



SYNTHESIS AND CHARACTERISATION OF BIMETALLIC [Al (III)Ba (II)]- μ -OXO-ISOPROPOXIDE,
 $BaO_2Al_2(OPr^i)_4$ AND ITS REACTIONS WITH SOME PROTIC LIGANDS

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Abstract- A new bimetallic [Al (III) Ba (II)]- μ -oxo-isopropoxide was prepared by the reaction of $Ba(OAc)_2$ with $Al(OPr^i)_3$ in 1:2 molar ratio. Reactions of this bimetallic- μ -oxo-isopropoxide, $BaO_2Al_2(OPr^i)_4$, were carried out with some protic ligands like water, alcohols, acetic acid, glycols and acetyl acetone in different stoichiometric ratios. The resultant products have been characterised by elemental analyses, Molecular weight determinations and spectroscopic (IR and NMR) studies. A plausible mechanism of the reactions has been proposed.

Metal alkoxides have been widely used as precursors for oxide ceramic materials (1,2), but in recent years soluble metal oxide alkoxide precursors are receiving considerable attention in view of their facile conversion to oxide ceramic materials and the presence of comparatively lesser residual organic component(3-6) in the final product(s). Presence of more than one metal atom linked together by μ -oxo bridges changes significantly the physical characteristics of the resultant products and induces active sites for insertion polymerisation reactions (7-14). In this communication, the preparation and characterisation of $BaO_2Al_2(OPr^i)_4$ and its hydrolysis and alcoholysis reactions as well as its reaction with protic ligands like glycols, acetic acid and acetylacetone are reported. Substitution reactions by less hydrolysable groups decrease the functionality of the precursors and thus promote a decoupling between substitution, hydrolysis and condensation. Substitution of isopropoxy groups by organic ligands influences the physical properties of bimetallic μ -oxo derivatives and controls the hydrolysis as well as thermal stability and also causes a modification in the coordination sphere of the metals, change in catalytic behaviour, solubility and the reactivity of the resulting complexes.

EXPERIMENTAL

All reactions were carried out under strictly anhydrous conditions.

Aluminium isopropoxide (Fluka) was redistilled at 80°C/0.3 mm before use. $Ba(OCOCH_3)_2$ (AR, BDH) was used as obtained after drying under vacuum. Isopropanol was estimated oxidimetrically using a 1 N $K_2Cr_2O_7$ solution in 12.5% sulphuric acid (15,16). Aluminium and barium were estimated gravimetrically as $Al(ONC_9H_{14})_3$ (17) and $BaSO_4$ (17).

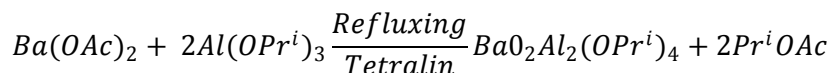
A semimicro Gallenkamp ebulliometer fitted with thermistor sensing was used for molecular weight measurements. Infrared spectra were recorded on a CARL ZEISS JENA Specord M80 in the range 4000-200 cm^{-1} in nujol mulls. The NMR spectra were recorded in $CDCl_3$ solution using TMS as an internal reference on a JeolFX90Q multinuclei spectrophotometer. ^{27}Al NMR spectra were recorded using $Al(NO_3)_3 \cdot xH_2O$ as reference.

The bimetallic [Al (III), Ba (II)]- μ -oxo-isopropoxide was prepared by refluxing $Al(OPr^i)_3$ with $Ba(OCOCH_3)_2$ (0.005mM) in stoichiometric ratio in tetralin solution for about 40h under a fractionating column. Isopropyl acetate formed during the course of reaction was fractionated off continuously from 80° C to 190 °C. After completion of the reaction and removal of all volatile fractions at 40-50° C/1mm, a yellow-coloured solid product was obtained. The isolated product was recrystallised from benzene solution. Yield 85%, Found: OPr^i , 48.2; Ba, 29.9; Al, 11.7: Calc: for $BaO_2Al_2(OPr^i)_4$: OPr^i , 51.4; Ba, 29.9; Al, 11.7%.

The hydrolysis and alcoholysis reactions of $BaO_2Al_2(OPr^i)_4$ under different experimental conditions and its reactions with ligands like acetic acid, acetyl acetone and glycols have been studied. The results are described under specific headings.

RESULTS AND DISCUSSIONS

The reaction of barium acetate with aluminium isopropoxide in 1:2 molar ratio in tetralin solution yields soluble bimetallic [Al (III), Ba (II)]- μ -oxo-isopropoxide, $BaO_2Al_2(OPr^i)_4$, in quantitative yield.



The reaction in low boiling solvents like toluene or xylene could not be pushed to completion.

In the I.R. spectra, the $\nu C=O$ frequency appearing at 1620 cm^{-1} in $Ba(OAc)_2$ was found to be absent indicating the removal of acetyl groups. A band observed at $\sim 1320\text{ cm}^{-1}$ is characteristic of gem dimethyl of the isopropoxy group(18). The bands at ~ 1190 and $\sim 1100\text{ cm}^{-1}$ may be assigned to vibrations(18)of the isopropoxy moiety and the one appearing at $\sim 950\text{ cm}^{-1}$ to $\nu C-O$ isopropoxy bridging group(19). The bands appearing in the region $430-450\text{ cm}^{-1}$ may be assigned to $\nu Al-O$ (20) and those appearing in the region $600-650\text{ cm}^{-1}$ to the combination bands like($\nu C-CH_3 + \nu Al-O$)and (ring deformation + $\nu Al-O$) respectively(20). $\nu Ba-O$ has been observed at $\sim 460\text{ cm}^{-1}$.

The 1H NMR spectrum of the compound $BaO_2Al_2(OPr^i)_4$ in $CDCl_3$ solution shows a broad overlapping doublet centred at $\delta 1.20$ ppm due to methyl protons of the fastly interchanging bridging and terminal isopropoxy groups and a multiplet centred at $\delta 4.30$ ppm due to methine protons of the isopropoxy group. The spectra could not be further resolved even up to $-60^\circ C$, indicating interchangeability of alkoxy groups even at lower temperatures.

This observation is further corroborated by the ^{13}C NMR spectrum in which 2 signals due to methine and methyl carbons are observed at $\delta 63.8$ ppm and $\delta 27.0$ ppm respectively.

The ^{27}Al NMR spectrum shows only one signal at $\delta 60.6$ ppm (line width at half height 480 Hz) indicating a tetrahedral geometry around the aluminium atom(21).

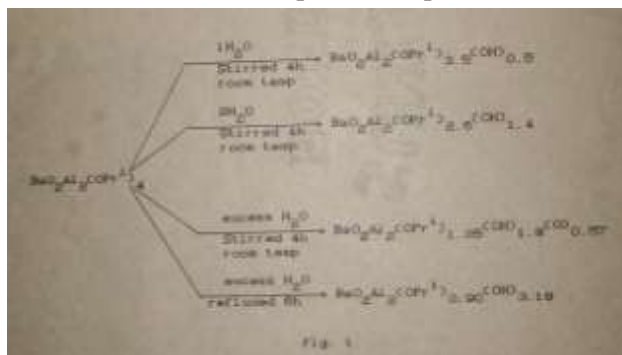
Repeated molecular weight measurements in boiling benzene solution in different concentration ranges confirm its dimeric nature, i.e., $Ba_2O_4Al_4(OPr^i)_8$.

Reactions of $Ba_2O_4Al_4(OPr^i)_8$ were carried out with water, alcohol and some protic ligands and the results are being described below:

Hydrolysis

The hydrolysis of $Ba_2O_4Al_4(OPr^i)_8$ in isopropanol solution has been studied under different experimental conditions and the hydrolysed products have been isolated after distilling off the volatile fractions under reduced pressure at ambient temperature and analysed.

On addition of water, slow hydrolysis occurs and the isopropoxy groups are replaced by $-OH$, which then undergo condensation. Initially no visible change is observed in the solution but on stirring for some time turbidity appears. The change from sol to gel occurs through condensation and the extent of condensation increases with time and temperature, yielding finally sparingly soluble polymeric compounds (yellowish solids). The isolated products are found to have non- stoichiometric ratios. However, under controlled experimental conditions, the elemental analyses of the final products are found to correspond (within 1-2%) to the respective empirical formulae shown in fig.1:



The 1HNMR spectra of freshly prepared derivatives show a doublet at $\delta 1.20$ ppm and a multiplet at $\delta 4.30$ ppm confirming the presence of isopropoxy group.

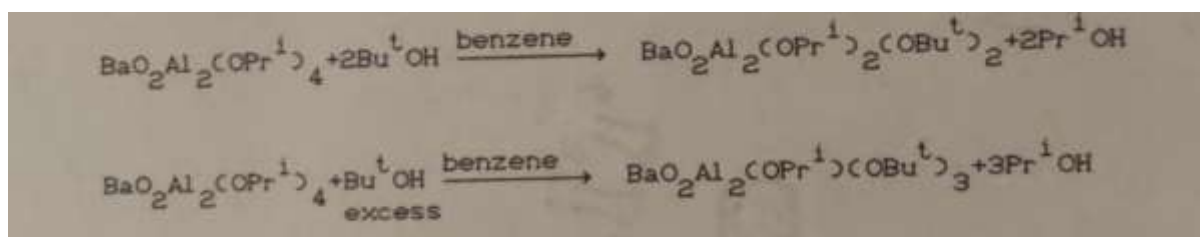
In IR spectra, absorptions at 610 and 460 cm^{-1} have been ascribed to $\nu\text{Al-O}$ and $\nu\text{Ba-O}$ respectively and the presence of a broad band in region 3200-3600 cm^{-1} bands confirms the presence of -OH group (22).

Alcoholysis

The treatment of $\text{BaO}_2\text{Al}_2(\text{OPr}^i)_4$ with excess MeOH, resulted in the formation of a product of the composition $\text{BaO}_2\text{Al}_2(\text{OPr}^i)_{1.3}(\text{OMe})_{2.7}$. However even on repeated treatment with MeOH, all isopropoxy groups could not be replaced and the final product was found to have the composition $\text{BaO}_2\text{Al}_2(\text{OPr}^i)(\text{OMe})_3$.

The reaction of $\text{BaO}_2\text{Al}_2(\text{OPr}^i)_4$ with tert-butanol in 1:2 and 1: >4 molar ratios and fractionating off the liberated isopropanol as an azeotrope with benzene resulted in the formation of $\text{BaO}_2\text{Al}_2(\text{OPr}^i)_2(\text{OBu}^t)_2$ and $\text{BaO}_2\text{Al}_2(\text{OPr}^i)(\text{OBu}^t)_3$ respectively.

Molecular weight measurement of $\text{BaO}_2\text{Al}_2(\text{OPr}^i)(\text{OBu}^t)_3$ in boiling benzene reveals its dimeric nature. The solubility of $\text{BaO}_2\text{Al}_2(\text{OPr}^i)(\text{OMe})_3$ was not found to be sufficient for molecular weight measurement.

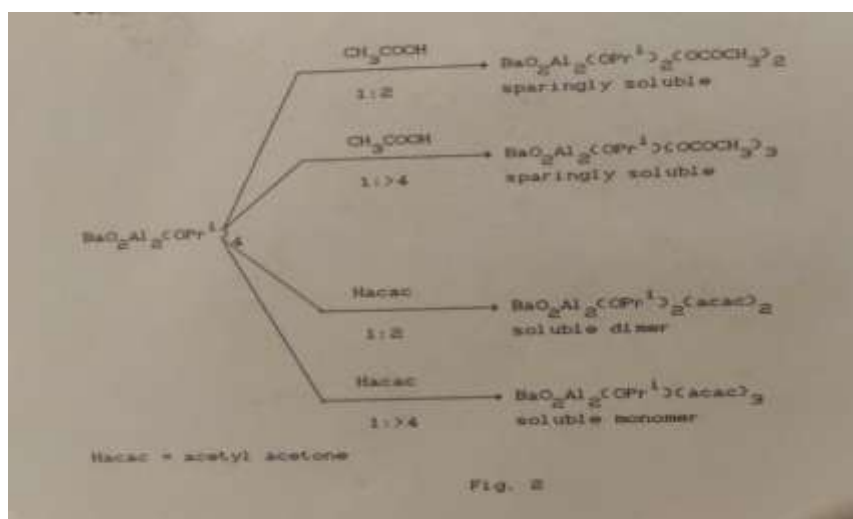


These alcoholysis reactions appear to indicate that one of the isopropoxy groups in the unit, $\text{BaO}_2\text{Al}_2(\text{OPr}^i)_4$ of the dimer may be triply bridging, making it resistant to replacement.

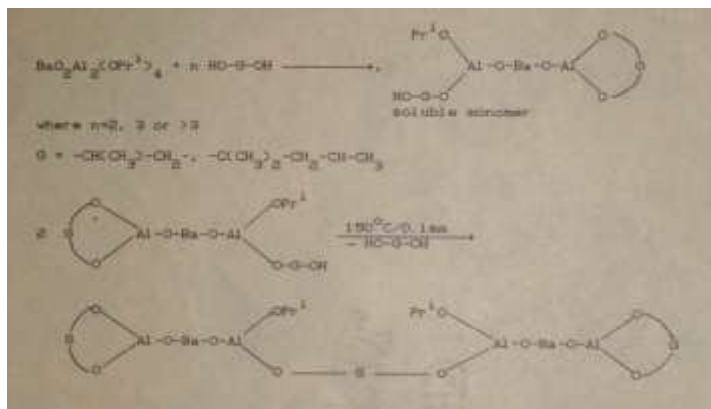
The ^1H NMR spectra of the t-butoxy derivative show a broad signal at δ 1.25 ppm due to the mixing of methyl protons of isopropoxy and butoxy groups along with a multiplet of methine protons. In the methylated products, a sharp doublet due to methoxy groups at δ 3.54 ppm, a fairly sharp doublet at δ 1.22 ppm and a multiplet at δ 4.30 ppm are observed.

The IR spectra of t- butoxy derivative show absorption bands at 1210 and 1200 cm^{-1} assignable to $\nu(\text{C-O})$ and bands at 1010, 910, 800 and 770 cm^{-1} due to isopropoxy (23) groups. The methoxy derivative shows a band at 1180 cm^{-1} (merged with the band of isopropoxy) and 1070 cm^{-1} due to $\nu(\text{C-O})$ of methoxy(23).

Reactions of $\text{BaO}_2\text{Al}_2(\text{OPr}^i)_4$ with acetic acid and acetyl acetone appear to proceed with the replacement of three out of four isopropoxy groups only. The liberated isopropanol was fractionated off azeotropically with benzene and the progress of the reaction was monitored by estimating the quantity of isopropanol in the azeotrope. The final products obtained in the reactions are shown below (fig. 2) and their elemental analyses and molecular weights of soluble products correspond (within $\pm 0.5\%$) to the empirical formulae indicated in each case:



Reactions of $BaO_2Al_2(OPr^i)_4$ with glycols in molar ratios 1:2, 1:3 or 1:>3 yield the products having the molecular composition $BaO_2Al_2(OPr^i)(OGO)(OGO)$ only:



The product obtained with hexylene glycol on heating at $150^\circ/0.1$ mm undergoes intermolecular condensation with the loss of one mole of glycol.

The 1H NMR spectra of carboxylic acid derivatives show a sharp doublet at δ 1.19 ppm and a multiplet at δ 4.18 ppm. In the analogous acetylacetonate derivatives two singlets at δ 2.03 and δ 5.56 ppm due to methyl and methine protons of acetylacetonate group along with a sharp doublet at δ 1.20 ppm and a multiplet at δ 4.30 ppm due to methyl and methine protons of the isopropoxy groups are observed. The disappearance of the signal at δ 13 ppm, confirms the interaction of the enolic -OH of acetylacetonate with isopropoxy group.

The propylene glycol derivative in $DMSO-d_6$ solution shows a doublet at δ 1.0 ppm due to methyl of isopropoxy and a multiplet at δ 3.8 ppm due to methine protons. A signal due to -OH was observed at δ 7.9 ppm. The corresponding hexylene glycol derivative in $CDCl_3$ solution shows three sets of doublets at δ 1.21, δ 1.30 and δ 1.53 ppm respectively due to methyl of hexylene glycol and isopropoxy groups.

The IR spectra of carboxylic acid derivative show bands at 1620 cm^{-1} and at 1270 cm^{-1} due to $\nu_{asym}(C-O)$ and $\nu_{sym}(C-O)$ stretching vibrations. The β -diketone derivative shows a strong band in the region $1600-1500\text{ cm}^{-1}$ along with the usual bands due to isopropoxy group (24). The glycol derivatives show a broad band in the region $3600-3240\text{ cm}^{-1}$ confirming the presence of a free -OH group (23).

The derivative $BaO_2Al_2(OPr^i)_2(acac)_2$ was found to be dimeric in nature and therefore it appears that acetyl acetone moieties replace the terminal isopropoxy groups without affecting the basic geometry of the parent compound.

Both IR and NMR spectral data confirm the presence of isopropoxy group in the molecule and the ^{27}Al NMR signal (line width at half height 180Hz) supports the six coordinated environment (21) around aluminium atoms.

Repeated crystallization attempts to develop a single crystal could not be successful. A number of plausible structures could be suggested for $BaO_2Al_2(OPr^i)_4$ and its substitution products on the basis of their spectral data and known structures of few compounds like:

$HBa_6O(Ph)_9(THF)_8$ (25), $H_3Ba_6O(OBu^t)_{11}(OCe_2CH_2O)(THF)_3$ (25),

$Ba_6O(OC_2H_4OMe)_{10}(HOC_2H_4OMe)_4$ (26), $H_2Ba_8(O)(OPH)_4(HMPA)_6$ (27) as well as $Ba_2(OCPh_3)_4(THF)_3$ (27). However, this effort might be too speculative at this stage particularly in view of a recent conclusion about the variation of coordination state of barium between 4 and 5 in the last compound.

It may, therefore, suffice to point out a few salient features for the same, e.g. (i) the reactions of $Ba_2O_4Al_4(OPr^i)_8$ dimer with Bu^tOH and CH_3COOH show that two out of eight isopropoxy groups in the molecule might be triply bridging, rendering them resistant to replacement and (ii) its reactions with acetylacetonate show that the original dimeric structure remains intact up to replacement of four isopropoxy groups but breaks down to the monomeric species $BaO_2Al_2(OPr^i)(acac)_3$ on

replacement of six OPr^i group. Further, ^{27}Al NMR spectra show that the last product has aluminium in 6 coordination state whereas in all other species it is 4 coordinated.

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Table 1. Reaction of [Al (III), Ba(II)] - μ - oxo – isopropoxide with water.

BaO ₂ Al ₂ (OPr ⁱ) ₄	H ₂ O	Molar Ratio	Reaction Condition	Product Formed*	Yield (g) Found (Calc)	Analysis % Found (Calc)		
						Ba	Al	OPr ⁱ
1.76	0.07	1:1	Stirred,4h Room Temp. Pr ⁱ OH 40ml	BaO ₂ Al ₂ (OPr ⁱ) _{3.5} (OH) _{0.5}	1.69 (1.68)	1.69 (31.3)	29.7 (12.3)	45.2 (47.4)
1.59	0.12	1:2	Stirred,4h Room Temp. Pr ⁱ OH 60ml	BaO ₂ Al ₂ (OPr ⁱ) _{2.6} (OH) _{1.4}	1.44 (1.38)	34.4 (34.3)	13.4 (13.5)	35.1 (38.3)
1.41	excess	1:>4	Refluxed 6h, Pr ⁱ OH 40 ml	BaO ₂ Al ₂ (OPr ⁱ) _{0.90} (OH) _{3.18}	0.98 (1.00)	41.6 (41.7)	16.3 (16.4)	14.7 (16.3)
1.22	excess	1:>4	Stirred 8h Room temp. Pr ⁱ OH 50 ml	BaO ₂ Al ₂ (OPr ⁱ) _{1.05} (OH) _{1.8} (O) _{0.57}	1.02 (0.96)	42.3 (42.1)	16.6 (16.6)	19.3 (19.0)

- Yellow Solids having poor solubility in organic solvents

Table 2. Reaction of [Al (III), Ba(II)] - μ - oxo – isopropoxide with some protic ligands.

BaO ₂ Al ₂ (OPr ⁱ) ₄ (g)	Ligand (g)	Molar Ratio	Pr ⁱ OH liberated Found (Calc)(g)	Product Formed	Yield (g) Found (Calc)	Analysis % Found (Calc)		
						Ba	Al	OPr ⁱ
MeOH 1.56	0.21	1:2	-	BaO ₂ Al ₂ (OPr ⁱ) _{1.3} (OMe) _{2.7}	1.32 (1.37)	34.0 (34.0)	13.2 (13.4)	-
1.63	4.8*	1:>4	-	BaO ₂ Al ₂ (OPr ⁱ)(OMe) ₃	1.31 (1.33)	36.1 (36.5)	14.3 (14.1)	-
1.68	Bu ^t OH 0.55	1:2	0.41 (0.43)	BaO ₂ Al ₂ (OPr ⁱ) ₂ (OBu ^t) ₂	1.71 (1.79)	28.0 (28.1)	10.9 (11.0)	-
1.55	4.2	1:>4	0.57 (0.59)	BaO ₂ Al ₂ (OPr ⁱ)(OBu ^t) ₃	1.69 (1.69)	20.1 (20.3)	10.4 (10.7)	-
1.30	CH ₃ COOH 0.34	1:2	0.25 (0.28)	BaO ₂ Al ₂ (OPr ⁱ) ₂ (OCOCH ₃) ₂	1.30 (1.30)	29.7 (29.9)	11.5 (11.8)	23.2 (25.7)
1.55	3.6	1:>4	0.58 (0.59)	BaO ₂ Al ₂ (OPr ⁱ)(OCOCH ₃) ₃	1.50 (1.55)	29.5 (29.9)	11.6 (11.8)	11.0 (12.8)
1.21	Hacac 0.53	1:2	0.38 (0.39)	BaO ₂ Al ₂ (OPr ⁱ) ₂ (acac) ₂	1.41 (1.42)	25.2 (25.4)	9.2 (9.9)	-
1.93	3.0	1:>4	0.73 (0.74)	BaO ₂ Al ₂ (OPr ⁱ)(acac) ₃	2.40 (2.41)	23.2 (23.6)	9.0 (9.3)	-
1.98	HO-G-OH 0.33	1:2	0.50 (0.51)	BaO ₂ Al ₂ (OPr ⁱ)(O-G-O) (O-G-O)	1.80 (1.86)	31.6 (31.8)	12.2 (12.5)	-
2.41	HO-G'-OH	1:2	0.61 (0.62)	BaO ₂ Al ₂ (OPr ⁱ)(O-G'-O) (O-G'-OH)	2.66 (2.71)	26.0 (26.6)	10.2 (10.4)	-

- - treated 3 times with methanol
- Hacac= acetyl acetone, G= CH(CH₃)-CH₂-, G' = C(CH₃)₂-CH₂-CH-CH₃