

## THE SYNTHESSES OF $[\text{BzMe}_3\text{N}]_2[\text{Mo}_4\text{O}_{10}(\text{OMe})_6]$

Ridla Bakri

The Department of Chemistry, Faculty of Mathematic and Natural Sciences, Universitas Indonesia,  
Depok 16424, Indonesia

E-mail : bakri@makara.cso.ui.ac.id.

### Abstract

In an attempt to synthesize  $[\text{BzMe}_3\text{N}]_2\text{Mo}_2\text{O}_5(\text{OMe})_5$  from the reaction of  $[\text{BzMe}_3\text{N}]_2\text{MoO}_4$  and  $\text{MoO}(\text{OMe})_4$  in the ratio of 1:1 in methanol has produced  $[\text{BzMe}_3\text{N}]_2\text{Mo}_4\text{O}_{10}(\text{OMe})_6$ . The formation of  $[\text{Mo}_4\text{O}_{10}(\text{OMe})_6]^{2-}$  anion suggests that ligand dissociation has occurred in solution. Suitable crystals for X-ray crystallographic were obtained from hot methanol and the crystal structure of  $[\text{BzMe}_3\text{N}]_2\text{Mo}_4\text{O}_{10}(\text{OMe})_6$  has been solved and reported here in.

*Keywords :* molybdenum oxoalkoxide,  $[\text{BzMe}_3\text{N}]^+$  cation =  $[(\text{C}_6\text{H}_5\text{CH}_2)\text{N}(\text{CH}_3)_3]^+$ , ligand dissociation, X-ray crystallographic structure.

### 1. Introduction

Study of the transition metal alkoxide complexes has aroused much interest recently and many aspects of the subject have been extensively reviewed by Bradley [1-4] and Chisholm [5-8]. The compound has been using, as a precursor, for preparation metal oxide [1,9], for ceramic materials in the electronic industry and catalyst [1,10].

Metal alkoxides or metal oxoalkoxides have been used as precursors in the preparation of soluble metal oxides in organic solvents and in the Sol-Gel process metal alkoxides are used for the preparation of metal oxides materials by hydrolysis in non-aqueous solvents [5,9,11].

For examples,  $[\text{Bu}^n_4\text{N}]_2\text{W}_2\text{O}_5(\text{OMe})_4$  has been prepared by Errington and co-workers [12], from the reaction of  $[\text{Bu}^n_4\text{N}]_2\text{WO}_4$  and  $\text{WO}(\text{OMe})_4$ , while Zubietta and co-workers [13] produced  $[\text{Ph}_3\text{MeP}]_2\text{Mo}_4\text{O}_{10}(\text{OMe})_6$  from reaction between  $[\text{Ph}_3\text{MeP}][\text{Mo}_8\text{O}_{26}]$  and 1-methyl-1-phenylhydrazine in a mixture of  $\text{CH}_2\text{Cl}_2$  and MeOH.

### 2. Experiment

The preparation was carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk technique.

Crystal of  $\text{Mo}(\text{OMe})_4$  (0.55 g, 2.33 mmol) and  $[\text{BzMe}_3\text{N}]_2\text{MoO}_4$  (1.06 g, 2.33 mmol) were placed in the Schlenk tube. MeOH (20 ml) was then added into the flask with vigorously stirring and the mixture was continued to stir overnight to give white suspension. The suspension was heated up to give clear solution and after cooled at room temperature a colourless crystal of  $[\text{BzMe}_3\text{N}]_2\text{Mo}_4\text{O}_{10}(\text{OMe})_6$  was produced giving 1.29 g, or 79.63 % yield. The spectra of the compound gives signal as follows, I.R. data : 275m, 315m, 360m, 380m, 405w, 430w, 445w, 460w, 515s, 535s, 570s, 605w, 615w, 625w, 700s, 725s, 780s, 810m, 855vw, 890s, 910s, 935s, 975m, 1000s, 1030s, 1070s, 1125w, 1155m, 1215m, 1245w, 1415w, 1490s  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  data :  $\delta_{\text{H}}$  7.8 (10H, m,  $\text{C}_6\text{H}_5\text{-CH}_2\text{-N}$ ), 5.1 (18H, s,  $(\text{CH}_3\text{O})_6\text{-Mo}$ ), 4.7 (4H, s,  $\text{C}_6\text{H}_5\text{-CH}_2\text{-N}$ ), and 3.3 ppm (9H, s,  $(\text{CH}_3)_3\text{-N}$ ) in the ratio of 5 : 9 : 2 : 9. The micro

analysis of crystals  $[\text{BzMe}_3\text{N}]_2\text{Mo}_4\text{O}_{10}(\text{OMe})_6$  found (calculation) % C 30,13 (30,24), %H 5,16 (5,08) and %N 2,66 (2,71).

### 3. Results and Discussions

In the attempt to synthesize  $[\text{BzMe}_3\text{N}]_2\text{Mo}_2\text{O}_5(\text{OMe})_4$  by following the work of Errington and co-workers [12], an equivalent of  $[\text{BzMe}_3\text{N}]_2\text{MoO}_4$  was reacted with  $\text{MoO}(\text{OMe})_4$  in MeOH. However, the reaction produced  $[\text{BzMe}_3\text{N}]_2\text{Mo}_4\text{O}_{10}(\text{OMe})_6$ , **1**, instead of  $[\text{BzMe}_3\text{N}]_2\text{Mo}_2\text{O}_5(\text{OMe})_4$ . The compound **1** has also been prepared by Zubietta and co-workers [13] from the the reaction of  $[\text{Ph}_3\text{MeP}][\text{Mo}_8\text{O}_{26}]$  and 1-methyl-1-phenylhydrazine in a mixture of  $\text{CH}_2\text{Cl}_2$  and MeOH. Compound **1** has similar structure to  $[\text{Pr}^n_4\text{N}]_2\text{W}_4\text{O}_{10}(\text{OMe})_6$  [14] (Figure 1) which produce from an attempted preparation of  $[\text{Pr}^n_4\text{N}]_2\text{W}_2\text{O}_5(\text{OMe})_4$  by using the same reaction, although the molybdenum methoxo compound has slightly different arrangement of ligands. The formation of  $[\text{Mo}_4\text{O}_{10}(\text{OMe})_6]^{2-}$ , **1** anion in this reaction suggests that ligand dissociation is occurred in solution, as in the case of,

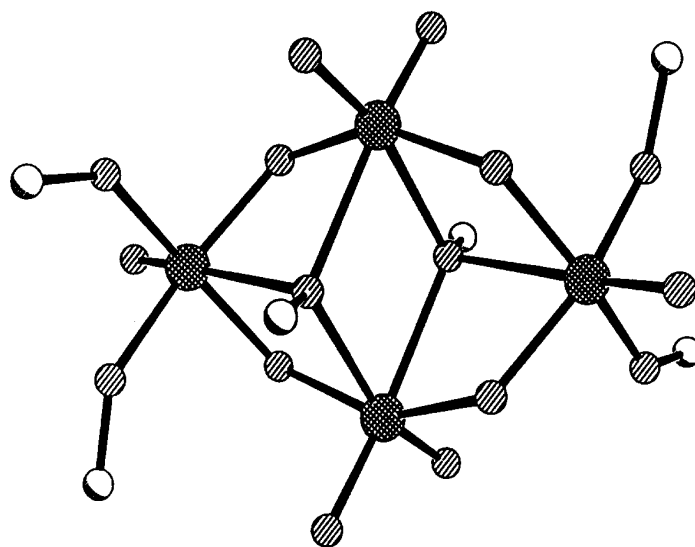


Figure 1 : The Structure of  $[\text{W}_4\text{O}_{10}(\text{OMe})_6]^{2-}$  anion

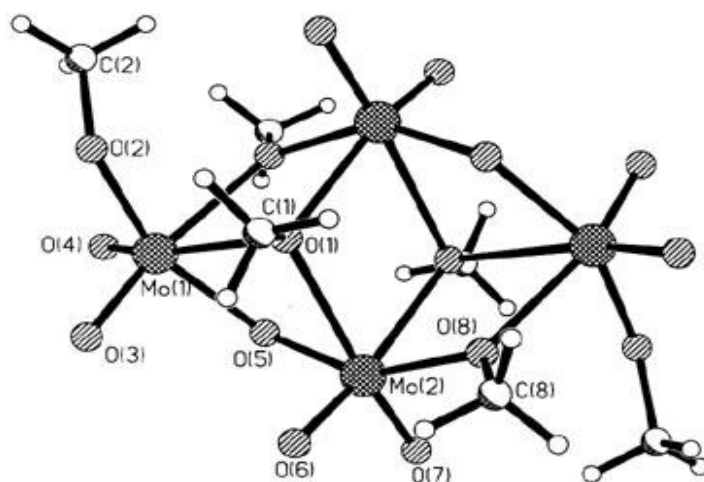


Figure 2. The Structure of  $[\text{Mo}_4\text{O}_{10}(\text{OMe})_6]^{2-}$  anion

The compound **1** which was produced from this reaction has similar features in the infrared spectrum to those described in the literature [13], and the following signal peaks may be assigned; the  $\nu(\text{Mo}=\text{O})$  stretching vibration at 890, 910, 935, 975, and  $1000\text{ cm}^{-1}$ , the  $\nu(\text{Mo}-\text{O}-\text{Mo})$  stretching at 700, 725, 780 and  $810\text{ cm}^{-1}$ , the  $\nu(\text{Mo}-\text{OR})$  stretching vibration at 605, 615 and  $625\text{ cm}^{-1}$ , the  $\nu(\text{O}-\text{Mo}-\text{O})$  bending vibration at 275, 315, 360 and  $380\text{ cm}^{-1}$ , and the  $\nu(\text{C}-\text{O})$  stretching at 1030 and  $1070\text{ cm}^{-1}$ . The  $^1\text{H-NMR}$  spectrum indicates the presence of  $[\text{BzMe}_3\text{N}]^+$  cation in the compound. The micro analysis also suggest that the formulation of the compound is  $[\text{BzMe}_3\text{N}]_2\text{Mo}_4\text{O}_{10}(\text{OMe})_6$ .

The structure of  $[\text{Mo}_4\text{O}_{10}(\text{OMe})_6]^{2-}$  anion with atomic numbering can be seen in Figure 2 and the selected bond distances and angles shown in Tabel 1. As shown in Figure 2, the Mo centers of compound **1** display  $[\text{MoO}_6]$  pseudooctahedral geometries through coordination to oxo and methoxo ligands. The structure of  $[\text{Mo}_4\text{O}_{10}(\text{OMe})_6]^{2-}$  displays two unique molybdenum centers, one displaying  $[\text{MoO}_2(\text{OCH}_3)(\mu\text{-O})(\mu\text{-OCH}_3)(\mu_3\text{-CH}_3)]$  coordination and the second  $[\text{MoO}_2(\mu\text{-O})(\mu\text{-OCH}_3)(\mu_3\text{-OCH}_3)_2]$  geometry. In other words, the compound consists of two similar units of  $[\text{Mo}_2\text{O}_4(\mu\text{-O})(\text{OCH}_3)(\mu\text{-OCH}_3)(\mu_3\text{-OCH}_3)]$  in the structure. The structure illustrates a common feature of the chemistry of polymolibdates in alcoholic solvents: the incorporation of alkoxy groups into the cluster.

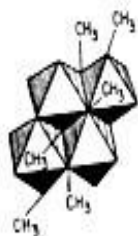
Tabel 1. Selected Bond Length ( $\text{\AA}$ ) and Angles (deg) for  $[\text{BzMe}_3\text{N}]_2\text{Mo}_4\text{O}_{10}(\text{OMe})_6$

Mo1-O1	2,272(2)	Mo2-O1	2,394(2)
Mo1-O2	1,909(2)	Mo2-O5	1,865(2)
Mo1-O3	1,715(2)	Mo2-O6	1,715(2)
Mo1-O4	1,704(2)	Mo2-O7	1,705(2)
Mo1-O5	1,993(2)	Mo2-O8	2,035(2)
O(1)-Mo(1)-O(2)	85,06(8)	O(1)-Mo(2)-O(5)	71,91(7)
O(1)-Mo(1)-O(3)	95,01(9)	O(1)-Mo(2)-O(6)	87,08(9)

O(1)-Mo(1)-O(4)	156,29(6)	O(1)-Mo(2)-O(7)	166,71(7)
O(1)-Mo(1)-O(5)	72,67(7)	O(1)-Mo(2)-O(8)	83,25(7)
O(2)-Mo(1)-O(3)	96,33(9)	O(5)-Mo(2)-O(6)	102,85(10)
O(2)-Mo(1)-O(4)	101,11(9)	O(5)-Mo(2)-O(7)	99,65(8)
O(2)-Mo(1)-O(5)	155,86(6)	O(5)-Mo(2)-O(8)	150,81(6)
O(3)-Mo(1)-O(4)	106,87(10)	O(6)-Mo(2)-O(7)	105,09(10)
O(3)-Mo(1)-O(5)	94,82(10)	O(6)-Mo(2)-O(8)	90,63(9)
O(4)-Mo(1)-O(5)	96,01(8)	O(7)-Mo(2)-O(8)	101,64(8)



a



b

**Figure 3. An arrangement of four edge-sharing octahedral**

The tetranuclear unit is the most common compositional pattern in the coordination chemistry of polyoxo-alkoxomolybdates and tungstates. The structure is that adopted by  $[\text{Mo}_4\text{O}_{10}(\text{OMe})_6]^{2-}$  consists of compact cluster of four edge-sharing octahedra as illustrated in Figure 3b.

Formation of the underivatized polyoxomolybdate parent structure,  $[\text{Mo}_4\text{O}_{16}]^{8-}$ , is most likely precluded by the high negative charge. Replacement of bridging oxo groups by alkoxy ligands serves to reduce the overall cluster charge and hence to stabilize the unit in alcoholic solvents [15].

## Conclusion

$\text{BzMe}_3\text{N}]_2\text{Mo}_4\text{O}_{10}(\text{OMe})_6$  has been produced by reaction of  $\text{Mo}(\text{OMe})_4$  with equimolar of  $\text{BzMe}_3\text{N}]_2\text{MoO}_4$ . The compound had produced from the ligand dissociation in solution and it has similar structure to  $[\text{Pr}^n_4\text{N}]_2\text{W}_4\text{O}_{10}(\text{OMe})_6$  with slightly different arrangement of ligands.

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