Oxotrichlorotriphenylphosphidesulphidemolybdenum(V) $[MoOCl_3(SPPh_3)]$, a Mononuclear Five-Co-ordinate Oxomolybdenum(V) Complex

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Summary $[MoOCl_3(SPPh_3)]$ has been synthesised and shown by *X*-ray crystallography to exist as discrete five co-ordinate molecules which have a distorted square pyramidal geometry.

The structures and reactions of molybdenum(V) complexes are of considerable current interest because of the identification of this oxidation state in certain molybdenum-containing enzymes.[1] Attention has been focused on molybdenum(V) complexes containing *S*-donor ligands since the e.s.r. spectra obtained are consistent with the Mo^V centre being bound to at least one sulphur atom.[1,2] A number of binuclear Mo^V complexes of *S*-donor ligands have been characterised including examples of five co-ordinate oxomolybdenum(V) with L-cysteine ester.[3] However, it is usually considered that monomeric examples of such species are more likely to exhibit reactivities which resemble those of the natural systems.[1,4] We report here the first complete characterisation of a mononuclear oxo-molybdenum(V) complex, $[MoOCl_3(SPPh_3)]$.

$MoOCl_3$ and Ph_3PS (1 : 1—5) react in CH_2Cl_2 under anhydrous conditions to yield $[MoOCl_3(SPPh_3)]$ as an emerald green solid which, after recrystallisation from CH_2Cl_2, was found to be analytically pure. An *X*-ray crystallographic structure determination has been completed; *crystal data:* Orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 14{\cdot}243$, $b = 14{\cdot}353$, $c = 10{\cdot}021$ Å. 3122 Reflections were measured on a Hilger and Watts four-circle diffractometer using a graphite monochromator and the structure was solved using standard Patterson and Fourier techniques,

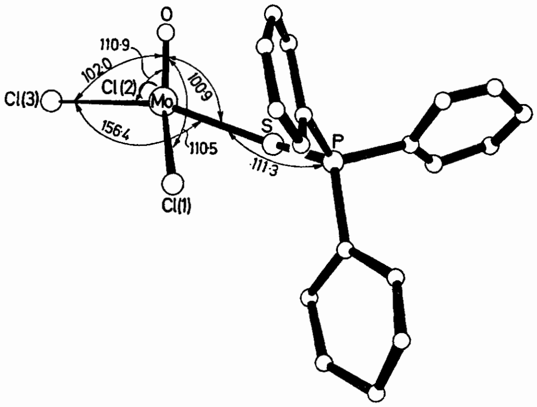

Figure. *X*-Ray crystal structure of $MoOCl_3(SPPh_3)$. Bond angles in degrees.

and refined by least-squares methods with anisotropic temperative factors for all the atoms (the positions of the hydrogen atoms were calculated from those of the carbons) to $R = 0{\cdot}045$. [$MoOCl_3(SPPh_3)$] exists as discrete five-co-ordinate molecules which have an essentially square pyramidal geometry (Figure) with the metal atom 0·65 Å above the best plane described by the atoms Cl(1), Cl(2), Cl(3), and S. There is, however, some distortion of this geometry towards a trigonal bipyramidal arrangement with the Cl(3) and S atoms in the apical positions. The length of the Mo–O bond (1·647 ± 0·003 Å) is significantly shorter than those determined with sufficient precision for related oxomolybdenum(v) complexes which contain a ligand *trans* to this group, [$MoOCl_3\{OP(NMe_2)_3\}_2$] (1·686 ± 0·005 Å)[5] and $Cs_2[Mo_2O_2S_2(EDTA)]$ (1·683 ± 0·006 Å).[6] The stronger nature of the Mo–O bond in [$MoOCl_3(SPPh_3)$] suggested by these data is supported by the value of the ν(Mo–O) stretching frequency of 1008 cm^{-1} which is higher than found for six-co-ordinate oxomolybdenum(v) complexes and close to the values (1007—1012 cm^{-1}) reported[7] for $[MoOX_4]^-$ (X = Cl or Br) which presumably have a square pyramidal C_{4v} structure. The length of the Mo–Cl bond *trans* to the sulphur atom (2·342 ± 0·001 Å) is slightly greater than those (2·305 and 2·325 ± 0·001 Å) of the other two Mo–Cl bonds. The bond-length data obtained in this study suggest that the Mo–S[8] and P–S[9] bonds of length 2·460 and 2·041 ± 0·001 Å, respectively should both be regarded as single bonds, with the change in the stretching frequency of the latter, from 637 (free ligand) to 575 (complex) cm^{-1} implying significant weakening of the P–S bond on co-ordination.

E.s.r. ($\bar{g} = 1{\cdot}957$), electronic spectra (λ_{max} 660 nm), and molecular weight data (detd. 499 ± 20 calcd. 513) are all consistent with [$MoOCl_3$ ($SPPh_3$)] dissolving unchanged into CH_2Cl_2 solution where it reacts readily with Lewis bases (halide ions, or neutral *O* or *N*- donor ligands). In all the reactions investigated so far the compound shows no tendency to form simple addition complexes but produces [$MoOCl_3L$] and/or [$MoOCl_3L_2$] derivatives.

The results obtained in this study suggest that the complexes $MoOCl_3(SR_2)$ (R = Me, Et, or Pr^n), previously considered to be six-co-ordinate *via* halo-bridges,[10] may in fact have five-co-ordinate structures related to that of [$MoOCl_3(SPPh_3)$].

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