



---

**HETEROCYCLIC COMPOUNDS OF ALUMINIUM (III) WITH GLYCOLS:**

**PART 3 - REACTION OF  $H[Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$  WITH  
 $MOCH_3$  (M= Li, Na, K) IN 1:1 MOLAR RATIO**

**Anita Kothari**

Department of Chemistry, Government College, Ajmer, 305001, India  
e-mail : anitajm1969@gmail.com

---

**Abstract**

Reaction of  $Al(OPr^i)_3$  with  $HOC(CH_3)_3C(CH_3)_2OH$  in 1:1 and 1:2 molar ratios in refluxing benzene, have resulted in the synthesis of  $[(Pr^iO)Al\{OC(CH_3)_2C(CH_3)_2O\}]$  and  $H[Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$ , respectively. These are insoluble/sparingly soluble in benzene and chloroform but soluble in dimethyl sulfoxide. Further reaction of  $H[Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$  with  $MOCH_3$  (M = Li, Na and K) in 1:1 molar ratio in refluxing methanol yields  $[(CH_3OH)M][Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$ . These are soluble in methanol and dimethyl sulfoxide. These bimetallic heterocyclic derivatives are dimeric in methanol and have slight ionic character. Plausible structures has been proposed on the basis of elemental analyses, molecular weight measurements, IR, NMR( $^1H$ ,  $^{13}C$  and  $^{27}Al$ ) spectral studies.  $^{27}Al$  NMR spectra show the presence of four coordinated aluminum site.

---

**Introduction**

A considerable amount of work has been carried out in the laboratories of the candidate on M-O-C derivatives, which has been summarized in three books namely, metal alkoxides<sup>1</sup>, metal  $\beta$ -diketonates and allied derivatives<sup>2</sup> and metal carboxylates<sup>3</sup>. In addition, the work on M-N-C bonded compounds has been summarized by Lappert et al.<sup>4</sup>. More recent research has focused on the synthesis and characterization of heterocyclic derivatives in which the labile alkoxy bridging ligands of metal alkoxides

are replaced by ligands<sup>5</sup>, such as oxo<sup>6-7</sup>,  $\beta$ -diketonate<sup>8-14</sup>, acetate<sup>15</sup>, glycolate<sup>16-17</sup>, siloxides and even hetrometallic alkoxides<sup>18</sup>.

Keeping this in view an effort has been made during the course of the present investigation to synthesize and characterize some interesting bimetallic heterocyclic derivatives of aluminium(III) with 2,3-dimethyl-2,3-butanediol.

## Experimental

All of the solvents used in the present investigation were of reagent grade and were made anhydrous by standard methods. Aluminium isopropoxide was prepared as described by Mehrotra<sup>19</sup>. 2,3-dimethyl-2,3-butanediol was distilled before use. Isopropanol was determined<sup>20</sup> by oxidation with normal  $K_2Cr_2O_7$  solution in 12.5%  $H_2SO_4$ . Aluminium was determined gravimetrically as oxinate.

$^1H$  NMR spectra were recorded on a JEOL FX 90Q spectrometer in  $CDCl_3$  using TMS as an internal reference.  $^{13}C$  NMR spectral studies were carried out in chloroform at 22.49 MHz using  $D_2O$  locks.  $^{27}Al$  NMR spectral studies were carried out in benzene or methanol on a JEOL FX 90Q at 23.79 MHz, using aluminium nitrate (in water) as standard reference. Molecular weight measurements were carried out on a Knauer vapour pressure osmometer in chloroform or methanol solution at 45°C. Infrared spectra were recorded as Nujol mulls on a Perkin Elmer 577 spectrophotometer in the range 4000-200 $cm^{-1}$ .

## Synthesis of compounds of 2,3-dimethyl-2,3-butanediol

### 1. Reaction of $Al(OPr^i)_3$ with $HOC(CH_3)_2C(CH_3)_2OH$ in 1:2 molar ratio in benzene.

To the benzene solution of  $Al(OPr^i)_3$  (4.45 g, 21.79 mmol),  $HOC(CH_3)_2C(CH_3)_2OH$  (5.17 g, 43.75 mmol) was added. Initially solution was clear for about 1½ hrs. refluxing time. But became insoluble after sometime. The whole contents were refluxed for about 5 hrs. The liberated isopropanol was estimated as benzene-isopropanol azeotrope. A white solid powder of the formula  $H[Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$  was obtained, after the removal of remaining solvent under reduced pressure.

The above product was purified by recrystallization from a mixture of dimethyl sulfoxide and dichloromethane. Yield found : 95%. Anal. found: Al, 10.30; C, 54.89; H, 9.50%. Calculated for  $C_{12}H_{25}O_4Al$  : Al, 10.36; C, 55.36; H, 9.68%.

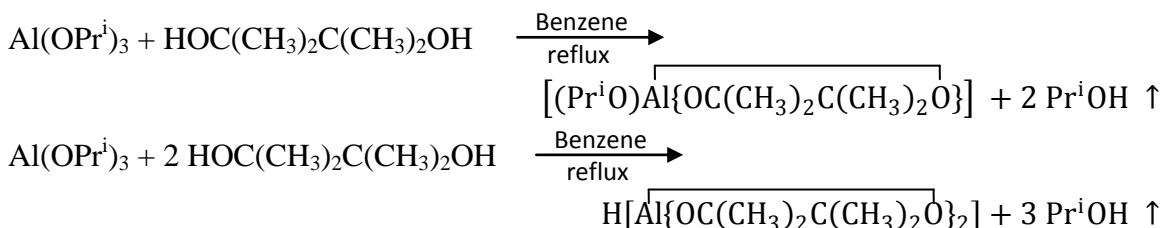
## 2. Reaction of $\text{H}[\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$ with $\text{LiOCH}_3$ in 1:1 molar ratio in methanol

A methanol solution of lithium methoxide [prepared by dissolution of 0.06 g (8.65 mmol) of lithium in ~20ml of methanol] was added to a suspension of  $\text{H}[\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$  (2.27 g, 8.71 mmol) in methanol (~~~30 ml~~). The mixture was refluxed for about 2 hrs., until a clear solution was obtained, Excess methanol was removed under vacuum giving a white solid  $[(\text{CH}_3\text{OH})\text{Li}][\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$ . The product was washed with dichloromethane. Yield found: 96%. Anal. found: Al, 8.99; C, 51.86; H, 9.39%. Calculated for  $\text{C}_{13}\text{H}_{28}\text{O}_5\text{LiAl}$  : Al, 9.04; C, 52.34; H, 9.46%. Similarly, the reactions of  $\text{Al}(\text{OPr}^i)_3$  with  $\text{HOC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{OH}$  in 1:1 molar ratio in benzene and of  $\text{H}[\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$  with sodium and potassium methoxide in 1:1 molar ratio in methanol were carried out (Table-1)

## Result and Discussion

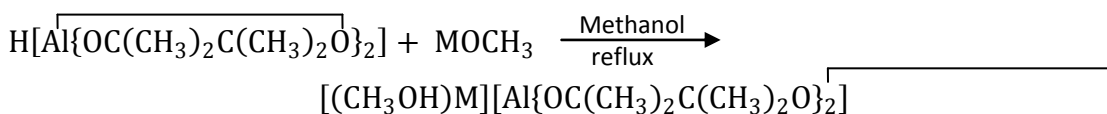
### Compounds of 2,3-dimethyl-2,3-butanediol

$\text{Al}(\text{OPr}^i)_3$  reacts with  $\text{HOC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{OH}$  in 1:1 and 1:2 molar ratios in refluxing benzene to yield  $[(\text{Pr}^i\text{O})\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}]$  and  $\text{H}[\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$ , respectively:



Two moles of isopropanol could be collected easily in the above reactions and for the removal of third mole of isopropanol, the reactions are pushed to completion by continuously removing the liberated isopropanol azeotropically. Completion of these reactions was checked by estimating the liberated isopropanol in a mixture of benzene and isopropanol. All the above products are white solids and insoluble/sparingly soluble in benzene and chloroform but soluble in dimethyl sulfoxide.

Reaction of  $\text{H}[\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$  with alkali metal methoxide in 1:1 molar ratio in methanol are facile and give soluble products of the type,  $[(\text{CH}_3\text{OH})\text{M}][\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$  (M=Li, Na and K) :



**Table - 1 : Reaction of  $\text{Al}(\text{OPr}^i)_3$ , with  $\text{HOC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{OH}$  in 1:1 and 1:2 molar ratios and reaction of  $\text{H}[\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$  with  $\text{MOCH}_3$  (M=Li, Na and K)**

S. No	Reactants (g)		Molar Ratio	Product	Pr <sup>i</sup> OH (g) found (calcd.)	Yield %	Analysis % found (calcd.)		
	a	b					Al	C	H
1.	$\text{Al}(\text{OPr}^i)_3$ 3.06	$\text{HOC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{OH}$ 1.78	1:1	$[(\text{Pr}^i\text{O})\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}]$	1.72 (1.80)	98	13.31 (13.34)	-	-
2.	4.45	5.17	1:2	$\text{H}[\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	3.89 (3.93)	95	10.30 (10.36)	54.89 (55.36)	9.50 (9.68)
3.	$\text{H}[\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$ 2.27	$\text{LiOCH}_3$ 0.06	1:1	$[(\text{CH}_3\text{OH})\text{Li}][\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	-	96	8.99 (9.04)	51.86 (52.34)	9.39 (9.46)
4.	2.01	$\text{NaOCH}_3$ 0.18	1:1	$[(\text{CH}_3\text{OH})\text{Na}][\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	-	98	8.53 (8.58)	48.89 (49.67)	8.61 (8.98)
5.	2.26	$\text{KOCH}_3$ 0.34	1:1	$[(\text{CH}_3\text{OH})\text{K}][\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	-	99	8.13 (8.16)	46.62 (47.25)	8.61 (8.54)

These bimetallic heterocyclic derivatives are white solids, soluble in methanol and dimethyl sulfoxide. These derivatives exhibit dimeric nature in methanol. The molar conductance<sup>21</sup> values in 0.001 M methanol solution suggest slight ionic nature of these derivatives (Table - 2).

**Table - 2 : Properties of  $[(Pr^iO)Al\{OC(CH_3)_2C(CH_3)_2O\}]$ ,  $H[Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$  and  $[(CH_3OH)M][Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$  (M = Li, Na and K).**

S.No.	Compound	Nature of the product	Molar Conductance $ohm^{-1}cm^2mol^{-1}$ (methanol)	Molecular weight found (calcd.)
1.	$[(Pr^iO)Al\{OC(CH_3)_2C(CH_3)_2O\}]$	White solid	-	- (202)
2.	$H[Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$	White solid	-	- (260)
3.	$[(CH_3OH)Li][Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$	White solid	84	510 (298)
4.	$[(CH_3OH)Na][Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$	White solid	92	530 (314)
5.	$[(CH_3OH)K][Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$	White solid	99	545 (331)

### IR Spectra

Infrared spectra of these bimetallic heterocyclic derivatives and 2,3-dimethyl-2,3-butanediol have been recorded in the range 4000-200  $cm^{-1}$  and the relevant data are summarized in Table - 3.

A perusal of this table indicate the presence of a broad stretching vibration (3400-3420  $cm^{-1}$ ) in all the above compounds, except in the case of  $[(Pr^iO)Al\{OC(CH_3)_2C(CH_3)_2O\}]$ . These broad bands are ascribed to the -O-H group coordinated to aluminium in  $H[Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$ . Presence of a broad band in the range 3417-3420 $cm^{-1}$  in  $[(CH_3OH)M][Al\{OC(CH_3)_2C(CH_3)_2O\}_2]$  may be ascribed to the -O-H group of the methanol molecule.

The medium to weak intensity band in the region 1040-1052  $\text{cm}^{-1}$  are assigned to  $\nu$  C-O vibration<sup>22-24</sup>. The band in the region 648-666  $\text{cm}^{-1}$  may tentatively be assigned to  $\nu$  Al-O vibration<sup>25</sup>.

**Table 3 : IR spectral data ( $\text{cm}^{-1}$ ) of  $[(\text{Pr}^i\text{O})\text{Al}\{\overline{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}}\}]$ ,  $\text{H}[\overline{\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2}]$  and  $[(\text{CH}_3\text{OH})\text{M}][\overline{\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2}]$  ( $\text{M} = \text{Li, Na and K}$ ).**

S.No.	Compound	$\nu$ O-H	Glycolic $\nu$ C-O	Ring vib.	$\nu$ Al-O
1.	Ligand $\text{HOC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{OH}$	3420 br	1165 m	-	-
2.	$[(\text{Pr}^i\text{O})\overline{\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}}]$	-	1045 m	996 m	660 w
3.	$\text{H}[\overline{\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2}]$	3400 br	1048 m	989 m	659 m
4.	$[(\text{CH}_3\text{OH})\text{Li}][\overline{\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2}]$	3418 br	1040 m	970 m	666 m
5.	$[(\text{CH}_3\text{OH})\text{Na}][\overline{\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2}]$	3420 br	1050 w	969 m	652 w
6.	$[(\text{CH}_3\text{OH})\text{K}][\overline{\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2}]$	3417 br	1052 w	972 m	648 w

**br = broad, m = medium, w = weak**

### <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR spectral<sup>26</sup> data for these derivatives and 2,3-dimethyl-2,3-butanediol have been summarized in Table-4.

The hydroxy proton resonance at  $\delta$  2.68 ppm in 2,3-dimethyl-2,3-butanediol does not appear in the spectra of  $[(\text{CH}_3\text{OH})\text{M}][\overline{\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2}]$  derivative, indicating the formation of Al-O bond. However, this proton resonance signal appears only in the derivative  $\text{H}[\overline{\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2}]$  at  $\delta$  2.61 ppm.

Methyl protons of pinacolate moiety appear at  $\delta$  1.21-1.27 ppm.

Signals at  $\delta$  1.14 and  $\delta$  3.97 ppm in the <sup>1</sup>H NMR spectra of the derivative  $[(\text{Pr}^i\text{O})\overline{\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}}]$  are assigned to the methyl and the methine protons of the isopropoxy group.

**Table 4 :  $^1\text{H}$  NMR spectral data ( $\delta\text{ppm}$ ) of  $[(\text{Pr}^i\text{O})\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}]$ ,  
 $\text{H}[\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$  and  $[(\text{CH}_3\text{OH})\text{M}][\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$   
(M = Li, Na and K).**

S.No.	Compound	Glycolate moiety		Isopropoxy group		Methanol
		-CH <sub>3</sub>	-OH	-CH <sub>3</sub>	-CH<	
1.	Ligand $\text{HOC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{OH}$	1.27, s (12H)	2.68, s (2H)	-	-	-
2.	$[(\text{Pr}^i\text{O})\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}]$	1.23, s (12H)	-	1.14, d (6H)	3.97, m (1H)	-
3.	$\text{H}[\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	1.21, s (24H)	2.61, br (1H)	-	-	-
4.	$[(\text{CH}_3\text{OH})\text{Li}][\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	1.24, s (24H)	-	-	-	3.49, u (4H)
5.	$[(\text{CH}_3\text{OH})\text{Na}][\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	1.25, s (24H)	-	-	-	3.49, u (4H)
6.	$[(\text{CH}_3\text{OH})\text{K}][\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$	1.27, s (24H)	-	-	-	3.48, u (4H)

**s = singlet, d = doublet, m = multiplet, br = broad, u = unresolved**

## <sup>13</sup>C NMR Spectra

The <sup>13</sup>C NMR spectra of bimetallic heterocyclic derivatives and 2,3-dimethyl-2,3-butanediol are summarized in Table-5. The positions of <sup>13</sup>C NMR signals correspond well to the number of chemically different carbon atoms present in these compounds. There is no significant chemical shift of the various <sup>13</sup>C signals present in these derivatives as compared to the free ligand.

Methyl protons of pinacolate moiety and methanol appear at δ 23.20 - 24.79 and δ 47.73 - 49.02 ppm, respectively. The carbonyl carbon appears at δ 74.05 - 74.76 ppm.

**Table 5 : <sup>13</sup>C NMR spectral data (δppm) of [(Pr<sup>i</sup>O)Al{OC(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>O}], H[Al{OC(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>O}<sub>2</sub>] and [(CH<sub>3</sub>OH)M][Al{OC(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>O}<sub>2</sub>] (M = Li, Na and K).**

S.No.	Compound	Glycolate moiety		Methanol
		-CH <sub>3</sub>	>C<	-CH <sub>3</sub>
1.	Ligand HOC(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> OH	25.08	75.19	-
2.	[(CH <sub>3</sub> OH)Li][Al{OC(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> O} <sub>2</sub> ]	23.20	74.05	49.20
3.	[(CH <sub>3</sub> OH)Na][Al{OC(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> O} <sub>2</sub> ]	24.79	74.60	47.73
4.	[(CH <sub>3</sub> OH)K][Al{OC(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> O} <sub>2</sub> ]	24.69	74.76	48.06

## <sup>27</sup>Al NMR Spectra

<sup>27</sup>Al NMR Spectra of [(CH<sub>3</sub>OH)K][Al{OC(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>O}<sub>2</sub>] show a sharp signal at δ 71.79 ppm indicating<sup>27</sup> a tetrahedral environment around aluminium (III) atom (Fig.-1).

## Structural Features

In view of the above studies, the following tentative structures may be proposed for these derivatives (Fig.-2)



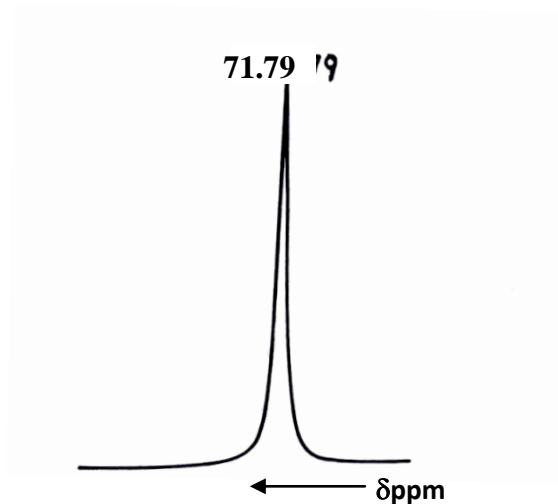


Fig. - 1 :  $^{27}\text{Al}$  NMR Spectra of  $[(\text{CH}_3\text{OH})\text{K}][\text{Al}\{\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O}\}_2]$

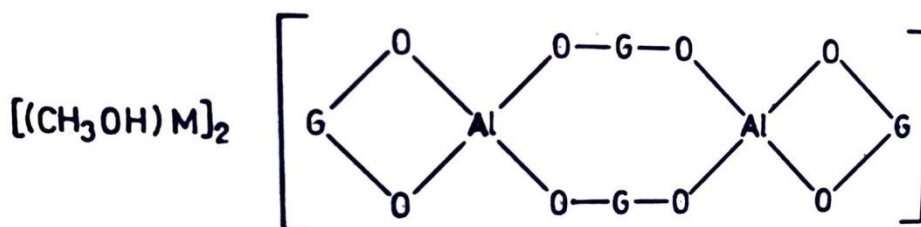
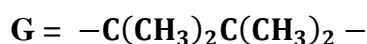


Fig. - 2 : Structure of  $[(\text{CH}_3\text{OH})\text{M}]_2[\text{Al}(\text{O-G-O})_2]_2$



## References

1. D. C. Bradley, R. C. Mehrotra and D. P. Gaur, Metal Alkoxides. Academic Press, London (1978).
2. R. C. Mehrotra, R. Bohra and D. P. Gaur, Metal  $\beta$ -Diketonates & Allied Derivatives. Academic Press, London (1978).
3. R. C. Mehrotra and R. Bohra, Metal Carboxylates. Academic Press, London (1983).
4. M. F. Lappert, A. R. Sanger, R. C. Srivastev and P. P. Power, Metal and Metalloid Amides, Horwood-Wiley, New York (1979).
5. M. H. Chishom. Polyhedron Symposium in Print No.19. Polyhedron, 17, 623-1034 (1998).
6. D. W. Stephen, T. T. Nadasdi, Coord. Chem. Rev., 147, 147-208. (1996)
7. T. R. Athar, R. Bohra, R. C. Mehrotra, J. Indian. Chem. Soc., 67, 535-537 (1990).
8. L. R. Sita, R. Xi, G. P. A. Yap J. Am. Chem. Soc., 119, 756-760 (1997).
9. S. Parola, R. Papiernik, L. G. Hubert-Pfuzgraf, S. Jagner, M. Hakansson, J. Chem. Soc. Dalton Trans., 4631-4635 (1997).

10. A. Dhammani, R. Bohra and R. C. Mehrotra, *Polyhedron* 14, 733-739 (1995).
11. A. Dhammani, R. Bohra and R. C. Mehrotra, *Main Group Metal Chemistry*, 18(12), 687-695 (1995).
12. A. Dhammani, R. Bohra and R. C. Mehrotra, *Polyhedron* 15, 733-737 (1996).
13. A. Dhammani, R. Bohra and R. C. Mehrotra, *Polyhedron* 17, 163-171 (1998).
14. S. Nagar, A. Dhammani, R. Bohra and R. C. Mehrotra, *J. Coord. Chem.*, 55(4), 381-392 (2002).
15. V. G. Kessler, L. G. Hubert-Pfalzgraf, S. Halut, J. C. Daran, *J. Chem. Soc. Chem. Commun.*, 705-726 (1994).
16. L. B. Archer, M. J. H. Smith, E. N. Duester, *Polyhedron*, 15, 929-946 (1996).
17. G. J. Gainsford, T. Kemmitt, N. B. Milestone, *Coordination. Inorg. Chem.*, 34, 5244-5251 (1995).
18. R. C. Mehrotra and A. Singh, *Prog. Inorg. Chem*, 46, 239 (1997).
19. R. C. Mehrotra, *J. Indian Chem. Soc.*, 30, 585-591 (1953)
20. D. C. Bradley, F. M. A. Halim, W. Wardlaw, *J. Chem. Soc.*, 3450-3454 (1950)
21. D. J. Phillips and S. Y. Tyree, *J. Am. Chem. Soc.*, 83, 1806 (1961).
22. A. K. Sen Gupta, R. Bohra and R. C. Mehrotra, *Inorg. Chim. Acta*, 170, 191 (1990).
23. A. K. Sen Gupta, R. Bohra and R. C. Mehrotra, *Synth. React. Inorg. Metal-Org. Chem.*, 21(3), 445-455 (1991).
24. S. Bhargava, Ph.D. Thesis, University of Rajasthan, Jaipur (1992).
25. A. Singh, A. K. Rai and R. C. Mehrotra, *Indian J. Chem.*, 11, 478-480 (1973).
26. R. M. Silverstein, G. C. Bassler and T. C. Morrill, *Spectrometric Identification of Organic Compounds* (1991).
27. J. H. Wengrovius, M. F. Garbaskas, E. A. Williams, R. C. Going, P. E. Donahue and J. F. Smith, *J. Am. Chem. Soc.*, 108, 982-989 (1986).