SYNTHESES AND STRUCTURAL ELUCIDATIONS OF SOME NOVEL HETEROCYCLIC COMPOUNDS CONTAINING ALUMINIUM(III) ATOMS AT BRIDGE-HEAD POSITIONS.1.REACTIONS OF BIS(ACETYLACETONATO)ALUMINIUM(III)-DI-μ-ISOPROPOXO-DI-ISOPROPOXO ALUMINIUM(III) WITH SIMPLE AND INTERNALLY FUNCTIONALLIZED OXIMES

Nikita Sharma, Rajnish K.Sharma and Rakesh Bohra*

Department of Chemistry, University of Rajasthan, Jaipur-302 004, India
rkbohra@satyam.net.in

Abstract

Reactions of bis(acetylacetonato)aluminium(III)-di-μ-isopropoxo-di-isopropoxo-aluminium(III), $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ with simple and internally functionallized oximes (RR'C=NOH) in 1:1 and 1:2 molar ratios in refluxing anhydrous benzene yielded binuclear complexes of the types, $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(ON{=}CRR')(OPr^i)]$ and $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(ON{=}CRR')_2]$ (where R = R' = CH_3 or C_6H_5; R = CH_3 , R' = $CH_2C_6H_5$; R = CH_3, R'= C_4H_3O-2, C_4H_3S-2, C_5H_4N-2),respectively.All these binuclear derivatives have been characterised by elemental analyses, molecular weight measurements, IR and (^1H and ^{13}C)NMR spectral studies.The binuclear nature of all these compounds gets support from the FAB mass spectrum of a representative compound,$[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_2]$ and ^{27}Al NMR spectrum of $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al\{ON{=}C(CH_3)C_4H_3S\text{-}2\}_2]$.

Introduction

The chemistry of metal alkoxides is quite facinating due to their interesting structural features(1-5) as well as their applicability as potential precursors for low temperature metal-oxide based advanced materials(6-8). The interest in these precursors is growing continously and this has recently led to the synthesis of alkoxide based heteroleptic derivatives containing oxo or chelating ligands(9-12).

It is worthwhile to mention here that in the case of the mixed aluminium(alkoxide)-β-diketonate systems both steric as well as electronic factors play a vital role(13).For example, the structure of the dimer $[Al(OPr^i)_2\{CH_3C(O)CHC(O)CH_3\}]_2$ is unique, as it prefers unsymmetrical 6- and 4- coordination geometries around the two aluminium(III) atoms,(13) $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ rather than the symmetrical 5-coordination geometries, $[\{CH_3C(O)CHC(O)CH_3\}(OPr^i)Al(\mu\text{-}OPr^i)_2Al\{CH_3C(O)CHC(O)CH_3\}(OPr^i)]$.

In view of above we carried out a systematic study on the syntheses and structural elucidations of some novel heterocyclic compounds containing aluminium(III) atoms at bridge-head positions(14-17).In this paper, we report the preparation and characterization of some novel heterocyclic compounds of aluminium(III) by the reaction of $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ with simple and internally functionalized oximes.(18)

Materials and Methods

All the chemicals were of reagent grade and dried prior to use.Moisture was carefully excluded throughout the experimental manipulations.Aluminium isopropoxide was prepared as described in the literature(1).Aluminium was estimated gravimetrically as the oxinate(19).Nitrogen and isopropanol were estimated as reported in the literature(19).The starting material $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ was prepared by the reported method(15).

Infrared spectra were recorded as Nujol mull on a Nicolet Magna- 550 spectrophotometer in the range 4000-400cm^{-1}.^1H and ^{13}C NMR spectra were recorded on a Jeol FX 90Q spectrometer in $CDCl_3$ using TMS as an internal reference. ^{27}Al NMR spectral study has been carried out in toluene using aluminium nitrate as a standard reference. 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, m-nitrobenzyl alcohol was used as the matrix. Molecular weight measurements were carried out by elevation in boiling point method using Beckmann's Thermometer(Einstellthermometer n-Beckmann,Labortherm-N,Skalewert, 0.01K. made in GDR) fitted in a glass assembly(supplied by JSGW, India) in anhydrous benzene.All manipulations were carried out under anhydrous conditions using anhydrous $CaCl_2$ guard/side tubes.The instrument was calibrated using samples of known molecular weights like Naphthalene/Benzophenone/Benzil in anhydrous benzene($M = 1000 \times K_b \times w/ W \times \Delta T_b$, where M = molecular weight, w = weight of solute in gms, K_b = molar elevation constant, W = weight of solvent in gms, ΔT_b = elevation in boiling point) .

Preparation of $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al\{ON{=}C(CH_3)C_4H_3O\text{-}2\}(OPr^i)]$

The reaction mixture containing $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ (2.11g,4.43mmol) and $[2\text{-}OC_4H_3C(CH_3){=}NOH]$ (0.54g,4.34mmol) in anhydrous benzene (~60ml) was refluxed for ~ 4h under a fractionating column. The liberated isopropanol was continuously fractionated out azeotropically with benzene. Progress as well as completion of the reaction was checked by the estimation of isopropanol in the azeotrope by oxidemetric titration. After stripping of the excess solvent under reduced pressure, a yellowish solid compound was obtained, which was recrystallized from dichloromethan and n-hexan mixture. All the complexes were prepared by a similar route and the details are summarised in Table I.

TABLE-I Synthetic and analytical data of $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(ON{=}CRR')(OPr^i)]$ and $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(ON{=}CRR')_2]$

Mass $[Al(OPr^i)_2acac]_2$ Mass RR'C=NOH	Molar ratios	Pr'OH Found (calcd.) g	Cpd No. Yield %	OPr' %	Elemental-Analysis				M.Wt. Found (Calcd.)	M.P. °C
					C %	H %	N %	Al%		
2.11g , $[2\text{-}OC_4H_3C(CH_3){=}NOH]$ 0.54g	1:1	0.20 (0.26)	**(1)** 92.5	31.6 (31.9)	53.6 (54.2)	6.9 (7.4)	2.4 (2.5)	9.7 (9.7)	573 (553.36)	100
2.22g , $[2\text{-}OC_4H_3C(CH_3){=}NOH]$ 1. 15g	1:2	0.51 (0.54)	**(2)** 97.4	18.8 (19.0)	53.9 (54.3)	5.3 (5.5)	4.4 (4.5)	8.5 (8.6)	547 (618.3)	93
2.11g , $[2\text{-}SC_4H_3C(CH_3){=}NOH]$ 0.62g	1:1	0.23 (0.25)	**(3)** 97.2	30.9 (31.0)	51.9 (52.6)	6.9 (7.1)	2.2 (2.4)	9.3 (9.4)	538 (569.5)	109
2.13g , $[2\text{-}SC_4H_3C(CH_3){=}NOH]$ 1.25g	1:2	0.49 (0.52)	**(4)** 98	18.1 (18.1)	50.5 (51.6)	4.7 (5.2)	4.2 (4.3)	8.1 (8.3)	610 (650.64)	90
2.70g , $[2\text{-}NC_5H_4C(CH_3){=}NOH]$ 0.76g	1:1	0.33 (0.33)	**(5)** 98.5	31.0 (31.3)	54.6 (55.2)	7.2 (7.4)	4.6 (4.9)	9.1 (9.5)	609 (564.4)	180
2.42g , $[2\text{-}NC_5H_4C(CH_3){=}NOH]$ 1 35g	1:2	0.50 (0.59)	**(6)** 99.2	18.0 (18 4)	56.0 (56.1)	6.0 (6.5)	8.7 (8.7)	8.3 (8.4)	622 (640.46)	103
1.69g , $(CH_3)_2C{=}NOH$ 0.26g	1:1	0.20 (0.20)	**(7)** 97.6	35.0 (35.3)	51.9 (52.6)	7.9 (8.1)	2.5 (2.9)	10.2 (10.7)	540 (501.35)	Visc ous
1.92g , $(CH_3)_2C{=}NOH$ 0.58g	1:2	0.52 (0.57)	**(8)** 98.3	22.5 (22.9)	50.9 (51.3)	7.1 (7.7)	4.7 (5.4)	10.4 (10.5)	550 (514.36)	Visc ous
2.23g , $[C_6H_5CH_2C(CH_3){=}NOH]$ 0.75g	1:1	0.19 (0.21)	**(9)** 99.5	29.5 (29.9)	56.3 (56.8)	7.1 (7.6)	2.2 (2.4)	9.0 (9.1)	561 (591)	Visc ous
1.81g , $[C_6H_5CH_2C(CH_3){=}NOH]$ 1.23g	1:2	0.43 (0.44)	**(10)** 99	16.6 (16.9)	57.9 (58.7)	6.2 (6.9)	3.9 (4.0)	7.5 (7.7)	704 (694.56)	Visc ous
1.96g , $(C_6H_5)_2C{=}NOH$ 0.79g	1:1	0.23 (0.24)	**(11)** 98.1	27.9 (28.2)	61.2 (61.3)	6.9 (7.1)	2.2 (2.2)	8.6 (8.6)	617 (625.49)	118
1 96g , $(C_6H_5)_2C{=}NOH$ 1.58g	1:2	0.43 (0.48)	**(12)** 97.6	15.1 (15.5)	46.5 (46.6)	5.0 (5.0)	3.4 (3 6)	(17.1) (17.0)	720 (762.64)	110

Results and Discussion

The reactions of $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ with simple and internally functionallized oximes (RR'C=NOH) in 1:1 and 1:2 molar ratios in refluxing anhydrous benzene yield the following products :

$$[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]+nRR'C{=}NOH \longrightarrow [\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(ON{=}CRR')_n(OPr^i)_{2-n} + nPr^iOH$$

where R = R' = CH_3 , C_6H_5 and R = CH_3 , R' = $CH_2C_6H_5$; R = CH_3 , R' = C_4H_3O-2 , C_4H_3S-2 , C_5H_4N-2 and n = 1or 2.

These reactions are quite facile and quantitative. All these derivatives are yellowish solids, hygroscopic in nature and are soluble in common organic solvents (benzene, chloroform, carbon tetrachloride etc.). Molecular weight measurements indicate their dimeric nature in refluxing benzene (Table-I).

IR spectra

The tentative assignment of some of the important bands have been made and are summarized in Table-II . Broad stretching vibrations at ~ 3300 cm^{-1} due to -OH group of the free oximes disappeared in the IR spectra of these derivatives suggesting the deprotonation of -OH group and formation of Al-O bond. Bands in the region 610-695 cm^{-1}may tentatively be assigned to Al-O stretching vibrations.(17) The appearance of νN-O(20) and νC=N(21) stretching vibrations towards lower frequencies (~20 cm^{-1}) further supports the formation of Al-O bond.In all these derivatives,the absence of any band at 1720cm^{-1}(due to the carbonyl stretching frequency of free acetylacetone) and the presence of strong bands in the range1590-1600 and 1420-1470cm^{-1} due to ν(C–O) and ν(C–C) stretching vibrations(22),respectively,of the acetylacetone moiety suggest the bidentate quasi-aromatic nature of the ligand. The medium intensity band observed in the region of 995-1010 cm^{-1} is assigned to ν C-O of bridging isopropoxy group. The Al-O-Al vibrations have been observed in the region 750-765 cm^{-1}.

TABLE-II: IR spectral data (cm^{-1}) of [$\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(ON{=}CRR')(OPr^i)$] and [$\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(ON{=}CRR')_2$]

Cpd. No.*	Acetylacetonate Moiety νC = O	νC = C	Oximate Moiety νC = N	νN–O	Isopropoxy Group ν C-O	νAl-O	ν Al-O-Al
1.	1600s	1450s	1525s	1360m	1010m	655m	760w
2.	1595s	1435s	1525s	1300m	1010m	650m	750w
3.	1600s	1460s	1545s	1370m	1010m	650m	760w
4.	1600s	1430s	1530s	1360m	1000m	695m	755w
5.	1600s	1460s	1520s	1360m	1000m	620m	760w
6.	1595s	1470s	1545s	1375m	1000m	610m	765w
7.	1590s	1420s	1525s	1380m	1000m	650	760w
8.	1600s	1465s	1520s	1375m	995m	675m	750w
9.	1600s	1460s	1520s	1370m	1010m	695m	750w
10.	1590s	1450s	1545s	1365m	1010m	650m	750w
11.	1600s	1455s	1530s	1380m	995m	650m	755w
12.	1595s	1440s	1525s	1370m	995m	655m	750w

- Compound Nos. as in Table IV.

^{1}H NMR Spectra

The important signals in ^{1}H NMR spectra of these derivatives are summarized in Table-III . A comparision of the spectra of the free oximes with the spectra of the corresponding derivatives show the absence of -OH signals, indicating deprotonation of the hydroxy group of the oxime ligand and formation of Al-O bond. This gets support from the significant shifting of the positions of methyl and phenyl signals of the ligand moiety. However, no appreciable shift was observed in the position of ring protons of the functionallized oximes ruling out the possibility of the coordination through hetero(N,O or S) atom .The methine proton of the bridging and terminal isopropoxy groups get merged to give a multiplet in the range δ3.80-4.31ppm.The presence of the methyl protons of bridging isopropoxy groups(compound **1-12**) as a doublet at δ1.17-1.27 ppm and methyl protons of the terminal isopropoxy (compound **1,3,5,7,9** and **11**) at δ1.51-1.87 ppm, indicates the nonequivalent nature of the bridging and terminal isopropoxy groups. The methyl and the methine signals of acetylacetonate moiety appeared at δ1.93-2.06 and δ5.46-5.54 ppm, respectively.

TABLE-III: ^{1}H NMR spectral data (δ ppm) of [{$CH_3C(O)CHC(O)CH_3$}$_2$Al(μ-OPr^i)$_2$-Al(ON=CRR')(OPr^i)[and [{$CH_3C(O)CHC(O)CH_3$}$_2$Al(μ-OPr^i)$_2$Al(ON=CRR')$_2$]

Compound	Acetylacetonate moiety		Isopropoxy moiety		Oximate moiety
	CH_3	CH	CH_3	OCH	
(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)$C_4H_3O_2$)(OPr^i)]	2.06,s (12H)	5.52,s (2H)	1.26,d (12H) 1.58,d (6H)	3.93-4.31,m(3H)	2.25s(3H,CH_3);6.5,dd(1H,H-4); 6.84d(1H,H-3);7.84br(1H,H-5)
(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)C_4H_3O-2)$_2$]	1.98,s (12H)	5.54,s (2H)	1.24,d (12H)	4.12,m(2H)	2.25s(3H,CH_3);6.4,dd(1H,H-4); 6.48d(1H,H-3);7.56br(1H,H-5)
(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)C_4H_3S -2)(OPr^i)]	1.97,s (12H)	5.48,s (2H)	1.17,d (12H) 1.87,d (6H)	3.89-4.15,m(3H)	2.25s(3H,CH_3);7.13,dd(1H,H-4); 7.32,d(1H,H-3); 7.39br(1H,H-5)
(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)C_4H_3S -2)$_2$]	1.93,s (12H)	5.54,s (2H)	1.27,d (12H)	4.12,m(2H)	2.31s(3H,CH_3);7.1,dd(1H,H-4); 7.9,d(1H,H-3);7.35br(1H,H-5)
(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)C_5H_4N -2)(OPr^i)]	1.98,s (12H)	5.47,s (2H)	1.18,d (12H) 1.82,d (6H)	3.98-4.00,m(3H)	2.46s(3H,CH_3);7.25t (1H,H-4); 7.35,t(1H,H-3);7.75t(1H, H-5) 8.1m(1H,H-6)
(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)C_5H_4N -2)$_2$]	2.03,s (12H)	5.54,s (2H)	1.24,d (12H)	4.12,m(2H)	2.38s(3H,CH_3);7.25t(1H,H-4); 7.83,t(1H,H-3);7.68,t(1H, H-5); 8.14m(1H,H-6)
(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)$_2$)(OPr^i)]	2.05,s (12H)	5.52,s (2H)	1.22,d (12H) 1.51,d (6H)	3.90-4.12,m(3H)	1.97,s(6H,CH_3)
(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)$_2$)$_2$]	2.06,s (12H)	5.51,s (2H)	1.20,d (12H)	4.11,m(2H)	1.98,s(12H,CH_3)
(acac)$_2$Al(μOPr^i)$_2$Al(ON=C(CH_3)$CH_2C_6H_5$)(OPr^i)]	1.99,s (12H)	5.48,s (2H)	1.25,d (12H) 1.65,d (6H)	3.80-4.02m(3H)	1.87,s(3H,CH_3);2.6s(2H,CH_2); 7.25m(5H,C_6H_5)
(acac)$_2$Al(μOPr^i)$_2$Al(ON=C(CH_3)$CH_2C_6H_5$)$_2$]	1.97,s (12H)	5.46,s (2H)	1.26,d (12H)	4.01,m(2H)	1.90,s(3H,CH_3);2.7s(2H,CH_2); 7.25m(5H,C_6H_5)
(acac)$_2$Al(μOPr^i)$_2$Al(ON=C(C_6H_5)$_2$)(OPr^i)]	1.93,s (12H)	5.52,s (2H)	1.17,d (12H) 1.87,d (6H)	3.89-4.21,m(3H)	7.26-7.9m(C_6H_5)
(acac)$_2$Al(μOPr^i)$_2$Al(ON=C(C_6H_5)$_2$)$_2$]	1.97,s (12H)	5.46,s (2H)	1.20,d (12H)	4.08m(2H)	7.21-7.58m(C_6H_5)

^{13}C NMR Spectra

The mode of bonding suggested above has been confirmed on the basis of ^{13}C NMR spectral data (Table-IV).In the ^{13}C NMR spectra of these complexes, the C=N carbon signal in general is deshielded as compared to its position for the corresponding free oximes, indicating the formation of Al-O bond. The carbon signals due to heterocyclic ring of the functionallized oximes have been observed at their expected positions and do not show any appreciable shifts . This further supports the view that heteroatom(N,O or S) does not take part in the bonding. The signals at δ 26.0-26.7,100.8-101.4 and 191.0-191.5 ppm are assigned to methyl, methine and carbonyl carbon of the acetylacetonate moiety, respectively. Similarly,two signals each for methyl and methine carbons of bridging and terminal isopropoxy groups were observed in compounds 1,3,5,7,9 and 11 suggesting the unequivalent nature of isopropoxy groups in these derivatives.

TABLE - IV : ^{13}C NMR spectral data (δ ppm) of [{$CH_3C(O)CHC(O)CH_3$}$_2$Al(μOPr^i)$_2$-Al(ON=CRR')(OPr^i)] and[{$CH_3C(O)CHC(O)CH_3$}$_2$Al(μOPr^i)$_2$Al(ON=CRR')$_2$]

S. No.	Compound	Acetylacetone moiety			Isopropoxy Moiety		Oximate moiety
		CH_3	CH	C=O	CH_3	OCH	
(1)	[(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)C_4H_3O-2)(OPr^i)]	26.7	101.1	191.4	25.2, 23.9	64.3, 63.2	11.1(CH_3);111.2(C3); 143.2(C5);147.8(C2); 151.1(C=N);109.1(C4)
(2)	[(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)C_4H_3O-2)$_2$]	26.6	101.0	191.3	24.9	64.1	11.0(CH_3);111.1(C3); 143.3(C5);146.9(C2); 150.9(C=N);109.0(C4)
(3)	[(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)C_4H_3S -2)(OPr^i)]	26.7	101.2	191.5	25.0, 23.6	64.2, 63.2	12.41(CH_3);126.8(C4); 126.9(C3);127(C5); 140.4(C2);151.4(C=N)
(4)	[(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)C_4H_3S -2)$_2$]	26.7	101.2	191.5	24.9	64.0	12.41(CH_3);126.3(C4); 126.6(C3);127(C5); 140.3(C2);151.4(C=N)
(5)	[(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)C_5H_4N -2)(OPr^i)]	26.4	100.9	191.2	25.0, 23.5	64.3, 63.5	10.2(CH_3);122.8(C5); 124.4(C3);137.5(C4); 148.8(C6);153.1(C2); 156.9(C=N)
(6)	[(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)C_5H_4N -2)$_2$]	26.4	100.8	191.1	25.0	63.4	10.0(CH_3);123.6(C5); 126.0(C3);135.2(C4); 148.1(C6);153.0(C2); 157.0(C=N)
(7)	[(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)$_2$)(OPr^i)]	26 6	101.1	191.1	25.1, 23.7	64.6, 63.6	11.5(CH_3);159.2(C=N)
(8)	[(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)$_2$)$_2$]	26.5	101.1	191.0	24.9	64.1	11.4(CH_3);160.0(C=N)
(9)	[(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)$CH_2C_6H_5$)(OPr^i)]	26.0	101.4	191.4	25.0, 23.4	64.8, 63.8	12.0(CH_3);158.2(C=N); 127.8,129.9(C_6H_5); 17.1(CH_2);156.0(C=N)
(10)	[(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(CH_3)$CH_2C_6H_5$)$_2$]	26.6	101.1	191.3	25.0	64.5	12.0(CH_3);156.1(C=N); 127.8,129.9(C_6H_5); 17.0(CH_2);156.9(C=N)
(11)	[(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(C_6H_5)$_2$)(OPr^i)]	26.7	101.1	191.4	25.2, 23.6	64.3, 63.8	136.5,133.1,129.3, 126.7 (C_6H_5);157 (C=N)
(12)	[(acac)$_2$Al(μ-OPr^i)$_2$Al(ON=C(C_6H_5)$_2$)$_2$]	26.6	101.1	191.4	25.0	64.3	136.2,132.6, 130.0,126.2 (C_6H_5);157.2 (C=N)

FAB Mass

The tantative assignment of the important fragmentation ion peaks of a representative compound [{$CH_3C(O)CHC(O)CH_3$}$_2$Al(μ-OPr^i)$_2$Al{ON=C(CH_3)C_4H_3O-2}$_2$] has been made and tabulated in scheme-I. The FAB mass spectrum of [{$CH_3C(O)CHC(O)CH_3$}$_2$Al(μ-OPr^i)$_2$Al{ON=C(CH_3)C_4H_3O-2}$_2$] appears to indicate its binuclear nature.

Scheme 1: FAB Mass spectral data for $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_2]$

m/e
$689[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_2].C_3H_3O_2$;
$589[\{CH_3C(O)CHC(O)CH_3\}Al(\mu\text{-}OPr^i)\ \mu OCH(CH_3)CH_2Al\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_2].C_3H_3O_2$;
$557[\{CH_3C(O)CHC(O)CH_3\}\ Al(\mu\text{-}OPr^i)\ \mu OC(CH_3){=}CH_2Al\{ON{=}C(CH_3)C_4H_3O\text{-}2\}_2].C_2O$;
$489[\{CH_3C(O)CHC(O)CH_3\}\ Al(\mu\text{-}OPr^i)\ \mu OC(CH_3){=}CH_2Al\{ON{=}C(CH_3)C_4H_3O\text{-}2\}(OC_3H_4)].C_2O$;
$457[\{CH_3C(O)CHC(O)CH_3\}Al(\mu\text{-}OPr^i)\ \mu OC(CH_3){=}CH_2Al\{ON{=}C(CH_3)C_4H_3O\text{-}2\}].C_4O$;
$427[\{CH_3C(O)CHC(O)CH_3\}Al\{\mu\text{-}OC(CH_3){=}CH_2\}_2Al\{ON{=}C(CH_3)C_4H_3O\text{-}2\}].C_3$;
$387[\{CH_3C(O)CHC(O)CH_3\}Al\{\mu\text{-}OC(CH_3){=}CH_2\}_2Al\{N{=}C(CH_3)C_4H_3O\text{-}2\}].C$;
$345[\{CH_3C(O)CHC(O)CH_3\}Al(\mu\text{-}O)\ \mu OC(CH_3){=}CH_2Al\{N{=}C(CH_3)C_4H_3O\text{-}2\}].C$;
$333[\{CH_3C(O)CHC(O)CH_3\}Al(\mu\text{-}O)\ \mu OC(CH_3){=}CH_2Al\{N{=}C(CH_3)C_4H_3O\text{-}2\}]$;
$225[\{CH_3C(O)CHC(O)CH_3\}Al\text{-}O\text{-}\ Al\text{-}N{=}CH_2]$; 211 $[\{CH_3C(O)CHC(O)CH_3\}Al\text{-}O\text{-}\ Al{=}N]$;
$195[\{CH_3C(O)CHC(O)CH_3\}Al\text{-}\ Al{=}N]$; 126 $[Al\{OC(CH_3)C{=}O\}]$

^{27}Al NMR Spectra

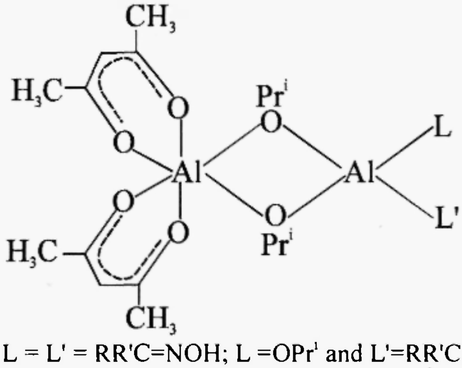
^{27}Al NMR spectrum of a representative compound, $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al\{ON{=}C(CH_3)C_4H_3S\text{-}2\}_2]$ at room temperature exhibits a broad signal at δ4.10-80.20ppm. On the basis of this result it may be concluded that the coordination number of both aluminium atoms is 4-,5-, or 6 or one aluminium atom is four coordinate and one is six coordinate,respectively(9).

It is worthwhile to mention here that ^{27}Al NMR spectrum of the starting compound$[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ at 120°C reveals a narrow signal at about δ 0 ppm and the broad signal at δ 57 ppm of six and four coordinate atoms,respectively.

Since in the above dinuclear complex, $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al\{ON{=}C(CH_3)C_4H_3S\text{-}2\}_2]$,the ligand moiety(2-acetylthiophenoxime) is behaving as a monodentate ligand,therefore,the presence of a broad ^{27}Al NMR signal may indicate the presence of 4- and 6- coordination geometries arounds both aluminium(III)atoms.

Conclusion

Although it is difficult to comment on the structural aspects of these derivatives without single crystal X-ray studies of atleast a representative compound yet in view of the dinuclear nature of all the above products as well as the monodentate behaviour of the oxime ligand moieties,the following tentative structure may be proposed for these derivatives.



where L = L' = RR'C=NOH; L =OPr^i and L'=RR'C=NOH

Fig.1. Proposed structure of $[\{CH_3C(O)CHC(O)CH_3\}_2Al(\mu\text{-}OPr^i)_2Al(ON{=}CRR')_n(OPr^i)_{2\text{-}n}]$ ($R{=}R'{=}CH_3$, C_6H_5 and $R{=}CH_3$, $R'{=}CH_2C_6H_5$; $R{=}CH_3$, $R'{=}C_4H_3O\text{-}2$, $C_4H_3S\text{-}2$, $C_5H_4N\text{-}2$ and n=1 or 2)

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