

## X-Ray Crystal Structure of Oxidichlorotris(dimethylphenylphosphine)molybdenum(IV), [MoOCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>]

By LJUBICA MANOJLOVIĆ-MUIR

(School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ)

**Summary** The blue isomer of [MoOCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>] is shown to be a meridional octahedral complex, with the oxygen atom *trans* to chlorine and the two chlorine atoms *cis* to each other.

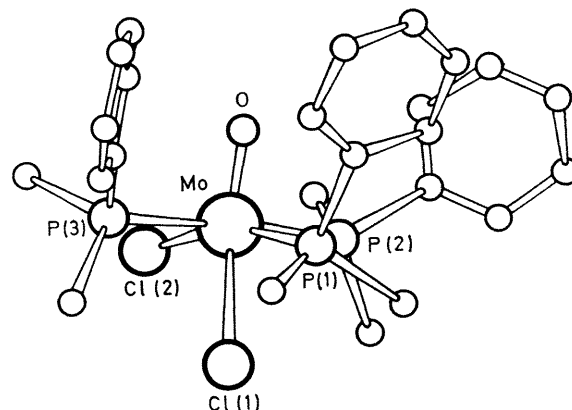
in the ionic complex of oxomolybdenum(IV) with ditertiary phosphine, [MoOCl{Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>}<sub>2</sub>]<sup>+</sup>[ZnCl<sub>3</sub>OC(CH<sub>3</sub>)<sub>2</sub>]<sup>-</sup>, OC(CH<sub>3</sub>)<sub>2</sub>.<sup>2</sup> The Mo-Cl distances are Mo-Cl(1) = 2.552(3) and Mo-Cl(2) = 2.463(4). The three Mo-P distances are

New diamagnetic complexes of oxomolybdenum(IV) with mono- and di-tertiary phosphines have been made recently.<sup>1</sup> Butcher and Chatt have characterised a series of blue, and green, complexes of the type MoOX<sub>2</sub>L<sub>3</sub>, where X = Cl, Br, I, NCS, or NCO and L = monotertiary phosphine; for the compound [MoOCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>], a blue isomer and a green isomer have been observed. Butcher and Chatt suggest that the colour of a complex, green or blue, depends on whether the oxygen atom is *trans* to L or X, respectively. The X-ray crystal structure analysis of blue [MoOCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>] was undertaken to verify this suggestion and elucidate details of molecular geometry.

**Crystal data:** C<sub>24</sub>H<sub>33</sub>Cl<sub>2</sub>MoOP<sub>3</sub>, *M* 597.3, orthorhombic, space group *Pbca*, *a* = 17.009(6), *b* = 16.528(5), *c* = 19.311(8) Å (Mo-K<sub>α</sub> radiation, λ = 0.7107 Å), *D<sub>m</sub>* (flotation) = 1.47, *Z* = 8, *D<sub>c</sub>* = 1.46.

The analysis is based on 2280 independent reflexions with *I* ≥ 3σ(*I*). The intensities were measured with Mo-K<sub>α</sub> radiation on a Hilger and Watt's four-circle diffractometer. The structure was solved by the heavy-atom method, and refined by full-matrix least-squares to an *R* value of 0.067. The established molecular geometry, (Figure), confirms the configuration suggested by Butcher and Chatt.

The co-ordination polyhedron around molybdenum is a distorted octahedron, with a meridional arrangement of three phosphine ligands. The oxygen atom is *trans* to chlorine, and the two chlorine atoms are *cis* to each other. The Mo-O distance of 1.674(8) Å agrees with that of 1.69 Å



FIGURE

Mo-P(1) = 2.503, Mo-P(2) = 2.541, and Mo-P(3) = 2.558 Å, each with a standard deviation of ±0.004 Å. These distances can be explained on the basis of an O > PMe<sub>2</sub>Ph > Cl relative *trans*-influence series in the octahedral molybdenum(IV) complexes, but a more detailed rationalisation is being considered.

I thank Professor J. Chatt for samples of the complex and the S.R.C. for financial support.

(Received, November 23rd, 1970; Com. 2020.)

<sup>1</sup> A. V. Butcher and J. Chatt, *J. Chem. Soc. (A)*, 1970, 2652, and unpublished work; L. K. Atkinson, A. H. Mawby, and D. C. Smith, *Chem. Comm.*, 1970, 1399.

<sup>2</sup> V. C. Adam, U. A. Gregory, and B. T. Kilbourn, *Chem. Comm.*, 1970, 1400.