Molybdenum Hexachloride

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MOLYBDENUM HEXACHLORIDE has not been reported previously, although the tungsten analogue, WCl_6, is well known. Standard methods of preparing chlorides in high oxidation states[1,2] result in the formation of $MoCl_5$, owing to thermal instability of the sexivalent chloride at the temperatures required.

$$MoCl_6 \rightarrow MoCl_5 + \tfrac{1}{2}Cl_2$$

Colton *et al.*,[3-5] have shown recently that thionyl chloride may be used to replace oxygen atoms in the conversion of transition-metal oxides into chlorides or oxychlorides. Molybdenum trioxide was converted into molybdenum oxytetrachloride, $MoOCl_4$.[4,5]

Molybdenum hexachloride was prepared by heating molybdic acid under reflux with thionyl chloride under absolutely anhydrous conditions for several hours. Removal of the excess of solvent, and fractional sublimation of the products was carried out under high vacuum. The products isolated were: $MoOCl_4$, $MoCl_6$, $MoOCl_3$, and $MoCl_5$.

Molybdenum hexachloride may also be obtained in small quantities by careful fractionation of the products of chlorinating molybdenum metal.

Like the pentachloride, the hexachloride is a black powder. It is distinguished by the formation of large single crystals with a silver–grey lustre. The structure of tungsten hexachloride has been reported.[6] Direct comparison of the powder photographs of WCl_6 and $MoCl_6$ indicates that the compounds are isostructural.

Molybdenum hexachloride is extremely sensitive to traces of moisture. The oxidation state was confirmed by titration with potassium permanganate or ceric sulphate.

Treatment of tungstic acid, H_2WO_4, with thionyl chloride provides a method of preparing $WOCl_4$ in almost quantitative yield. After three days, the products were $WOCl_4$ and traces of WCl_6.

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[1] F. A. Colton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience, New York, 1962.

[2] E. R. Eppierson, S. M. Horner, K. Knox, and S. Y. Tyree, "Inorganic Syntheses," McGraw-Hill, New York, 1963, Vol. 7, p. 163.

[3] D. Brown and R. Colton, *Nature*, 1963, **198**, 1300.

[4] R. Colton and I. B. Tomkins, *Austral. J. Chem.*, 1965, **18**, 447.

[5] R. Colton, I. B. Tomkins, and P. W. Wilson, *Austral. J. Chem.*, 1964, **17**, 496.

[6] R. W. G. Wykoff, "Crystal Structures", 2nd end., Vol. 2, Interscience, New York, 1964, p. 203.