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Aluminum Five- and Six-Coordination in Bis(acetylacetonato)aminoalkoxides

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ABSTRACT: *Reactions of bis(acetylacetonato)aluminum(III)-di-μ-isopropoxo-di-isopropoxo aluminum-(III), $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ with aminoalcohols, ($HO{-}R{-}NR^1R^2$) in 1:1 and 1:2 molar ratios in refluxing anhydrous benzene yielded binuclear complexes of the types $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al(O{-}R{-}NR^1R^2)(OPr^i)]$ and $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al(O{-}R{-}NR^1R^2)_2]$ ($R = -(CH_2)_3-$, $R^1 = R^2 = H$; $R = -CH_2C(CH_3)_2-$, $R^1 = R^2 = H$; $R = -(CH_2)_2-$, $R^1 = H$, $R^2 = -CH_3$; and $R = -(CH_2)_2-$, $R^1 = R^2 = CH_3$), respectively. All these compounds are soluble in common organic solvents and exhibit sharp melting points. Molecular weight determinations reveal their binuclear nature in refluxing benzene. Plausible structures have been proposed on the basis of elemental analysis, molecular weight measurements, IR, NMR (^1H, ^{13}C, and ^{27}Al), and FAB mass spectral studies. ^{27}Al NMR spectra show the presence of both five- and six-coordinated aluminum sites.* Heteroatom Chem 14:518–522, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10184

INTRODUCTION

Metal alkoxide chemistry has been growing continuously and systematically in recent years [1]. Homo- as well as heterometal alkoxides have been emerging as suitable precursors for low-temperature metal-oxide-based advanced materials by sol–gel or MOCVD (Metallo-Organic Chemical Vapour Deposition) [2] route. The reaction of aluminum isopropoxide with acetylacetone in 1:1 molar ratio yields an interesting derivative of the type $[Al(acac)(OPr^i)_2]_2$ (acac: $CH_3COCHCOCH_3$), which has been shown to be an unsymmetrical dimer [3] $(acac)_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2$ (**1**) involving the presence of both four- and six-coordinated aluminum(III) atoms. The replacement of the two terminal isopropoxy groups by chelating/sterically demanding ligands leads to products depicting similar unsymmetrical structures [4–10]. We report herein the synthesis and characterization of some novel heteroleptic derivatives of aluminum(III) by the reactions of **1** with a variety of aminoalcohols.

RESULTS AND DISCUSSION

The reactions of **1** with a number of aminoalcohols, ($HO{-}R{-}NR^1R^2$) in 1:1 and 1:2 molar ratios in refluxing anhydrous benzene, yielded binuclear complexes **2–9** represented by the following equation and Table 1.

$$\underset{\mathbf{1}}{[(acac)_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]} + n\,HO{-}R{-}NR^1R^2 \rightarrow \underset{\mathbf{2\text{–}9}}{[(acac)_2Al(\mu\text{-}OPr^i)_2Al(O{-}R{-}NR^1R^2)_n(OPr^i)_{2-n}]} + n\,Pr^iOH$$

All these reactions are quantitative and quite facile. Their progress has been followed by

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TABLE 1 Synthetic and Analytical Data of $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al(O\text{–}R\text{–}NR^1R^2)(OPr^i)]$ **2, 4, 6, 8** and $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2(O\text{–}R\text{–}NR^1R^2)_2]$ **3, 5, 7, 9**

	R	*R^1, R^2*	*n*	**1** *(g), Amino Alcohol (g)*	*Pr^iOH(g): Found (Calcd)*	*Yield (%)*	*m.p. (°C)*	*Analysis %: Found (Calcd)*			*M. Wt.: Found (Calcd)*
								Al	*OPr^i*	*N*	
2	$(CH_2)_3$	H, H	1	1.81, 0.27	0.22 (0.22)	98	140	10.66 (10.73)	34.98 (35.18)	2.40 (2.78)	500 (503)
3	$(CH_2)_3$	H, H	2	2.51, 0.77	0.61 (0.61)	97	145	10.27 (10.42)	22.58 (22.77)	5.23 (5.45)	510 (518)
4	$CH_2C(CH_3)_2$	H, H	1	3.05, 0.55	0.35 (0.37)	97	150	10.35 (10.44)	30.94 (31.16)	2.42 (2.70)	546 (555)
5	$CH_2C(CH_3)_2$	H, H	2	2.60, 0.95	0.64 (0.64)	98	155	9.67 (9.89)	21.20 (21.61)	4.98 (5.12)	518 (532)
6	$(CH_2)_2$	H, CH_3	1	2.86, 0.43	0.35 (0.35)	99	140	10.58 (10.73)	35.17 (35.18)	2.41 (2.78)	500 (503)
7	$(CH_2)_2$	H, CH_3	2	3.21, 0.98	0.76 (0.79)	99	148	10.15 (10.42)	22.63 (22.70)	4.99 (5.40)	528 (533)
8	$(CH_2)_2$	CH_3, CH_3	1	3.29, 0.60	0.40 (0.40)	98	150	10.09 (10.44)	33.94 (34.13)	2.65 (2.70)	500 (577)
9	$(CH_2)_2$	CH_3, CH_3	2	3.67, 1.33	0.89 (0.89)	98.5	153	9.89 (9.89)	21.31 (21.61)	4.98 (5.12)	518 (522)

estimating the isopropanol liberated azeotropically. All products are hygroscopic, pale yellow, sharp melting solids that are soluble in common organic solvents. They can be purified by recrystallization. Molecular weight determinations indicate their binuclear nature in refluxing benzene.

FAB MASS SPECTRA

The FAB mass spectrum of representative **2** indicates its binuclear nature (Table 2).

IR SPECTRA

The tentative assignments of some of the important bands are summarized in Table 3. The broad band at 3650 cm^{-1} due to —OH group of aminoalcohols disappeared in the spectra of **2–9**, suggesting the deprotonation of the —OH groups and the formation of Al—O bonds. The appearence of νNH stretching frequency toward lower frequencies (2945–2955 cm^{1}) as compared to the free ligand (~3400 cm^{1}) indicates the formation of coordinate bond through nitrogen to the aluminum atom. This gets support by the appearance of a new band in the region 495–510 cm^{-1} due to νAl—N and 655–672 cm^{-1} due to νAl—O bonds [10]. In **2–9**, the absence of a band at 1720 cm^{-1} (due to the carbonyl stretching frequency of free acetylacetone) and the presence of strong bands in the range 1600–1608 and 1518–1528 cm^{-1} due to νC—O and νC—C stretching vibrations of the acetylacetone moiety suggest the bidentate chelating nature of the ligand. The νC—O stretching vibrations due to the terminal and the bridging isopropoxy moieties shift to lower frequencies and appear in the range 1000–1015 cm^{-1}. The νAl—O—Al vibrations have been observed [4,5] in the region 748–762 cm^{-1}.

TABLE 2 Interpreted FAB Mass Spectra of $[(acac)_2Al\text{-}((\mu\text{-}OPr^i)_2Al\{O(CH_2)_3\text{-}NH_2\}(OPr^i)]$

Compound	*m/e*
$[(acac)_2Al(\mu\text{-}OPr^i)_2Al\{O(CH_2)_3\text{–}NH_2\}(OPr^i)]\cdot C_5H_6N$	583
$[(acac)_2Al(OPr^i)][Al(OPr^i)\{O(CH_2)_3\text{–}NH_2\}]^+C_5H_6N$	524
$[(acac)_2Al(OPr^i)][Al(OPr^i)\{O(CH_2)_3\text{–}NH_2\}]^+\cdot C_4H_3N$	509
$[(acac)_2Al(OPr^i)][Al(OPr^i)\{O(CH_2)_3NH_2\}]^+$	444
$[(acac)_2Al(OPr^i)][Al(OPr^i)]^{+2}\cdot CH_2$	384
$[(acac)_2Al(OPr^i)][(OH)Al]^{+2}\cdot CH_2$	342
$[(acac)Al(OPr^i)(OH)][Al(OH)]^{+2}\cdot C_3H_2$	285
$[(acac)Al(OH)]^+[Al(OH)]^{+2}\cdot CH$	225
$[(acac)Al(OH)]^+[Al(OH)]^{+2}$	187
$[(acac)Al(OH)]^+$	143

^1H NMR SPECTRA

The characteristic signals in the ^1H NMR spectra of **2–9** are summarized in Table 4. The absence of —OH signals indicates deprotonation of the hydroxy group of the aminoalcohols and formation of the Al—O bond. All these derivatives show upfield shifts of $-NH_2$ as well as $-NCH_3$ protons, suggesting the chelation through nitrogen to the aluminum. In 1:1 derivatives, the methyl and the methine signals of the terminal and the bridging isopropoxy groups appear as a doublet at δ 1.19–2.01 and δ 1.17–1.20 ppm and as a multiplet at δ 3.85–4.06 and δ 3.74–3.98 ppm, respectively. The presence of two sets of signals

TABLE 3 IR Spectral Data (cm^{-1}) of **2--9**

	β-Diketonate Moiety (νC═O)	*Isopropoxy Moiety*				*Aminoalkanolate Moiety*		
		νC═C	*νC–O*	*νC–O*	*νN–H*	*νAl–O–Al*	*νAl–O*	*νAl–N*
2	1605s	1528s	1005m	1360m	2950	760w	666w	495w
3	1602s	1525s	1010m	1355m	2945	755w	670w	500w
4	1600s	1520s	1009m	1345m	2948	758w	658w	505w
5	1605s	1522s	1011m	1352m	2952	762w	660w	498w
6	1608s	1528s	1008m	1348m	2955	760w	672w	502w
7	1603s	1520s	1015m	1350m	2946	748w	670w	500w
8	1602s	1523s	1012m	1358m	–	750w	659w	498w
9	1600s	1518s	1000m	1355m	–	757w	655w	510w

Note: s = strong, m = medium, w = weak.

indicates that these are unequivalent. In case of the 1:2 derivatives, the methyl and the methine protons of the bridging isopropoxy groups appeared as a doublet at δ 1.18–2.01 and as a multiplet at δ 4.02–4.05 ppm, respectively. The methyl and the methine signals of the acetylacetonate appeared at δ 1.94–2.01 and δ 5.45–5.51 ppm, respectively.

^{13}C NMR SPECTRA

^{13}C NMR chemical shifts of **2–9** were recorded in choloroform at ambient temperature and are summarized in Table 5. The carbon attached to the nitrogen atom is slightly deshielded as compared to that in the free aminoalcohols [10–12], supporting the bidentate nature of the aminoalkanolate moiety. The signals due to the methyl carbon atoms of the terminal and the bridging isopropoxy groups appeared at δ 25.21–26.44 and δ 25.13–27.11 ppm, respectively, while the methine carbons of the terminal and the bridging isopropoxy groups appeared at δ 61.09–61.32 and δ 63.96–71.70 ppm, respectively, indicating the nonequivalent nature of these groups. The methyl, the methine, and the carbonyl carbon atoms of the acetylacetonate moiety have been observed at δ 24.29–24.87, δ 100.21–100.95, and δ 191.21–191.42 ppm, respectively.

^{27}Al NMR SPECTRA

The ^{27}Al NMR spectrum of **2** at room temperature (25°C) exhibits signals at δ 1.90 and 14.0 ppm, indicating the presence [13] of hexa- and pentacoordinated aluminum(III) atoms. However, in the case of **3**, only one sharp signal at δ 0.31 ppm has been observed, suggesting the presence of hexacoordination around both the aluminum atoms.

On the basis of these results, plausible structures may be proposed (Figs. 1a and 1b).

EXPERIMENTAL

All the chemicals used were of reagent grade. Moisture was carefully excluded throughout experimental

TABLE 4 ^{1}H NMR Spectral Data (δ, ppm) of **2--9**

	Acetylacetonate Moiety		*Isopropoxy Moiety*		*Aminoalkanolate Moiety*		
	–CH$_3$	*–CH<*	*–CH$_3$*	*–OCH<*	*–OCH$_2$*	*NH<*	*–NCH$_3$*
2	2.00, s (12H)	5.48, s (2H)	1.18, d (12H) 1.20, d (6H)	3.97–4.01, m (3H)	3.95, t (6H)	2.92, s (2H)	–
3	2.01, s (12H)	5.49, s (2H)	1.19, d (12H)	4.05, m (2H)	3.92, t (12H)	2.90, s (4H)	–
4	1.99, s (12H)	5.47, s (2H)	1.20, d (12H) 1.21, d (6H)	3.98–4.06, m (3H)	3.94, t (2H)	2.91, s (2H)	–
5	2.00, s (12H)	5.50, s (2H)	1.18, d (12H)	4.04, m (2H)	3.95, t (4H)	2.94, s (4H)	–
6	1.98, s (12H)	5.51, s (2H)	1.17, d (12H) 1.19, d (6H)	3.95–4.03, m (3H)	3.75, t (4H)	2.33, s (1H)	2.52, s (3H)
7	1.97, s (12H)	5.48, s (2H)	2.01, d (12H)	4.02, m (2H)	3.72, t (8H)	2.37, s (2H)	2.50, s (6H)
8	1.94, s (12H)	5.45, s (2H)	1.18, d (12H) 2.01, d (6H)	3.74–3.85, m (3H)	3.29, t (4H)	–	2.25, s (6H)
9	2.01, s (12H)	5.49, s (2H)	2.00, d (12H)	4.05, m (2H)	3.92, t (8H)	–	2.27, s (12H)

Note: s = singlet, d = doublet, t = triplet, m = multiplet.

TABLE 5 ^{13}C NMR Spectral Data (δ, ppm) of **2--9**

	Acetylacetonate Moiety			*Isopropoxy Moiety*		*Aminoalkanolate Moiety*		
	$-CH_3$	$-CH<$	$-CO<$	$-CH_3$	$-OCH<$	$-OCH_2$	$-CN<$	$N(CH_3)$
2	24.35	100.92	191.35	25.29, 26.58	61.09, 64.08	60.78	44.89	–
3	24.29	100.79	191.21	25.13	64.54	60.90	44.80	–
4	24.37	100.21	191.42	25.21, 26.01	61.21, 64.64	60.17	41.59	–
5	24.48	100.86	191.37	26.05	64.57	59.99	41.69	–
6	24.51	100.93	191.35	25.31, 26.59	61.23, 63.96	59.40	45.40	59.99
7	24.87	100.95	191.38	26.60	64.47	59.32	45.60	60.14
8	24.80	100.80	191.24	26.44, 27.11	61.32, 63.98	58.99	47.55	59.50
9	24.86	100.81	191.25	26.45	71.70	59.21	47.70	61.45

manipulations. Aluminum isopropoxide was prepared by the literature method [14]. Acetylacetone and aminoalcohols were distilled before use. Solvents were carefully dried by usual methods. Aluminum was estimated as oxinate gravimetrically [15]. Isopropanol was estimated by oxidimetric method [16]. Nitrogen was estimated by Kjeldhals method [15]. The starting material **1** was prepared by reported method [4,5]. The IR spectra were recorded as Nujol mulls on a Nicolet Magna-550 spectrophotometer in the range 4000–400 cm^{-1}. The ^{1}H 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 spectra were recorded in toluene using aluminum nitrate as a reference. FAB mass spectra were recorded on a Jeol SX 102/DA-6000 mass spectrometer/Data system using argon/xenon (6 kV, 10 mA) as the FAB gas, *m*-nitrobenzylalcohol was used as the matrix. Molecular weight measurements were carried out by the boiling point elevation method in benzene using a Beckmann thermometer.

Synthesis of **2**

The reaction mixture containing **1** (1.81 g, 3.70 mmol) and $HO(CH_2)_3NH_2$ (0.27 g, 3.69 mmol) in anhydrous benzene (~65 ml) was refluxed for ~4 h under a fractionating column. The liberated isopropanol was continuously fractionated out azeotropically with benzene. Progress as well as the completion of the reaction was checked by the estimation of the isopropanol in the azeotrope by oxidimetry. The product was soluble in benzene. After stripping off the excess solvent under reduced pressure, a light pale yellow solid was obtained in a quantitative yield, which was purified by recrystallization from a mixture of dichloromethane and *n*-hexane (7:1). Similar procedure was adopted for the synthesis of all other compounds. Their physical and analytical data are summarized in Table 1.

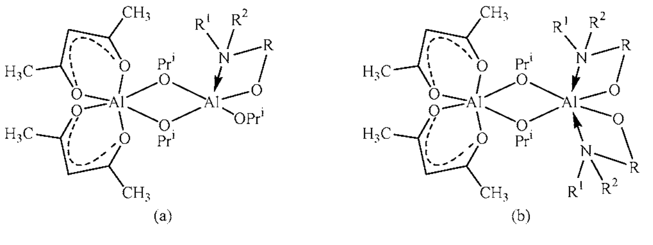

FIGURE 1 Proposed structures of (a) **2, 4, 6, 8** and (b) **3, 5, 7, 9**.

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