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Synthesis and characterization of some binuclear alkylene dithiophosphate complexes of bis(acetylacetonato)aluminium(III)-di-(μ-isopropoxo)di-isopropoxoaluminium(III) and sol-gel synthesis of nanosized θ-alumina

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Reactions of bis(acetylacetonato)aluminum(III)-di-(μ–isopropoxo)-di-isopropoxoaluminum(III) **(A)** with a variety of alkylenedithiophosphoric acids in different molar ratio yield products of the type $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al\{S(S)P(O\text{-}G\text{-}O)_n(OPr^i)_{2-n}]$ **(1-9)** {where G = $C(CH_3)_2C(CH_3)_2$, n=1[**1**], n=2[**2**]; $-CH_2CH(C_2H_5)$, n=1[**3**], n=2[**4**]; $CH_2CH(CH_3)$, n=1[**5**], n=2[**6**];$C(CH_3)_2CH_2CH(CH_3)$, n=1[**7**]; $CH(CH_3)CH(CH_3)$ n=1[**8**], n=2[**9**]}. Progress of the reaction is monitored by estimating liberated 2-propanol in benzene-2-propanol azeotrope by oxidimetric method. All pale coloured viscous products were soluble in common organic solvents and are characterized by elemental analyses, FT-IR and NMR (^1H and $^{13}C\{^1H\}$ NMR) spectral studies. Molecular weight measurements in refluxing anhydrous benzene indicated binuclear nature of the complexes. ^{27}Al NMR spectra of two of the derivatives, (**1**) and (**2**), suggested the presence of aluminium(III) atoms in different coordination states. ^{31}P NMR spectra of the representative derivatives (**1**) and (**2**) exhibited only a single peak at 95.71 and 90.59 ppm, respectively, suggesting tetra-coordination around phosphorus atom and a bidentate mode of chelation of the dithio ligand. Sol-gel transformation of $Al(OPr^i)_3$ and $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ **(A)** followed by sintering at ~850 °C yield alumina **(a)** and **(b)**, respectively. The powder X-ray diffraction patterns, SEM images and FT-IR spectral studies of **(a)** and **(b)** has indicated formation of nano-crystallites of θ -Al_2O_3 [PDF # 110517] in both the cases. The energy band gaps of 4.78 eV and 5.01 eV for (a) and (b), respectively are obtained from the absorption spectra.

Keywords: Bis(acetylacetonato)aluminum(III))-di-(μ–isopropoxo)-di-isopropoxoaluminum(III), alkylenedithiophosphoric acid, sol-gel transformation, nano-sized θ -Al_2O_3

The role of metal-alkoxides as precursors for pure materials by sol–gel technique is very well established, but to get targeted materials having suitable shape, size and porous structure, a good control over the rate of hydrolysis of the alkoxide appears to be essential[1-3]. This could be achieved by partial substitution of some of the alkoxy groups in metal alkoxides by chelating/sterically demanding ligands, such as oximes[4,5], glycols[6,7], Schiff bases[8,9] etc. The chemical modifications help in modifying the solubility and reactivity of the resulting alkoxide derivatives to make them better precursors for their applications in high-purity metal-oxide based ceramic materials[10,11]. Aluminum being a hard acid, is expected to bond strongly to hard bases[12-14] as compared to soft bases like sulphur containing ligands[15,16]. The dithiophosphate ligand system gained a great deal of attention due to their ability to stabilize metals in higher oxidation state[17-19]. The dithiophosphatate derivatives of metals are found to be biologically active[20-21] and hence find extensive potential applications in agriculture, medicine and also in chemical industries[22,23], yet corresponding aluminium(III) derivatives are comparatively less known.

Alumina, which is an important material due to its high thermal and mechanical stability, its chemical inertness with non-toxic nature[24] exist in a variety of structural polymorph such as η-, γ-, δ-, θ- and α-alumina. Aluminium hydroxide converts into the most stable form α-alumina (corundum, sapphire) via different transition phases as γ, δ and θ with increase of temperature upto 1100 °C[25]. Although the atomic structures of transition alumina are still matter of discussion, it has been found that the structure γ, δ and η phases possess a defected spinel structure[26]. It is interesting to mention here that sol-gel transformation of $Al(OPr^i)_3$ as well as its chemically modified derivatives as precursors for transition alumina, at different sintering temperatures, have been done successfully [10, 13,14]. Transition alumina are versatile ceramic oxides known for exhibiting a wide variety of applications in engineering, biochemical areas, as building and refractory materials, electric and heat insulators etc.[27-29]. Among various transition aluminas, the θ- alumina phase is very important due to its specific structure and is widely used as catalyst and adsorbent[30-32].

In this article we report synthesis and characterization of some binuclear alkylenedithiophosphate complexes of bis(acetylacetonato)aluminium(III)-di-(μ-isopropoxo)di-isopropoxoaluminium(III) (**A**) along with the sol-gel transformation of aluminium isopropoxide and its acetylacetone modified precursor (**A**) into nano-sized θ-alumina.

Materials and Methods

All the experiments (except hydrolysis reaction) were carried out under strictly anhydrous conditions. The solvent and reagents were purified and dried according to the standard procedures[33]. Due precautions were taken while handling hazardous chemicals and solvents such as benzene. Aluminium was estimated gravimetrically as the oxinate[34], sulphur and isopropanol were estimated as reported in the literature[33]. Aluminium (III) isopropoxide was synthesized and purified as reported in the literature[35]. The precursor material $[(acac)_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ (**A**) was prepared by the reported method[36]. IR spectra were obtained as Nujol mulls on a Nicolet Magna 550 spectrophotometer in the range 4000 – 400 cm^{-1}. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL FX 90Q spectrometer using TMS as an internal reference in $CDCl_3$ and $CHCl_3$, respectively. The ^{27}Al NMR studies were carried out in toluene using aluminum nitrate as an external reference in aqueous solution and ^{31}P NMR spectra were recorded in $CDCl_3$. The molecular weight measurements were carried out by the elevation in boiling point method using a Beckmann thermometer fitted in a glass assembly (supplied by JSGW, India) in anhydrous benzene. The XRD patterns were recorded on Panalytical make X'Pert PRO MPD diffractometer (model 3040). SEM was performed on Carl -Zeiss (30keV) make and model EVO. The optical absorption spectra of samples have been recorded over wavelength 200 to 800 nm in solution using spectrophotometer JASCO Corp., UV-530, Rev.1.00 at room temperature.

Preparation of $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)\{S(S)P(O(CH_3)_2C(CH_3)_2CO\}]$

Benzene solutions of $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2]$ (**A**) (2.52 g; 5.15 mmol in 40 mL) and $[(OC(CH_3)_2C(CH_3)_2\ O)P(S)SH]$ (1.09 g; 5.14 mmol in 20 mL) were refluxed for 4 h. The liberated 2-propanol was continuously fractionated out azeotropically with benzene. The progress as well as the completion of the reaction was checked by the estimation of the 2-propanol in the azeotrope by oxidimetric titration[33]. After stripping off the excess solvent under reduced pressure, a pale viscous compound was obtained. The purification as well as the formation of good quality crystals of the compound from a mixture of dichloromethane and *n*-hexane (1:1) could not be achieved. The other derivatives were prepared using similar procedure. Their analytical data are summarized in Table 1.

Hydrolysis of (A) using sol-gel technique

To the clear 2-propanolic solution of (**A**) (2 g in ~30 mL 2-propanol) a drop of distilled water- 2-propanol mixture (1 mL water and 4 mL anhydrous 2-propanol) was added and stirred on a magnetic stirrer. Sol formation occurred immediately. Excess amount of water was added in small lots with continuous stirring for 4-5 h to ensure complete hydrolysis. The yellow gel formed during this process was dried in a preheated oven (at ~120 °C). The powder obtained was washed with acetone and n-hexane (1:1) mixture to remove any organic impurity. The resulting yellow powder was sintered at ~ 850 °C for 3 h in a muffle furnace to give a white powder, which was characterized as θ–alumina by powder XRD [PDF # 110517]. Hydrolysis of the other precursor $Al(OPr^i)_3$ was also carried out separately by similar route.

Results and Discussion

Synthesis and characterization of alkylene dithiophosphate complexes of bis(acetylacetonato)aluminium(III)di(μ-isopropoxo) di(isopropoxo)aluminium(III)

Reaction of the precursor, (**A**) with $[(O\text{-}G\text{-}O)P(S)SH]$ in 1:1 and 1:2 molar ratio in refluxing anhydrous benzene yield products of the following type $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al\{S(S)P(O\text{-}G\text{-}O)\}(OPr^i)]$ and $[(CH_3COCHCOCH_3)_2Al(\mu\ \text{-}OPr^i)_2Al\{S(S)P(O\text{-}G\text{-}O)\}_2]$, respectively:

$$[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al(OPr^i)_2] + n[(O\text{-}G\text{-}O)P(S)SH] \xrightarrow[\text{Reflux}]{\text{Benzene}}$$

$$[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al\{S(S)P(O\text{-}G\text{-}O)\}_n(OPr^i)_{2-n}] + Pr^iOH\uparrow$$

Table 1 — Analytical data for$[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al\{S(S)P(O\text{-}G\text{-}O)_n(OPr^i)_{2-n}]$ (n = 1 or 2)

*Complex	Pr^{i}OH(g) Found (Calcd.)	Yield %	Analysis % Found (Calcd.)					Mol. wt. Found (Calcd.)
			Al	OPr$_{ii}$	C	H	S	
(1)	0.43	99	8.4	27.01	46.72	7.21	9.5	659
	(0.43)		(8.4)	(27.60)	(46.87)	(7.34)	(9.9)	(640)
(2)	0.49	99.9	6.29	14.43	42.22	6.61	16.13	725
	(0.51)		(6.81)	(14.89)	(42.42)	(6.56)	(16.15)	(792)
(3)	0.40	98	8.1	28.21	45.14	7.07	10.21	628
	(0.43)		(8.8)	(28.85)	(45.02)	(7.01)	(10.43)	(613)
(4)	0.50	98.5	7.3	15.59	45.38	6.02	17.28	654
	(0.51)		(7.3)	(15.96)	(45.12)	(6.89)	(17.33)	(638)
(5)	0.27	99.6	9.7	28.99	44.14	6.90	10.74	590
	(0.27)		(9.8)	(29.63)	(44.12)	(6.86)	(10.75)	(597)
(6)	0.60	99.5	7.59	16.01	37.28	5.69	17.92	684
	(0.69)		(7.64)	(16.71)	(37.34)	(5.65)	(18.12)	(707)
(7)	0.31	96.2	8.25	27.02	46.07	7.39	9.7	638
	(8.32)		(8.43)	(27.63)	(46.87)	(7.34)	(9.9)	(640)
(8)	0.61	99	8.6	28.1	45.32	7.09	10.41	630
	(0.62)		(8.8)	(28.9)	(45.09)	(7.03)	(10.43)	(612)
(9)	0.49	99	7.2	16.2	39.17	6.01	17.03	718
	(0.50)		(7.3)	(16.02)	(39.13)	(5.97)	(17.30)	(736)

*$[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al[S(S)P(OC(CH_3)_2C(CH_3)_2O)](OPr^i)]$(1),$[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al[S(S)P(OC(CH_3)_2C(CH_3)_2O)]_2]$ (2), $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al[S(S)P(OCH_2CH(C_2H_5)O)](OPr^i)]$ (3), $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al[S(S)P(OCH_2CH(C_2H_5)O)]_2]$ (4), $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al[S(S)P(OCH_2CH(CH_3)O)](OPr^i)]$ (5),$[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al[S(S)P(OCH_2CH(CH_3)O)]_2]$ (6), $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al[S(S)P(OC(CH_3)_2CH_2CH(CH_3)O)](OPr^i)]$ (7), $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al[S(S)P(OCH(CH_3)_2CH(CH_3)O)](OPr^i)]$ (8) and $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al[S(S)P(OC(CH_3)CH(CH_3)O)_2]]$ (9)

[where G = $C(CH_3)_2C(CH_3)_2$, $-CH_2CH(C_2H_5)$, $CH_2CH(CH_3)$, $C(CH_3)_2CH_2CH(CH_3)$ and $CH(CH_3)CH(CH_3)$; n= 1 or 2]

These reactions are quite facile and can be pushed to completion by fractionating the liberated 2-propanol azeotropically with benzene. The progress of the reactions was monitored by estimating the liberated 2-propanol present in the azeotrope oxidimetrically. All these derivatives are pale viscous solids and are soluble in common organic solvents. Molecular weight measurements in refluxing anhydrous benzene indicated their binuclear nature (Table 1).

IR spectra

The tentative assignments of some of the important bands have been made and are summarized in Table 2. Medium intensity band at 2500 cm^{-1} in the free ligand due to $\upsilon_{(SH)}$ is absent in the IR spectra of these complexes, indicating deprotonation of –SH group and formation of Al-S bond[34]. Medium intensity band in the region 975-998 cm^{-1} due to $\upsilon_{(P\text{-}O\text{-}C)}$, in the alkylenedithiphosphoric acid, do not show any significant shift in the aluminium(III) complexes. Band due to $\upsilon_{(P=S)}$ present[35] at 660-685 cm^{-1} show shifting to lower frequencies in the aluminium (III) complexes indicating the bidentate nature of the ligand[16].

The presence of strong bands in the region 1600–1610 and 1510–1545 cm^{-1} due to ν(C=O) and ν(C=C) stretching vibrations, respectively, suggest the bi-dentate quansi-aromatic nature of the acetylacetonate moiety[36]. The medium intensity band observed in the region 1000–1020 cm^{-1} have been assigned ν(C-O) of isopropoxy group[36]. A band at 515-575 cm^{-1} may be assigned to be ν(Al-S)[16]. The Al-O-Al vibrations have been observed[36] in the region 760-790 cm^{-1}.

^{1}H NMR spectra

The important signals in the ^{1}H NMR spectra of these derivatives are summarized in Table 3. A comparison of the spectra of the free ligand (alkylenedithiophosphoric acid) with the spectra of the corresponding derivatives show the absence of –SH signals, again indicating deprotonation of the –SH group of the ligand and formation of Al-S bond[16,37]. The methine protons of the bridging and

Table 2 — IR spectral data (cm^{-1}) of $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al\{S(S)P(O\text{-}G\text{-}O)_n(OPr^i)_{2-n}]$ (n = 1 or 2)

*Complex	Acetylacetonate moeity		Isopropoxy moiety	Alkylenedithio Phosphate moiety				
	*v*C=O	*v*C=C	*v*C-O	*v*P-O-C	*v*P=S	*v*Al-S	*v*Al-O	*v*Al-O-Al
(1)	1600s	1540s	1005m	975m	685w	535w	620w	780w
(2)	1605s	1535s	1010m	995m	680w	525w	610w	790w
(3)	1605s	1525s	1020m	975m	660w	550w	635w	775w
(4)	1600s	1545s	1000m	995m	675w	560w	635w	760w
(5)	1610s	1535s	1020m	998m	685w	515w	625w	780w
(6)	1605s	1530s	1015m	975m	680w	525w	630w	770w
(7)	1600s	1520s	1010m	998m	675w	575w	630w	760w
(8)	1605s	1510s	1015m	995m	670w	520w	630w	775w
(9)	1605s	1520s	1020m	998m	660w	520w	635w	775

*Complex numbers are as in Table 1

Table 3 — ^{1}HNMR spectral data (in ppm) of $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al\{S(S)P(O\text{-}G\text{-}O)_n(OPr^i)_{2-n}]$ (n = 1 or 2)

*Complex	Acetylacetonate moeity		Isopropoxy moeity		Alkylenedithiophosphate moiety
	$-CH_3$	-CH	$-CH_3$	-OCH	
(1)	1.97,s (12H)	5.48,s (2H)	1.27,d (12H)[J 6.1Hz] 1.30, d (6H) [J 5.8Hz]	3.64-4.12, br (3H)	1.40, s (12H, CH_3)
(2)	2.30, s (12H)	5.48, s (2H)	1.24, d (12H) [J 6.2Hz]	4.12, br (2H)	1.45, s (24H, CH_3)
(3)	1.97, s (12H)	5.45, s (2H)	1.17, d (12H) [J 6.0Hz] 1.23, d (6H) [J 5.9Hz]	3.67-3.93, br (3H)	1.04, t (3H, CH_3) [J 7.3Hz] ; 1.86, m (2H, CH_2); 3.40-3.51, m (1H, OCH) [J 13.6Hz] ; 4.04, m (2H, OCH_2) [J 10.4Hz]
(4)	1.95, s (12H)	5.44, s (2H)	1.19, d (12H) [J 6.1Hz]	3.86, br (2H)	1.06, t (6H, CH_3) [J 7.4Hz] ; 1.88, m (4H, CH_2); 3.46-3.54, m (2H, OCH) [J 14.1Hz] ; 4.08, m (4H, OCH_2) [J 10.5Hz]
(5)	1.98, s (12H)	5.51, s (2H)	1.17, d (12H) [J 6.3Hz] 1.19, d (6H) [J 5.8Hz]	3.95-4.03, br (3H)	1.38,d(3H,CH_3) [J 7.2Hz]; 4.33 m (2H, OCH_2) [J 10.8Hz] ; 4.78, m (1H, OCH) [J 14.2Hz]
(6)	1.97, s (12H)	5.48,s (2H)	1.20, d (12H) [J 6.2Hz]	4.02, br (2H)	1.40, d(6H, CH_3) [J 7.1Hz]; 4.35, m (4H, OCH_2) [J 10.6Hz] ; 4.79, m (2H, OCH) [J 14.1Hz]
(7)	1.93, s (12H)	5.48,s (2H)	1.14,d (12H) [J 6.4Hz] 1.33, d (6H) [J 5.9Hz]	3.94-4.08, br(3H)	1.55,s (6H, CH_3) [J 7.6Hz]; 1.46, d (3H, CH_3) [J 7.1Hz]; 4.54, m (1H, OCH) [J 14.8Hz] ; 1.63, d (2H, CH_2)
(8)	1.94,s (12H)	5.45,s (2H)	1.18,d (12H) [J 6.1Hz] 1.20,d (6H) [J 5.8Hz]	3.74-3.85, br (3H)	1.34, d (6H, CH_3) [J 7.8Hz] ; 4.26, m (2H, OCH) [J 14.9Hz]
(9)	2.01, s (12H)	5.49,s (2H)	1.26,d (6H) [J 6.4Hz]	3.98, br (2H)	1.36, d (12H, CH_3) [J 7.2Hz] ; 4.34, m (4H, OCH) [J 15.0Hz]

*Complex numbers are as in Table 1; s- Singlet, d-doublet, t-triplet, m-multiplet, br-broad

terminal isopropoxy groups get merged to give a broad signal in the range of 3.64-4.08 ppm. The methyl protons of the bridging isopropoxy groups appear at 1.14–1.27 ppm, while the methyl protons of the terminal isopropoxy groups appear at 1.19–1.33 ppm as a doublet, indicating the nonequivalent nature of the bridging and terminal isopropoxy groups. The methyl and the methine signals of the acetylacetonate moieties appeared at 1.93–2.30 and 5.44–5.51 ppm, respectively[36,37].

$^{13}C\{^1H\}$ NMR spectra

The $^{13}C\{^1H\}$ NMR spectra of aluminum(III) complexes (Table 4) confirmed the mode of bonding as indicates by ^{1}H NMR spectra. The signal at 26.0–26.9, 100.8–101.4 and 191.2–191.6 ppm may be assigned to methyl, methine and carbonyl carbon of the acetylacetonate moieties, respectively[37]. Characteristic chemical shift values of isopropoxy groups observed at 23.2–25.5 and 63.1–64.8 ppm have been assigned to the methyl and methine carbons, respectively. Similarly, presence of two signals each for the methyl and the methine carbons of the bridging and terminal isopropoxy groups indicate nonequivalent nature of the isopropoxy groups in these derivatives[37].

Table 4 — $^{13}C\{^{1}H\}$ NMR spectral data (δ, ppm) of $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al\{S(S)P(O\text{-}G\text{-}O)_n(OPr^i)_{2-n}]$ (n = 1 or 2)

*Complex	Acetylacetonate moeity			Isopropoxy moeity		Alkylenedithiophosphate moiety
	$-CH_3$	-CH	C=O	$-CH_3$	-OCH	
(1)	26.9	101.3	191.3	25.4 23.2	64.2 63.1	24.3 (CH_3); 90.5 (OC)
(2)	26.7	100.9	191.3	24.5	64.1	24.3(CH_3); 91.1(OC)
(3)	26.8	101.4	191.6	25.1 23.7	64.3 63.1	15.9(CH_3); 23.3(CH_2); 72.8(OCH); 76.9(OCH_2)
(4)	26.9	101.2	191.5	24.9	64.2	15.8(CH_3); 23.9 (CH_2); 72.8(OCH); 76.7(OCH_2)
(5)	26.5	100.8	191.2	25.0 23.5	64.3 63.5	23.8(CH_3); 73.4(OCH_2); 77.5(OCH)
(6)	26.3	100.9	191.4	25.5	63.3	23.5(CH_3);74.1(OCH); 73.4(OCH_2)
(7)	26.0	101.4	191.4	25.1 23.4	64.8 63.8	23.9(CH_3); 27.8 (CH_2); 82.4(OCH); 90.8 (OC)
(8)	26.7	101.1	191.5	25.2 23.6	64.3 63.8	17.9(CH_3); 82.9 (OCH)
(9)	26.6	101.1	191.4	25.0	64.3	17.8(OCH_3); 83.1 (OCH)

*Complex numbers are as in Table 1

^{27}Al NMR spectra

In ^{27}Al NMR (I = 5/2 for ^{27}Al) additional quadrupolar interactions are present and these are not completely averaged out in magic angle spinning. Hence, ^{27}Al NMR spectra provide information only about the first coordination sphere of Al(III) ions[38]. The ^{27}Al NMR spectrum of **(1)** [Fig. 1 (a)] at room temperature exhibits two signals at ~1.8 and at ~20.4 ppm, indicating the presence of both hexa- and penta-coordination around aluminum(III) atoms. The ^{27}Al NMR spectrum of **(2)** at room temperature [Fig-1 (b)] exhibits a signal at ~ 0.78 ppm indicating the presence of hexa-coordination around both the aluminium(III) atoms[13].

^{31}P NMR spectra

In proton decoupled ^{31}P NMR spectra of the representative derivatives (**1**) and (**2**) presence of only one single peak at 95.71 and 90.59 ppm, respectively, strongly suggested tetra-coordination around phosphorus atom and a bidentate mode of chelation of the dithio ligand[39] (Fig. 2). In the absence of single crystal X-ray diffraction study, it is difficult to comment on the exact molecular structure of such derivatives, yet above studies do suggest the possibility of a binuclear structure in all the similar derivatives in solution Fig. 3 (a) and (b) are proposed structures of $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al\{S(S)P(O\text{-}G\text{-}O)\}(OPr^i)]$ and $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al\{S(S)P(O\text{-}G\text{-}O)\}_2]$, respectively.

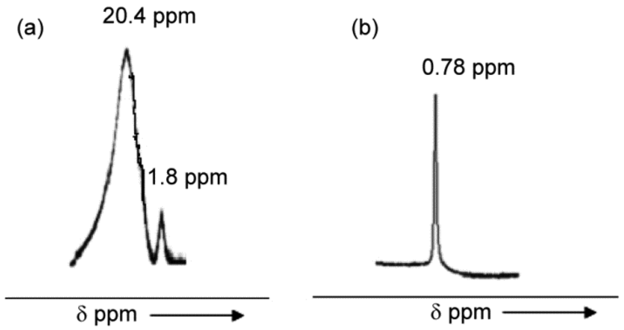

Fig. 1 — ^{27}Al NMR spectra of representative derivatives (a) for complex (1) and (b) for complex (2)

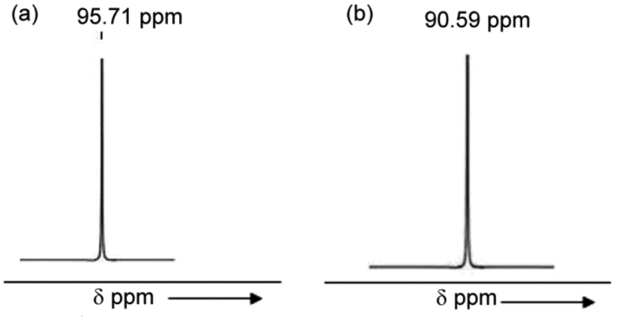

Fig. 2 — ^{31}P NMR spectrum of representative derivatives (a) for complex (1) and (b) for complex (2)

Hydrolytic studies of $Al(OPr^i)_3$ and (A) by the sol-gel technique

The hydrolysis of $Al(OPr^i)_3$ and (**A**) followed by sintering at 850 °C for 3 h afford homogenous formation of θ-alumina. These θ-alumina were

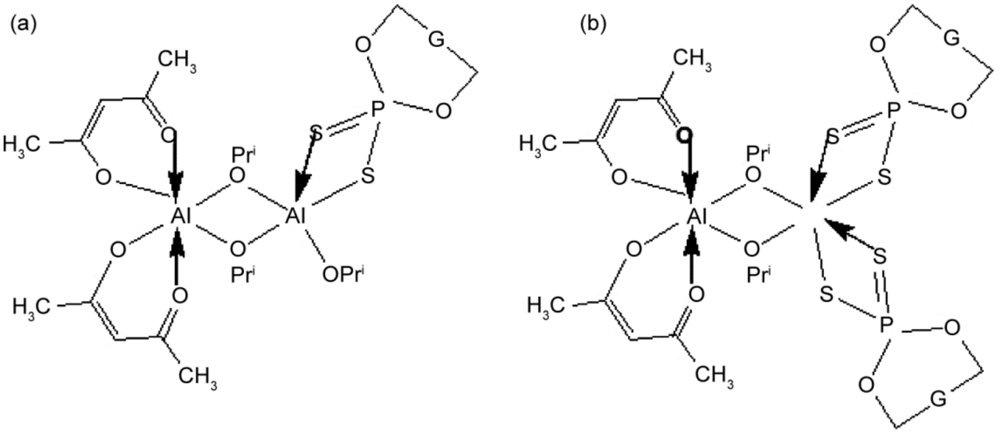

Fig. 3 — (a) and (b) are proposed structure of $[(CH_3COCHCOCH_3)_2Al(\mu\text{-}OPr^i)_2Al\{S(S)P(O\text{-}G\text{-}O)_n(OPr^i)_{2\text{-}n}]$ (n = 1 or 2), respectively

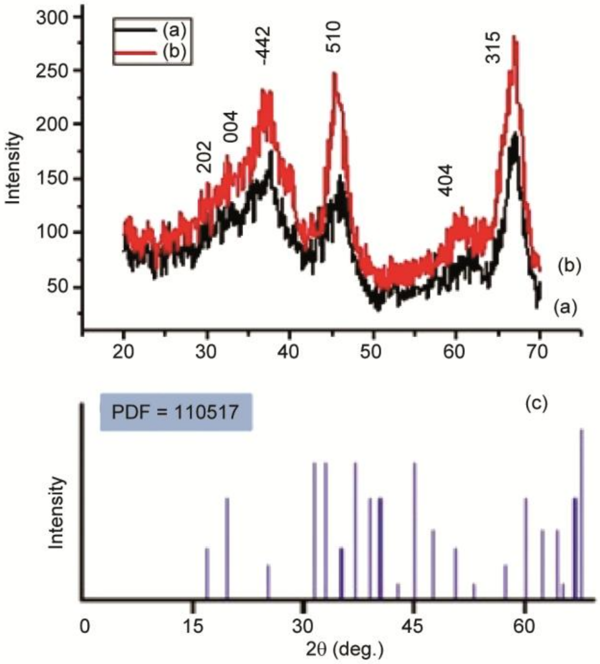

Fig. 4 — XRD patterns of alumina samples (a) and (b) obtained from $Al(OPr^i)_3$ and complex (**A**), respectively and (c) reference pattern for θ-alumina

characterized by FT-IR spectra, powder XRD and SEM analysis. The XRD patterns of nano-size θ-alumina obtained from $Al(OPr^i)_3$ and (**A**), respectively, along with the reported θ-alumina (PDF # 110517) are shown in Fig. 4. In these oxides the 2θ values 27.41^{o}, 32.93°, 37.61°, 42.85^{o}, 56.54 ^{o} and 66.90° corresponding to diffraction from (2 0 2), (0 0 4), (-4 4 2), (5 1 0), (4 0 4) and (3 1 5), respectively, are in good agreement with reported values suggesting the formation of monoclinic end-centered phase of transition alumina with lattice parameters a = 11.74 Å, b= 5.72 Å, c = 11.24 Å and β = 103.34°. It has been shown that the fcc arrangement of oxygen sublattices plays an important role in stabilization of θ phase[40].

The average particle sizes of the θ-Al_2O_3 obtained from $Al(OPr^i)_3$ and **(A)** were ~12 nm and ~10 nm, respectively**,** evaluated from Debye-Scherrer equation[41]. Scanning electron microscopic images of the oxides (Fig. 5) has shown formation of agglomerated micro crystallites of nano-sized particles in both the cases. In FT-IR absorption spectra of the θ-Al_2O_3 powders, the medium intensity band between 1000 and 400 cm^{-1} is a characteristic absorption band of transition alumina[32]. It is attributed to stretching vibration of the Al-O-Al bond. In addition to alumina bands, there are bands due to chemisorbed and adsorbed species at the surface, which is very obvious at this scale. A very large (medium intensity) band at 3300-3500 cm^{-1} is due to a superposition of vibration bands of bonded hydroxyl groups, isolated OH groups, and stretching vibrations of adsorbed water molecules. The band at 1650 cm^{-1} attributed to the bending of molecular water. The two week intensity bands between 1650,1500 and 1450 cm^{-1} are attributed to chemically adsorbed impurities of CO_2, CO_3^{2-}, or HCO_3^- that are very difficult to remove, even at temperatures of 850°C [15]. Energy band gaps were determined using *Tauc relation*[42]. The absorption spectra for θ-Al_2O_3 obtained from $Al(OPr^i)_3$ and **(A)** are shown in Fig. 6 (a) and (b), respectively along with the corresponding Tauc's plots [hv verses $(\alpha hv)^2$] in (c) and (d), respectively. From these plots, the energy band gaps for the θ-Al_2O_3 obtained from $Al(OPr^i)_3$ and **(A)** are found to be 4.82 eV and 5.01 eV, respectively.

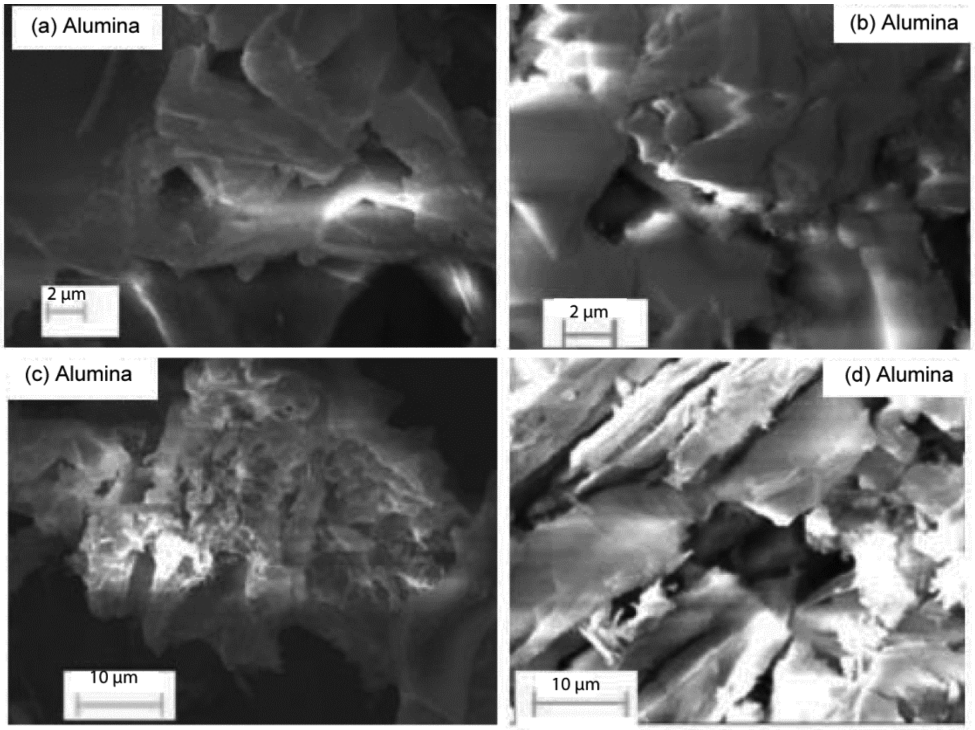

Fig. 5 — SEM images of alumina samples (a,c) obtained from Al(OPr^i)$_3$ and (b,d) from complex (**A**)

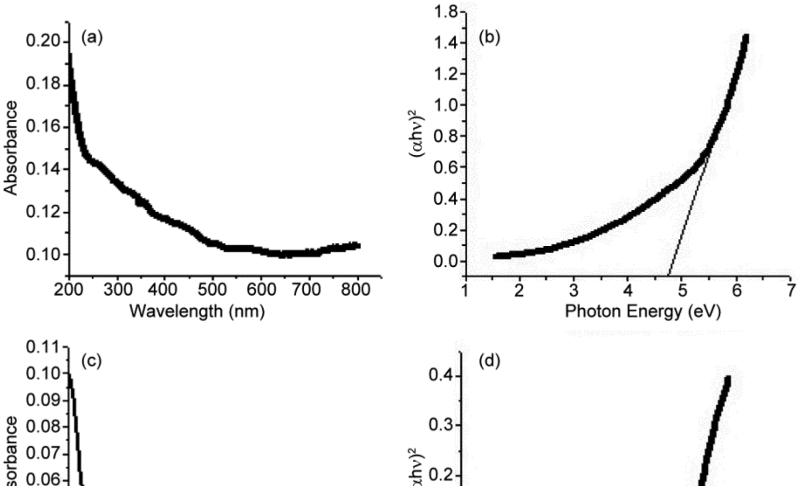

Fig. 6 — Absorption spectra (a) & (b) and corresponding *Tauc*-Plots, (c) & (d) of alumina obtained from Al(OPr^i)$_3$ & (**A**), respectively

Conclusions

The above studies suggest the formation of unsymmetrical binuclear complexes containing aluminium(III) atoms in different coordination environment. Spectroscopic studies suggest chelating mode of attachment of dialkylenedithio ligands. Sol-gel hydrolysis in organic media of aluminium isopropoxide as well as its chemically modified precursors exhibit interesting structural variations around aluminum(III) atoms. These appear to be potential precursors for the preparation of nanosized alumina by sol-gel technique.

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