

## Studies on the Preparation of Some Oxychloride Alkoxides of Hexavalent Molybdenum and their Coordination Complexes with $\alpha\alpha'$ Dipyridyl

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Reactions of molybdenum oxide tetrachloride,  $\text{MoOCl}_4$ , with primary and secondary alcohols have been carried out and the oxychloride alkoxides having the general formula  $\text{MoOCl}_2(\text{OR})_2$  (where  $\text{R} = \text{Me}, \text{Pr}^n, \text{Pr}^1$  and  $\text{Bu}^n$ ) have been isolated. These oxychloride alkoxides form coordination complexes with dipyridyl having the general formula  $\text{MoOCl}_2(\text{OR})_2 \cdot \text{dipy}$ . (dipy. = dipyridyl).

Very little work has been done on oxychloride alkoxides of metals. Bradley, Multani and Wardlaw<sup>1</sup> obtained  $\text{V}_2\text{OCl}_8(\text{OR})_8$  by heating  $\text{VCl}_2(\text{OR})_2 \cdot \text{ROH}$  and  $\text{MoOCl}_2(\text{OEt})$  by heating  $\text{MoCl}_2(\text{OEt})_3$  at 80-85° in vacuo. Coordination complexes of molybdenum (V) chloride alkoxides with dipyridyl have been reported by Anand, Multani and Jain<sup>2</sup>. These were prepared by the direct interaction of chloride alkoxides of molybdenum with dipyridyl in alcohol medium, and by alcohol interchange method.

The present studies deal with (i) the preparation of molybdenum oxydichloride dialkoxides by the direct interaction of  $\text{MoOCl}_4$  with different alcohols as well as by the alcohol interchange method and (ii) the preparation of dipyridyl complexes of the above oxychloride alkoxides. The present investigation shows that the above oxychloride alkoxides of molybdenum (VI) form coordination complexes with dipyridyl [as seen from the I. R. spectra of dipyridyl complexes of molybdenum oxychloride ethoxide and molybdenum oxychloride isopropoxide with absorption maxima in the region 1600-1610  $\text{cm}^{-1}$  and their analysis and analysis of other compounds], having the general formula  $\text{MoOCl}_2(\text{OR})_2 \cdot \text{dipy}$  (dipy. = dipyridyl). Even when a large excess of dipyridyl is used, not more than one molecule of it is attached to the oxychloride alkoxides. The above complexes have been readily obtained both by the direct interaction of the oxy-chloride alkoxides with dipyridyl in corresponding alcohol medium as well as by the alcohol interchange method.

### EXPERIMENTAL

Molybdenum oxide tetrachloride,  $\text{MoOCl}_4$  was prepared by the method described by Colton, Tomkins and Wilson<sup>3</sup>. Alcohols used were completely dried and distilled. Infrared spectra were taken in nujol using Perkin Elmer spectrophotometer.

1. D. C. Bradley, R. K. Multani and W. Wardlaw, *J. Chem. Soc.*, 1958, 4647.
2. S. K. Anand, R. K. Multani and B. D. Jain, *Curr. Sci.*, 1967, 36, 121-23.
3. R. Colton, I. B. Tomkins and P. W. Wilosn, *Aust. J. Chem.*, 1964, 17, 496-7.

*Analysis*: Molybdenum and chloride were determined as oxinate and silver chloride respectively. Methoxide, ethoxide and isopropoxide were analysed by the chromic acid method<sup>4,5</sup>.

*Preparation of molybdenum oxy-chloride alkoxides.*

(a) *Direct interaction method*: To molybdenum oxide tetrachloride,  $\text{MoOCl}_4$  (3.0 g) added ethyl alcohol (100 g) and refluxed the solution for about 4 hr. The greenish solution thus obtained on evaporation under reduced pressure gave a dark blue product having composition  $\text{MoOCl}_2(\text{OEt})_2$  (Found: Mo, 34.85; Cl, 25.67; OEt, 32.05%; requires for  $\text{MoOCl}_2(\text{OEt})_2$  Mo, 35.16; Cl, 25.98; OEt, 32.98%). Other oxychloride alkoxides were prepared similarly.

(b) *Alcohol interchange Method*: A suspension of molybdenum oxydichloride diethoxide,  $\text{MoOCl}_2(\text{OEt})_2$ , (2.0 g) in a mixture of isopropyl alcohol (50 g) and benzene (80 g) was refluxed for about 4 hr. and the greenish blue solution thus obtained was then fractionally distilled. The ethyl alcohol liberated in the reaction was removed as benzene-alcohol azeotrope. The solution was then evaporated under reduced pressure and molybdenum oxydichloride di-isopropoxide,  $\text{MoOCl}_2(\text{OPr}^i)_2$ , was obtained as a dark blue solid (Found: Mo, 31.07; Cl, 23.15,  $\text{OPr}^i$ , 38.70%; requires for  $\text{MoOCl}_2(\text{OPr}^i)_2$  Mo, 31.89; Cl, 23.56;  $\text{OPr}^i$ , 39.22%). Molybdenum oxydichloride di-n-propoxide and molybdenum oxydichloride di-n-butoxide were prepared similarly and their analysis agreed with the general formula given above.

*Preparation of the dipyriddy complexes of molybdenum oxychloride alkoxides.*

(a) *Direct interaction Method*: 80 g of ethyl alcohol containing 2.5 g of molybdenum oxide tetrachloride was refluxed for about 4 hr. and then treated with 1.5 g of dipyriddy in 30 g of ethyl alcohol. This resulted in the formation of a reddish precipitate which after separation by decantation was repeatedly washed with anhydrous ethyl alcohol and then dried under reduced pressure. On analysis it gave the following composition,  $\text{MoOCl}_2(\text{OEt})_2 \cdot \text{dipy}$ . (Found: Mo, 22.0; Cl, 16.24; OEt, 20.6; N, 6.25% requires for  $\text{MoOCl}_2(\text{OEt})_2 \cdot \text{dipy}$ ; Mo, 22.37; Cl, 16.53; OEt, 20.98; N, 6.52%).

(b) *Alcohol interchange Method*: A suspension of molybdenum oxydichloride diethoxide dipyriddy complex (2.0 g) in a mixture of isopropyl alcohol (50 g) and benzene (80 g) was refluxed and later fractionally distilled to remove the liberated ethyl alcohol as benzene-alcohol azeotrope. The resultant solution on evaporation under reduced pressure yielded reddish brown molybdenum oxydichloride di-isopropoxide dipyriddy complex which on analysis was found to have composition  $\text{MoOCl}_2(\text{OPr}^i)_2 \cdot \text{dipy}$  (Found: Mo, 20.75, Cl, 15.10;  $\text{OPr}^i$ , 25.50; N, 5.92%; requires for  $\text{MoOCl}_2(\text{OPr}^i)_2 \cdot \text{dipy}$  Mo, 21.00; Cl, 15.5;  $\text{OPr}^i$ , 25.84; N, 6.12%). Dipyriddy

4. C. A. Adams and J. R. Nicholls, *Analyst*, 1929, 54, 2.

5. D. C. Bradley, F. M. Abdel Halim and W. Wardlaw, *J. Chem. Soc.*, 1950, 3450.

complexes of molybdenum oxydichloride di-n-propoxide, di-n-butoxide and di-isobutoxide were prepared similarly and their analysis agreed with the general formula given above.

#### DISCUSSION

The formation of co-ordination complexes of metal alkoxides has been observed in a few cases only<sup>6</sup>, whereas the chloride alkoxides of metals readily form such complex compounds with alcohols<sup>6</sup>, esters<sup>6</sup>, ammonia<sup>7</sup>, amines<sup>7</sup> and dipyriddy<sup>8</sup>. The present investigation shows that molybdenum oxychloride alkoxides also form co-ordination complexes with dipyriddy, thereby illustrating the enhanced tendency of a metal chloride alkoxide to form co-ordination complexes when an electronegative group is already attached to the metal.

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6. D. C. Bradley, *Prog. Inorg. Chem.*, 1960, 2, 303.
7. H. Gilman, *J. Amer. Chem. Soc.*, 1956, 78, 6027.