$ or H and $\text{Ar} = \text{C}_5\text{H}_4\text{N}-2$, $\text{C}_4\text{H}_3\text{S}-2$, $\text{C}_4\text{H}_3\text{O}-2$). All the above complexes are soluble in common organic solvents, which have been characterized by elemental analysis, IR and multinuclear NMR (^1H , ^{13}C and ^{27}Al). Spectral studies. The ^{27}Al NMR chemical shift values indicate penta-coordination around aluminium(III) atom in both the above types of complexes. Molecular weight measurements in refluxing benzene exhibit monomeric and dimeric nature for the monoethyl and the diethyl complexes, respectively, which gets further support from the FAB mass spectra of the two representative compounds, $\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\}$ and $\text{EtAl}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2\}_2$.

INTRODUCTION

Organoaluminium compounds are used widely as reagents in organic synthesis and as catalysts in many synthetic processes /1,2/. For a better understanding of their role in synthesis and catalysis, it is essential to know the coordination ability of aluminium in such types of derivatives. Generally coordination numbers four and six are more common /3-7/ than five /8-10/ in such compounds.

It has also been shown recently /11-16/ that aluminium atoms in binuclear metallo-organic complexes usually acquire unsymmetrical structures containing aluminium(III) atoms in four- and six-coordination states rather than a symmetrical five-coordinated structure /13/.

In view of the increasing interest in penta-coordinated organoaluminium(III) complexes /8-10/, we have also reported probably the first known example of a five-coordinated heteroleptic metallo-organic compound of $\text{Al}(\text{III})$: $[\{\text{C}_6\text{H}_4\text{O}(\text{CH}=\text{NC}_6\text{H}_5)\}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\}]$ /17/.

Further, amongst multidentate organic ligands, oximes have been known to have biological functions /18-20/ such as growth regulatory, antimicrobial and fungicidal activities. The oxime groups are also present in the althiomycin antibiotic molecule /21/.

In view of the above, we report here the chemistry of a series of ethylaluminium(III) complexes with internally functionalized oximes.

MATERIALS AND METHODS

All the experimental manipulations were carried out under strictly inert conditions in anhydrous argon atmosphere. The solvents and reagents were purified by conventional techniques. The $\text{Et}_3\text{Al}.\text{Et}_2\text{O}$ /22/ and oximes /23/ were synthesized and purified according to literature methods. Aluminium was estimated gravimetrically as oxinate /24/. Microanalyses were carried out on a Perkin Elmer-C, H, N & S II series analyzer. The IR spectra were recorded as Nujol mull on a Nicolet Magna-550 spectrometers in the range $4000\text{--}400\text{ cm}^{-1}$. ^1H , ^{13}C and ^{27}Al NMR spectra were recorded in 5 mm NMR tubes as freshly prepared CDCl_3 solutions on a Bruker DPX-300 spectrometer operating at 300, 75.5 and 111.9 MHz, respectively. Spectra were referenced with internal chloroform peak ($\delta 7.26\text{ ppm}$ for ^1H and 77.0 ppm for ^{13}C). FAB mass spectra were recorded on a Jeol SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 KV, 10MA) as the FAB gas, m-nitrobenzyl alcohol was used as the matrix. Molecular weight measurements were carried out by elevation in boiling point method, using a Beckmann's Thermometer fitted in a glass assembly in anhydrous benzene. The instrument was calibrated using samples of known molecular weight like naphthalene/benzophenone/benzil in anhydrous benzene ($M = 1000 K_b \cdot w / \Delta T_b \cdot W$, where M = molecular weight, w = weight of solute in gms, K_b = molar elevation constant, W = weight of solvents in gms, ΔT_b = elevation in boiling point).

Preparation of $\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2\}$

A solution of $\text{Et}_3\text{Al}.\text{Et}_2\text{O}$ (1.75g, 9.32 mmol) in 20 ml of anhydrous diethyl ether was slowly added to an ethereal solution of $\text{HON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2$ (1.27 gm, 9.32 mmol) under argon atmosphere. The reaction mixture was stirred at room temperature for 4 h. After stirring, the solvents were evaporated under vacuum and dried to give a yellow-coloured paste. The product was washed ($2 \times 10\text{ ml}$) with petroleum ether. Further, it was dried in vacuum to afford a yellow solid (yield 98%). This was recrystallized from a mixture of dichloromethane and n-hexane (7:1).

All other diethylaluminium(III) complexes (3, 5, 7 and 9) were prepared using a similar route. Their synthetic details and analytical data are summarized in Table I.

Preparation of $\text{EtAl}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2\}$

An ethereal solution of $\text{Et}_3\text{Al}.\text{Et}_2\text{O}$ (1.29 g, 6.85 mmol) was gradually added to another ethereal solution of $\text{HON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2$ (1.87 gm, 13.7 mmol) under argon atmosphere. The contents were allowed to remain at room temperature for 4 h. After removal of the solvent under reduced pressure, the product obtained was washed ($2 \times 10\text{ ml}$) with n-hexane. Further it was dried under vacuum to afford a yellow solid (yield 98%).

The product obtained was recrystallized from a mixture of dichloromethane and n-hexane (7:1).

Table I
Synthetic and analytical data of ethylaluminium(III) complexes

S. No.	Complexes	Yield (%)	Colour and State	Elemental analysis (%)				M.Wt. Found (Calcd.)	M.P. (°C)
				C	H	N	Al		
1.	Et ₃ Al{ON=C(Me)C ₅ H ₄ N-2}	98	Yellow solid	58.8 (60.0)	7.75 (7.78)	12.5 (12.7)	12.0 (12.3)	447 (220)	242 dec.
2.	EtAl{ON=C(Me)C ₅ H ₄ N-2} ₂	98	Yellow Solid	58.4 (58.9)	5.84 (5.87)	17.0 (17.2)	8.24 (8.27)	320 (326)	218
3.	Et ₂ Al{ON=C(Me)C ₄ H ₃ S-2}	93	Yellow Solid	53.0 (53.3)	7.10 (7.16)	6.18 (6.22)	11.9 (12.0)	460 (225)	148 dec.
4.	EtAl{ON=C(Me)C ₄ H ₃ S-2} ₂	93	Cream Solid	49.4 (49.9)	5.00 (5.09)	8.18 (8.33)	8.00 (8.03)	328 (336)	135
5.	Et ₂ Al{ON=C(Me)C ₄ H ₃ O-2}	96	Yellow Solid	57.0 (57.4)	7.68 (7.71)	6.67 (6.69)	12.8 (12.9)	422 (209)	192 dec.
6.	EtAl{ON=C(Me)C ₄ H ₃ O-2} ₂	95	Brown Solid	55.1 (55.3)	5.60 (5.63)	9.06 (9.21)	8.81 (8.87)	296 (304)	130
7.	Et ₂ Al{ON=CH(C ₄ H ₃ S-2)}	96	White Solid	50.8 (51.2)	6.62 (6.68)	6.60 (6.63)	12.8 (12.8)	418 (211)	252 dec.
8.	EtAl{ON=CH(C ₄ H ₃ S-2)} ₂	96	White Solid	46.2 (46.7)	4.21 (4.25)	9.00 (9.08)	8.75 (8.77)	298 (308)	254 dec.
9.	Et ₂ Al{ON=CH(C ₄ H ₃ O-2)}	98	White Solid	54.8 (55.4)	7.21 (7.23)	7.02 (7.18)	13.8 (13.8)	400 (195)	220 dec.
10.	EtAl{ON=CH(C ₄ H ₃ O-2)} ₂	98	White Solid	52.0 (52.2)	4.70 (4.74)	10.1 (10.2)	9.75 (9.77)	264 (276)	234 dec.

Other remaining monoethylaluminium(III) complexes (**4**, **6**, **8** and **10**) were prepared using a similar route. Their synthetic details and analytical data are summarized in Table I.

RESULTS AND DISCUSSION

All the above reactions were carried out under strictly anhydrous and inert atmosphere. Reactions of Et₃Al.Et₂O with the corresponding internally functionalized oximes in 1:1 and 1:2 molar ratios in diethyl ether afforded products of the types, Et₂Al{ON=C(R)Ar} and EtAl{ON=C(R)Ar}₂ (where R = CH₃ or H and Ar = C₅H₄N-2, C₄H₃S-2, C₄H₃O-2). The general reaction may be illustrated schematically as:

(where R = CH₃ or H and Ar = C₅H₄N-2, C₄H₃S-2, C₄H₃O-2, n = 1 or 2)

All the above complexes are yellow, brown or white solids (Table I) and are soluble in common organic solvents. These compounds were purified by recrystallization from a mixture of dichloromethane and n-hexane. Molecular weight measurements in refluxing benzene exhibit monomeric and dimeric nature for the monoethyl and the diethyl complexes, respectively.

IR Spectra

Tentative assignments of some of the important IR bands have been made and are summarized in Table II. Broad stretching vibrations at $\sim 3300\text{ cm}^{-1}$ due to $-\text{OH}$ group of the free oximes disappeared in the IR spectra of these derivatives, suggesting the deprotonation of $-\text{OH}$ group and formation of Al-O bond. Formation of Al-O /25,26/ bond is further supported by the appearance of a weak-to-strong intensity band in the region $708\text{--}766\text{ cm}^{-1}$. The appearance of $\nu\text{N-O}$ /27/ and $\nu\text{C=N}$ /28/ stretching vibrations towards lower frequencies ($\sim 20\text{ cm}^{-1}$) further supports the formation of Al-O bond. The appearance of $\nu(\text{C=N})$ stretching frequencies at lower wave number, as compared to the free ligand moieties, indicates the coordination of aluminium to the nitrogen atom of the ligand. This was further confirmed by the appearance of a new weak-to-strong intensity band in the region $641\text{--}700\text{ cm}^{-1}$, which may be assigned to $\nu(\text{Al-N})$ mode /12,13,16/. The weak-to-strong intensity bands in the region $550\text{--}616\text{ cm}^{-1}$ were assigned to $\nu(\text{Al-C})$. The Al-O-Al /12,13/16/ vibrations have been observed in the region $766\text{--}841\text{ cm}^{-1}$.

Table II
Some relevant IR spectral data of ethylaluminium(III) complexes

S. No.	Compound	Oximate moiety		$\nu\text{Al-C}$	$\nu\text{Al-O}$	$\nu\text{Al-N}$	$\nu\text{Al-O-Al}$
		$\nu\text{N-O}$	$\nu\text{C=N}$				
1.	$\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{Me})\text{C}_3\text{H}_4\text{N-2}\}$	916m	1550m	600s	733s	650s	783s
2.	$\text{EtAl}\{\text{ON}=\text{C}(\text{Me})\text{C}_3\text{H}_4\text{N-2}\}_2$	916w	1583w	583w	766w	700m	-
3.	$\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{Me})\text{C}_4\text{H}_3\text{S-2}\}$	900m	1566w	583m	716s	641m	783m
4.	$\text{EtAl}\{\text{ON}=\text{C}(\text{Me})\text{C}_4\text{H}_3\text{S-2}\}_2$	883w	1566w	550w	716s	675m	-
5.	$\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{Me})\text{C}_4\text{H}_3\text{O-2}\}$	891w	1541w	600w	716s	675w	766w
6.	$\text{EtAl}\{\text{ON}=\text{C}(\text{Me})\text{C}_4\text{H}_3\text{O-2}\}_2$	900s	1566m	600s	733vs	650s	-
7.	$\text{Et}_2\text{Al}\{\text{ON}=\text{CH}(\text{C}_4\text{H}_3\text{S-2})\}$	891vs	1583s	616vs	708vs	666vs	841vs
8.	$\text{EtAl}\{\text{ON}=\text{CH}(\text{C}_4\text{H}_3\text{S-2})\}_2$	883vs	1600s	616vs	716vs	666vs	-
9.	$\text{Et}_2\text{Al}\{\text{ON}=\text{CH}(\text{C}_4\text{H}_3\text{O-2})\}$	875vs	1591s	600vs	750vs	650vs	800s
10.	$\text{EtAl}\{\text{ON}=\text{CH}(\text{C}_4\text{H}_3\text{O-2})\}_2$	866vs	1600s	583vs	733vs	675s	-

 ^1H NMR Spectra

The important signals in ^1H NMR spectra of these derivatives are summarized in Table III. A comparison of the spectra of the free oximes with the spectra of the corresponding derivatives shows the absence of $-\text{OH}$ signals, indicating deprotonation of the hydroxy group of the oxime ligands and formation of Al-O bond.

Table IH
NMR (^1H , ^{13}C and ^{27}Al) spectral data of ethylaluminium(III) complexes

Complex No.	^1H NMR in δ ppm		^{13}C NMR in δ ppm		^{27}Al NMR in δ ppm
	Ethyl moiety	Oximate moiety	Ethyl moiety	Oximate moiety	
1.	0.06 (m, CH_2); 1.07 (t, CH_3)	2.12 (s, CH_3); 7.35 (t, H-4); 7.57 (t, H-5); 8.05 (d, H-3); 8.62 (br, H-6)	0.92 (CH_2); 18.3 (CH_3)	9.65 (CH_3); 119.7 (C-5); 120.2 (C-3); 121.8 (C-4); 125.1 (C-6); 140.4 (C-2); 148.3 (C=N)	68.3
2.	0.09 (m, CH_2); 1.23 (t, CH_3)	2.12 (s, CH_3); 7.38 (t, H-4); 7.79 (br, H-5); 8.52 (br, H-3); 9.38 (br, H-6)	10.4 (CH_2); 17.8 (CH_3)	15.2 (CH_3); 120.1 (C-5); 122.5 (C-3); 134.9 (C-4); 147.8 (C-6); 148.5 (C-2); 149.5 (C=N)	66.6
3.	0.44 (br, CH_2); 1.72 (br, CH_3)	2.64 (s, CH_3); 7.51 (d, H-4); 7.73 (s, H-3); 7.82 (s, H-5)	1.11 (CH_2); 18.2 (CH_3)	12.1 (CH_3); 126.1 (C-4); 126.7 (C-3); 127.0 (C-5); 140.0 (C-2); 152.5 (C=N)	70.0
4.	0.85 (m, CH_2); 1.33 (t, CH_3)	2.18 (s, CH_3); 6.94 (br, H-4); 7.29 (s, H-3); 7.38 (s, H-5)	13.0 (CH_2); 18.2 (CH_3)	14.0 (CH_3); 126.1 (C-4); 126.7 (C-3); 130.1 (C-5); 141.4 (C-2); 152.5 (C=N)	65.0
5.	0.91 (br, CH_2); 1.33 (br, CH_3)	2.18 (s, CH_3); 6.59 (d, H-4); 7.41 (s, H-3); 7.54 (br, H-5)	13.9 (CH_2); 17.6 (CH_3)	11.1 (CH_3); 109.0 (C-4); 111.1 (C-3); 142.5 (C-5); 147.8 (C-2); 150.9 (C=N)	70.0
6.	0.88 (m, CH_2); 1.26 (br, CH_3)	2.15 (s, CH_3); 6.27 (br, H-4); 6.53 (br, H-3); 7.29 (br, H-5)	11.5 (CH_2); 17.6 (CH_3)	12.1 (CH_3); 108.3 (C-4); 111.1 (C-3); 142.6 (C-5); 148.8 (C-2); 151.7 (C=N)	63.7
7.	0.09 (m, CH_2); 1.17 (t, CH_3)	7.29 (s, CH); 7.41 (t, H-4); 7.60 (d, H-3); 7.70 (d, H-5)	0.92 (CH_2); 18.5 (CH_3)	126.4 (C-4); 131.4 (C-3); 131.6 (C-5); 139.8 (C-2); 150.4 (C=N)	70.4
8.	0.09 (m, CH_2); 1.26 (br, CH_3)	7.35 (s, CH); 7.48 (t, H-4); 7.54 (d, H-3); 7.79 (d, H-5)	0.89 (CH_2); 18.0 (CH_3)	125.7 (C-4); 131.4 (C-3); 131.6 (C-5); 139.9 (C-2); 151.8 (C=N)	71.1
9.	0.95 (m, CH_2); 1.20 (br, CH_3)	6.49 (br, H-4); 7.29 (s, CH); 7.41 (br, H-3); 7.73 (br, H-5)	0.81 (CH_2); 18.3 (CH_3)	111.2 (C-4); 112.4 (C-3); 144.2 (C-5); 146.9 (C-2); 152.0 (C=N)	67.9
10.	0.12 (m, CH_2); 1.20 (t, CH_3)	6.40 (br, H-4); 7.29 (s, CH); 7.51 (br, H-3); 7.76 (br, H-5)	0.81 (CH_2); 18.2 (CH_3)	111.7 (C-4); 112.1 (C-3); 144.3 (C-5); 146.6 (C-2); 155.0 (C=N)	71.0

*Complexes no. as in Table I

This gets support from the significant upfield shifting of the positions of methyl and CH signals of the ligand moiety. However, no appreciable shift was observed in the position of ring protons of the functionalized oximes, ruling out the possibility of coordination through the hetero (N, O or S) atom. ^1H NMR spectra of these derivatives exhibit characteristic peaks and peak multiplicities for Et-Al and ligand protons /6, 29, 30/. In the ^1H NMR spectra of the complexes, the CH_2 and CH_3 protons of Et-Al group appear in the range δ 0.06-0.95 ppm and δ 1.07-1.72 ppm, respectively. The methyl as well as CH proton resonance of ligands are shielded on complexation. Shielding effect is greater in 1:2 complexes as compared to 1:1 complexes. Other resonances are almost unaffected and appear at their expected positions (Table III).

^{13}C NMR Spectra

The mode of bonding suggested above has also been confirmed by the ^{13}C NMR spectral data (Table III). In the ^{13}C NMR spectra of these complexes the CH_2 and CH_3 carbon signals of EtAl group appear in the ranges δ 0.81-13.9 ppm and δ 17.6-18.5 ppm, respectively. The $\text{C}=\text{N}$ carbon resonance of ligands is shielded on complexation as compared to the free oximes, which suggests that there may be coordination of aluminium through nitrogen atom as evinced by IR spectra. The carbon signals due to heterocyclic rings of the functionalized oximes have been observed at their expected positions and do not show any appreciable shift. This further supports the view that heteroatom (N, O or S) does not take part in bonding.

FAB Mass Spectra

The FAB mass spectra of two representative compounds, $\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\}$ and $\text{EtAl}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2\}_2$, indicate that the largest number of mass ion peaks are present in both the monomeric and dimeric form. However, the FAB mass spectra of the above compounds show fragmentation ion peaks with higher $m/4$ than the molecular ion, suggesting that the complexes are associated in the solid state.

The characteristic fragmentation ion peaks of the compounds $\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\}$ and $\text{EtAl}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2\}_2$ are summarized in Schemes 1 and 2.

Scheme 1: FAB Mass spectral data for $\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\}$

m/e	
488	$\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\} \cdot (\text{C}_4\text{H}_3\text{S}-2)_3 \cdot \text{CH}_2$
391	$\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\} \cdot (\text{C}_4\text{H}_3\text{S}-2)_2$
308	$\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\} \cdot \text{C}_4\text{H}_3\text{S}-2$
295	$\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\} \cdot \text{C}_3\text{H}_2\text{S}$
232	$\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\} \cdot \text{C}_3$
220	$\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_4\text{H}_3\text{S}-2\} \cdot \text{C}_2$
157	$\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{CS}\}$
142	$\text{CH}_2\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{CS}\}$
124	$\text{CH}_2\text{Al}\{\text{N}=\text{C}(\text{CH})\text{CS}\}$

Scheme 2: FAB Mass spectral data for $\text{EtAl}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2\}_2$

m/4	
460	$\text{EtAl}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2\}_2 \cdot \text{C}_5\text{H}_4\text{N} \cdot \text{C}_3\text{H}_6\text{N}$
443	$\text{EtAl}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2\}_2 \cdot \text{C}_5\text{H}_4\text{N} \cdot \text{C}_3\text{H}_3$
391	$\text{EtAl}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_5\text{H}_4\text{N}-2\}_2 \cdot \text{C}_5\text{H}_5$
307	$\text{EtAl}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_3\}_2 \cdot \text{C}_5\text{H}_5$
242	$\text{EtAl}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}_3\}_2$
165	$\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}\}_2$
153	$\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}\}\{\text{ON}=\text{C}(\text{CH}_3)\}$
136	$\text{Al}\{\text{ON}=\text{C}(\text{CH}_3)\text{C}\}\{\text{N}=\text{C}(\text{CH}_2)\}$
120	$\text{Al}\{\text{N}=\text{C}(\text{CH}_3)\text{C}\}\{\text{N}=\text{C}(\text{CH}_2)\}$
107	$\text{Al}\{\text{N}=\text{C}(\text{CH}_3)\text{C}\}\{\text{N}=\text{CH}\}$

^{27}Al NMR Spectra

^{27}Al NMR spectra of these complexes exhibit a broad signal at 63.7-71.1 ppm, suggesting penta-coordination around aluminium(III) atom /8,31,32/.

CONCLUSION

Attempts to get good quality crystals of at least one representative compound for single crystal X-ray diffraction studies were not successful.

It is interesting to mention here that single crystal structure of an oximato complex, $[(\text{acac})_2\text{Zr}\{\text{ON}=\text{C}(\text{Me})\text{C}_5\text{H}_4\text{N}-2\}_2]$, indicates clearly that the oximato ligands bind Zr atom via N and O in a dihepto (η 2-N,O) manner /33/.

In view of the above studies as well as the observed dimeric nature of 1:1 and monomeric nature of 1:2 complexes, and the absence of the coordination through hetero (N, O or S) atom, the following plausible structures may be proposed tentatively for the types of derivatives (2a and 2b).

Fig.: Proposed structures for $\text{Et}_2\text{Al}\{\text{ON}=\text{C}(\text{R})\text{Ar}\}$ (2a) and $\text{EtAl}\{\text{ON}=\text{C}(\text{R})\text{Ar}\}_2$ (2b)

(where $\text{R} = \text{CH}_3$ or H and $\text{Ar} = \text{C}_5\text{H}_4\text{N}-2$, $\text{C}_4\text{H}_3\text{S}-2$, $\text{C}_4\text{H}_3\text{O}-2$)

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