

The Crystal Structure of an Adduct of Trichlorosulphidoniobium(V) with Triphenylphosphinesulphine: Coexistence of Five-co-ordinate Monomers and Six-co-ordinate Dimers

M. G. B. DREW, G. W. A. FOWLES, R. J. HOBSON and D. A. RICE

Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, U.K.

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The reactions of the oxohalides of the early transition metals have been extensively investigated; NbCl_3O and MoCl_3O form 1:1 and 1:2 adducts with monodentate ligands [1, 2], some of which have been studied by single crystal X-ray methods [3, 4]. Solution n.m.r. studies on $\text{NbCl}_3\text{O}/\text{OP}(\text{NMe}_2)_3$ have been interpreted in terms of 1:1, 1:2 and 1:3 complexes [5]. Few reports have been made on the adducts of the sulphidohalides [6] whilst single crystal X-ray studies on the parent sulphidohalides have been confined to $(\text{WX}_4\text{S})_2$ ($\text{X} = \text{Cl}$ or Br) [7], MoCl_3S_2 [8], $\text{Mo}_3\text{Cl}_4\text{S}_7$ [8], NbCl_2S_2 [9], and MoXS ($\text{X} = \text{Cl}$ or Br) [10]. Of these, $(\text{WX}_4\text{S})_2$ ($\text{X} = \text{Cl}$ or Br) [7] is unique in possessing a terminal multiple metal-sulphur bond.

The sulphidohalides MX_3S ($\text{M} = \text{Nb}$ or Ta , $\text{X} = \text{Cl}$ or Br) can be prepared by the reaction between stoichiometric quantities of the pentahalides and Sb_2S_3 in CS_2 [11], but our attempts to obtain single crystals for a structural study have been unsuccessful. However, the reaction between NbCl_3S and Ph_3PS yielded a 2:3 species which on recrystallisation from CS_2 gave crystals of the 1:1 adduct suitable for an X-ray analysis.

Crystal data: $\text{C}_{18}\text{H}_{15}\text{Cl}_3\text{NbPS}_2$, $M = 525.69$, triclinic, space group $\text{P}1$, $a = 12.524(5)$, $b = 10.193(4)$, $c = 17.823(6)$ Å, $\alpha = 103.80(3)$, $\beta = 102.60(4)$, $\gamma = 72.02(4)$ Å, $Z = 4$, $U = 2075.8$ Å³, $d_m = 1.69$, $d_c = 1.68$. The intensities of 3831 independent reflections ($2\theta < 40^\circ$) were recorded using zirconium-filtered $\text{Mo-K}\alpha$ radiation on a G.E.XRD-5 manual diffractometer by the stationary-crystal-stationary-counter method. The structure was solved by Patterson and Fourier methods, and least squares refinement on the 2880 non-zero reflections had reached $R 0.058$.

The unit cell contains two identical monomers $[\text{NbCl}_3\text{S}\cdot\text{SPPPh}_3]$ (Figure 1) and a centrosymmetric dimer $[\text{NbCl}_3\text{S}\cdot\text{SPPPh}_3]_2$ (Figure 2). The tendency of adducts of the type $\text{MCl}_4\cdot\text{L}$ ($\text{M} = \text{Ti}$ or Zr , $\text{L} =$ monodentate ligand) to be dimeric through halogen bridges is well-known [2, 12-14]. It can be argued that adducts $\text{MX}_3\text{S}\cdot\text{L}$ are more likely to be five-co-

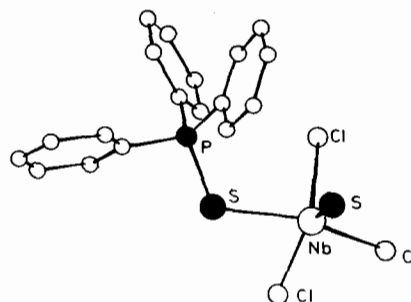


Figure 1. The five-coordinate species $\text{NbCl}_3\text{S}\cdot\text{SPPPh}_3$.

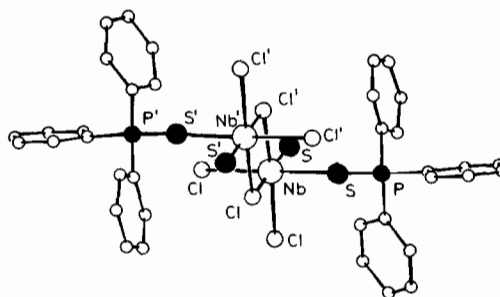


Figure 2. The dimeric species $[\text{NbCl}_3\text{S}\cdot\text{SPPPh}_3]_2$.

ordinate because of the presence of the M-S multiple bond. The resulting small energy differences between the monomeric and dimeric forms allows packing forces to determine which of the two forms (or both as in this unique case) is found in the solid state. In the monomer, the niobium atom is five-co-ordinate square-pyramidal with the terminal sulphur atom in the axial position (2.114(4) Å) and the three chlorine atoms (mean 2.34 Å) and the sulphur atom (2.577(3) Å) of the Ph_3PS molecule in the basal plane. The S-Nb-Cl , S angles range from 102.9(2) to 103.9(2) with the metal atom 0.55 Å above the plane of the four equatorial atoms. The overall stereochemistry resembles that of $\text{MoCl}_3\text{O}\cdot\text{SPPPh}_3$ [3] where the molybdenum atom is 0.65 Å above the basal plane and angles range from 100.9 to 110.9°.

The six-co-ordinate dimer can be considered to be formed by the linking of two five-co-ordinate species, one chlorine from each co-ordinating into the vacant sixth position of the other. There are few changes in geometry; the terminal Nb-S bond is 2.129(4) Å, the angles range from 97.0(2)-102.8(2) with the niobium atom 0.40 Å above the basal plane. The two bridging Nb-Cl bond lengths are 2.469(3) and 2.837(4) Å, the latter being *trans* to the terminal sulphur atom; the other Nb-Cl and Nb-S bonds are equivalent to those in the monomer. The difference between the two bridging Nb-Cl bond lengths is 0.368 Å, a value which can be solely attributed to the influence of the *trans* terminal sulphur atom. The niobium is thus in

a distorted octahedral environment in contrast with $[\text{WCl}_4\text{S}]_2$ where the difference in bond length is 0.683 Å and the structure consists of two weakly associated five-co-ordinate monomers [7].

The Nb-S-P angles in the monomer and dimer are 116.6(2) and 111.5(2) respectively compared to 111.3 in $\text{MoCl}_3\text{O}\cdot\text{SPPH}_3$ [3]. The configuration of the triphenylphosphine sulphide groups is slightly different in the two species suggesting packing effects are responsible for their detailed geometry. There are no close approaches to the vacant sixth position in the monomer.

These structures provide the first example of a Nb(V)-S terminal bond. The mean bond length of 2.121 Å represents considerable double bond character compared to single bond lengths of 2.526(5), and 2.540(4) in $\text{NbCl}_3[\text{SC}(\text{Me})\text{N}(\text{Me})_2]$ [15] and 2.575 Å (mean) in the present species.

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