Preparation, Crystal and Molecular Structure of Trichlorosulphido(triphenylphosphine sulphide)niobium(V)

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Received November 23, 1982

The reaction between $NbSCl_3$ and triphenylphosphine sulphide leads to the formation of the 1:1 adduct, crystals of which are triclinic, space group $P\bar{1}$, with $a = 12.524(5)$, $b = 10.193(4)$, $c = 17.823(6)$ Å, $\alpha = 103.80(3)$, $\beta = 102.60(4)$, $\gamma = 72.02(4)°$, $Z = 4$. The structure was solved by Patterson and Fourier methods using diffractometer data and refined to R 0.058 for 2880 significant reflections. The unit cell contains two five-co-ordinate monomers and one centrosymmetric six co-ordinate dimer, the co-existence of which is a most unusual feature in the solid state. The niobium atom is displaced from the plane formed by the three chlorine atoms and the ligand sulphur atom towards the sulphido sulphur atom [0.553(2) Å, monomer, 0.397(2) Å, dimer]. This displacement is larger than any yet found in adducts of $NbOCl_3$.

Introduction

Compounds of the general formula $MOX_3 \cdot L$ (M = early transition element, X = Cl or Br, L = monodentate ligand) are usually found [1, 2] to be five co-ordinate monomers; only one six-co-ordinate chlorine bridged dimer is known [3], $[NbOCl_4^-]_2$, but there is a large difference (0.573 Å) between the two Nb–Cl (bridging) bond lengths. On the other hand, $NbOCl_3 \cdot POCl_3$ [4] has been unequivocally shown to contain an oxygen bridged tetrameric unit.

Structural data on MSX_3 complexes are very limited. The dithiahexane adduct [5] of $WSCl_3$ contains a discrete six co-ordinate unit, as do the *bis*-tetrahydrothiophen adducts [6] $MSBr_3 \cdot 2tht$ (M = Nb or Ta). $NbSCl_3$ gives both five and six co-ordinate 1:1 and 1:2 anionic adducts with chloride ion [7]. In order to extend the knowledge and understanding of the structural aspects of this field of chemistry, we now report the single-crystal structure, infra-red and Raman spectra of $NbSCl_3 \cdot (Ph_3PS)$. This work has been the subject of a preliminary communication [8].

Experimental

Preparation and Purification of Starting Materials

$NbSCl_3$ was prepared as previously described [9]. Triphenylphosphine sulphide (tppS) was recrystallised from 1:1 toluene/petrol (100–120 °C) and pre-dried in a vacuum desiccator, and CS_2 was twice distilled from P_4O_{10} before use.

Synthesis

In view of the extreme moisture sensitivity of one of the starting materials and the product, the preparation was carried out using an all glass vacuum line and sealed ampoule techniques. The title compound was prepared by allowing equimolar quantities of $NbSCl_3$ and tppS to react in dry CS_2 for about five days, after which the ampoule was opened and the product removed by filtration and washed three times with redistilled solvent. The product was a bright yellow, moisture sensitive solid (Found: C, 40.8; H, 3.0; Cl, 20.3. Calcd. for $C_{18}H_{15}Cl_3NbPS_2$: C, 41.1; H, 2.9; Cl, 20.2%). The use of excess tppS and extended reaction times leads only to the isolation of the 1:1 adduct.

Single-crystals suitable for X-ray measurements were obtained as orange needles from CS_2 solution using a double-ampoule technique.

Spectra

All sample preparation was carried out in a nitrogen filled dry box. Infra-red spectra were measured as nujol mulls using a Perkin Elmer 577 spectrophotometer. Raman spectra were obtained by the spinning-sample technique using a specially designed cell on a Spex Ramalog machine equipped with a Krypton ion laser (568.2 nm excitation).

Crystal Data

$C_{18}H_{15}Cl_3NbPS_2$, $M = 525.69$, Triclinic, $a = 12.524(5)$, $b = 10.193(4)$, $c = 17.823(6)$ Å, $\alpha = 103.80(3)$, $\beta = 102.60(4)$, $\gamma = 72.02(4)°$, $U = 2075.8$ Å^3, $D_m = 1.69$ g cm^{-3}, $Z = 4$, $D_c = 1.68$ g cm^{-3}, $F(000) = 1048$, Mo-K_α radiation, $\lambda = 0.7107$ Å,

0020-1693/83/$3.00

$\mu(\text{Mo-K}_\alpha) = 15.1\ \text{cm}^{-1}$. No systematic absences, space group $P1$ or $P\bar{1}$. The latter gave a successful solution and refinement of the structure.

Crystallographic Measurements

A crystal with dimensions *ca.* 0.4 × 0.5 × 0.7 mm was mounted with the (013) planes perpendicular to the instrument axis of a General Electric XRD5 diffractometer which was used to measure diffraction intensities and cell dimensions. The instrument was equipped with a manual goniostat, a scintillation counter, and pulse-height discriminator, and employed zirconium-filtered molybdenum X-radiation. The stationary-crystal stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. Backgrounds were taken from plots of background as a function of 2θ. A standard reflection $(\overline{51}5)$ monitored during the course of the experiment showed only minor variance with time (±4%). 3831 independent reflections were measured with $2\theta \leq 40°$. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0.03I^2)]^{1/2}$, where E is the estimated background of the reflection. 2880 reflections with $I > 2\sigma(I)$ were used in subsequent calculations. The data were not corrected for absorption or extinction.

Structure Determination

The positions of the niobium atoms were determined from the Patterson function. A Fourier synthesis phased on these gave the positions of the chlorine, sulphur and phosphorus atoms. A second Fourier synthesis revealed the carbon atoms. The structure was refined by full-matrix least squares with the atoms divided into three blocks. In the latter stages of the refinement hydrogen atoms were included in trigonal positions. These corresponded to positive regions of electron density in a difference Fourier map and were included in the structure-factor calculations but were not refined. They were given thermal parameters equivalent to those of the atoms to which they were bonded.

The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $\sin\theta/\lambda$, was $\sqrt{w} = 1$ for $F_o < 90$ and $\sqrt{w} = 90/F_o$ for $F_o > 90$. Calculations were made at the University of London Computer Centre on the CDC 7600 computer [10] and with some of our own programs on an ICL 1904S at this university. Atomic scattering factors for niobium, chlorine, phosphorus, sulphur and carbon were taken from ref. 11 together with corrections for the real and imaginary part of the anomalous dispersion for niobium, chlorine, sulphur and phosphorus. Hydrogen scattering factors were taken from ref. 12.

The niobium, chlorine, sulphur and phosphorus atoms were refined anisotropically and the carbon atoms isotropically to R 0.058 for the 2880 significant reflections. In the final cycle of refinement no shift was $>0.04\sigma$. The 951 reflections given zero weight showed no large discrepancies.

Final positional parameters with their standard deviations are given in Table I. Table II shows the

TABLE I. Positional Parameters (×10^4) with Estimated Standard Deviations in Parentheses.

Atom	x	y	z
Nb(A)	3310(1)	5747(1)	3425(1)
Cl(3A)	2085(3)	4500(3)	3566(2)
Cl(2A)	4627(3)	3638(4)	3026(2)
Cl(1A)	3873(3)	6982(4)	2707(2)
S(1A)	1325(3)	7502(3)	3280(2)
S(2A)	4026(3)	6434(4)	4586(2)
P(A)	1274(3)	9512(3)	3285(2)
C(11A)	1278(10)	9883(13)	2358(7)
C(12A)	1468(11)	8859(13)	1702(7)
C(13A)	1407(11)	9196(14)	0982(8)
C(14A)	1172(11)	10588(14)	0937(8)
C(15A)	0956(11)	11642(14)	1571(8)
C(16A)	1006(11)	11300(13)	2288(7)
C(21A)	2316(10)	10147(12)	3999(7)
C(22A)	2454(11)	9938(13)	4775(8)
C(23A)	3224(12)	10453(15)	5356(8)
C(24A)	3850(12)	11201(15)	5173(8)
C(25A)	3738(12)	11455(15)	4448(9)
C(26A)	2981(11)	10907(14)	3824(8)
C(31A)	−0102(10)	10495(12)	3513(7)
C(32A)	−0283(12)	11422(14)	4209(8)
C(33A)	−1387(13)	12187(15)	4343(9)
C(34A)	−2304(12)	11997(15)	3769(9)
C(35A)	−2123(13)	11072(16)	3105(9)
C(36A)	−1023(12)	10273(15)	2957(8)
Nb(B)	8203(1)	5473(1)	−0169(1)
Cl(1B)	9889(2)	3426(3)	−0154(2)
Cl(2B)	8258(3)	5302(4)	−1502(2)
Cl(3B)	7193(3)	7835(3)	−0022(2)
S(1B)	8707(3)	5753(4)	1329(2)
S(2B)	6908(3)	4447(4)	−0308(2)
P(B)	7402(3)	5704(3)	1813(2)
C(11B)	6971(10)	4094(13)	1463(7)
C(12B)	7814(11)	2854(13)	1283(7)
C(13B)	7532(12)	1585(15)	1069(8)
C(14B)	6437(13)	1544(15)	1041(8)
C(15B)	5600(11)	2791(14)	1222(8)
C(16B)	5886(11)	4067(13)	1423(7)
C(21B)	6197(10)	7210(12)	1737(7)
C(22B)	6157(12)	8364(15)	2365(8)
C(23B)	5280(13)	9569(16)	2323(9)
C(24B)	4426(12)	9678(16)	1671(8)
C(25B)	4492(12)	8522(15)	1048(8)
C(26B)	5372(11)	7290(14)	1074(7)
C(31B)	7881(9)	5737(12)	2837(6)
C(32B)	8917(11)	6010(14)	3211(8)
C(33B)	9221(11)	6069(14)	4014(8)
C(34B)	8526(11)	5899(14)	4449(8)
C(35B)	7517(12)	5613(14)	4089(8)
C(36B	7189(11)	5526(13)	3289(7)

TABLE II. Molecular Dimensions (distance Å; angles °).

	Molecule A	Molecule B
Nb–Cl(1)	2.331(5)	2.469(3)
Nb–Cl(2)	2.332(4)	2.355(4)
Nb–Cl(3)	2.357(5)	2.330(3)
Nb–S(1)	2.577(3)	2.573(4)
Nb–S(2)	2.114(4)	2.129(4)
Nb–Cl(1$^{\mathrm{I}}$)	–	2.837(4)
S(1)–P(1)	2.028(5)	2.026(6)
Cl(1)–Nb–Cl(2)	93.5(2)	88.0(1)
Cl(1)–Nb–Cl(3)	151.1(1)	157.2(1)
Cl(1)–Nb–S(1)	87.9(1)	83.8(1)
Cl(1)–Nb–S(2)	103.0(2)	99.6(1)
Cl(1)–Nb–Cl(1$^{\mathrm{I}}$)	–	74.1(1)
Cl(2)–Nb–Cl(3)	90.3(1)	93.1(1)
Cl(2)–Nb–S(1)	152.4(1)	163.8(1)
Cl(2)–Nb–S(2)	103.6(1)	98.2(1)
Cl(2)–Nb–Cl(1$^{\mathrm{I}}$)	–	86.7(1)
Cl(3)–Nb–S(1)	76.0(1)	89.1(1)
Cl(3)–Nb–S(2)	103.9(2)	102.8(1)
Cl(3)–Nb–Cl(1$^{\mathrm{I}}$)	–	83.1(1)
S(1)–Nb–S(2)	102.9(1)	97.0(1)
S(1)–Nb–Cl(1$^{\mathrm{I}}$)	–	77.6(1)
S(2)–Nb–Cl(1$^{\mathrm{I}}$)	–	172.0(1)
Nb–Cl(1)–Nb$^{\mathrm{I}}$	–	105.9(1)
Nb–S(1)–P	116.6(2)	111.5(2)
S(1)–P–C(11)	115.2(4)	113.6(4)
S(1)–P–C(21)	113.9(4)	113.3(5)
S(1)–P–C(31)	103.8(5)	108.0(5)
C(11)–P–C(21)	110.2(7)	110.8(6)
C(11)–P–C(31)	103.9(6)	104.5(6)
C(21)–P–C(31)	109.0(5)	105.9(5)

(I is 2 – x, 1 – y, –z)

molecular dimensions involving the heavier atoms. Observed and calculated structure factors (S1), thermal parameters (S2), and the dimensions of the phenyl rings (S3) are available as supplementary material from the Editor.

Discussion

The unit cell contains two $NbSCl_3·tppS$ monomers (A), Fig. 1, and one centrosymmetric $[NbSCl_3·tppS]_2$ dimer (B), Fig. 2. The co-existence of monomer and dimer is a most unusual feature and we believe this to be the first report of such co-ordination isomers in the same crystal.

The stereochemistry about niobium in the monomer (A) is best described as a square pyramid, with the sulphido [S(2)] sulphur at the apex. The angles subtended at niobium between the apical sulphur atom and the basal atoms [Cl(1–3), S(1)] are all around 103°, which can be attributed to repulsive interactions between the multiply bonded S(2) and the other atoms. Consequently, the niobium atom lies 0.553(2) Å out of the plane described by the equatorial atoms towards the apical sulphur atom (Table III). This is less than that found in similar five co-ordinate $MoCl_3O·L$ complexes (L = tppS [1], 0.65 Å, or Cl^- [2], 0.59 Å) but greater than that in $ReOCl_4^-$ [2], 0.41 Å, and $[NbOCl_4^-]_2$, 0.37 Å [3], in which there is a weak interaction *trans* to oxygen (see earlier).

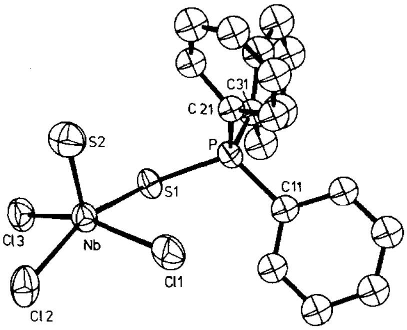

Fig. 1. An *ORTEP* drawing of the monomer viewed perpendicularly to the Cl(1), Cl(2), S(2) plane.

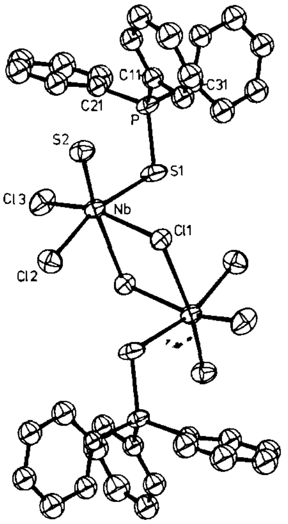

Fig. 2. An *ORTEP* drawing of the dimer viewed perpendicularly to the Cl(1), Cl(2), S(2) plane.

In the dimer (B) the niobium is in a distorted octahedral environment. This is attained by the linking of two monomeric units, one chlorine from each co-ordinating into the vacant sixth position of the other. The distance between the two niobium atoms is 4.240(4) Å. The bonds formed by the bridging chlorine atom [Cl(1B)] are both significantly longer than the other Nb–Cl bonds in the structure, indicating that this molecule is best considered as a dimer rather than two weakly associated monomers. The longer of the two bonds formed by Cl(1B) is *trans* to the multiply bonded sulphur atom, and the difference, 0.37 Å, can be attributed to the *trans* influence of this atom. Significantly, the bridging is not via the sulphido sulphur. Nb–O–Nb bridges have

TABLE III. Deviations of Atoms from Least-squares Planes (Å) (figures in bold type refer to atoms included in the calculation), and Torsion Angles (°).

	A	B
Nb	0.553(2)	0.397(2)
Cl(1)	**0.007(5)**	**−0.070(4)**
Cl(2)	**−0.008(6)**	**0.070(5)**
Cl(3)	**0.009(5)**	**−0.068(5)**
S(1)	**−0.008(4)**	**0.069(5)**
S(2)	2.666(6)	2.524(5)
Cl(1^I)	–	−2.418(4)
P	0.438(5)	1.708(5)

Torsion Angles (°)

	A	B
S(2)–Nb–S(1)–P	68.2(3)	−23.1(2)
Nb–S(1)–P–C(11)	86.3(8)	59.2(8)
Nb–S(1)–P–C(21)	−42.5(8)	−68.4(8)
Nb–S(1)–P–C(31)	−160.8(6)	174.6(6)

been shown to be present in $[NbOCl_3 \cdot POCl_3]_4$ [4], which contains a near planar Nb_4O_4 unit. The dimerisation is accompanied by a rotation about the Nb–S(1) bond (*cf.* Fig. 1 and 2) of *ca.* 90° as shown by the S(2)–Nb–S(1)–P torsion angles for the monomer and dimer (Table III). This presumably avoids a close approach between Cl(2B) and the carbons of the ligand in the dimer, although packing may also be important (see later), particularly since there are no Cl(2B)...C(3nB^I) contacts <4.0 Å in the dimer. The Raman spectrum shows two P=S stretching frequencies (582 and 586 cm^{-1}). Since there is no significant difference between the P=S bond lengths (0.002(8) Å) this must reflect the different configurations adopted by the tppS ligands.

The angles subtended at niobium by the multiply bonded sulphur atom and the equatorial ligands are between 97.0(1) and 102.8(1)°, less than in the monomer but still appreciably greater than 90° (Table II). This can be largely accounted for in the equalisation of repulsive effects between the axial ligands, S(2B) and Cl(1B^I), and the equatorial ligands. The average distance between S(2B) and the equatorial ligands is 3.48 Å, whereas that for Cl(1B^I) is 3.41 Å. Since the Nb(B)–S(2B) bond is much shorter than the Nb(B)–Cl(1B^I) bond the niobium atom is displaced from the equatorial plane by 0.397(2) Å towards the apical sulphur atom (Table III). This is greater than that found [5] in $WSCl_3 \cdot CH_3SCH_2CH_2SCH_3$, 0.32 Å, S at 2.668 Å, and [3] $[NbOCl_4^-]_2$, 0.37 Å, Cl at 3.011 Å.

The smaller displacement in the tungsten compound would be expected because of the shorter bond *trans* to the multiply bonded sulphur atom, whereas that in $[NbOCl_4^-]_2$ is surprising but perhaps reflects the size of oxygen compared with sulphur. The shortening of the multiple bond (1.70(2) compared to 2.129(4) Å) might be expected to compensate for the size difference, but all six co-ordinate $NbOCl_3 \cdot 2L$ structures [13] determined to date show relatively small displacements (0.15 to 0.31 Å) of the metal atom from the equatorial plane.

The Nb=S bond in the monomer is 0.015(6) Å shorter than that in the dimer, a difference that may be significant and which can be attributed to the influence of the *trans* chlorine in the dimer. This difference in bond length is not reflected in the Infra Red or Raman spectra, which both show a single band which may be assigned to the Nb=S stretch (536 and 537 cm^{-1} respectively). The Nb–S(1) distances do not differ significantly although they are signifiantly longer than the equivalent bond in $MoCl_3O \cdot tppS$ [1] (2.460 Å). The average of the Mo–Cl bond lengths in the latter structure is 2.324 Å, whereas that for the 'normal' Nb–Cl bonds in the present structure is 2.341 Å, reflecting the smaller covalent radius of Mo(V). However, this difference (*ca.* 0.02 Å) does not account for a difference in M–S bond length of 0.115 Å. The most likely explanation is that the ligand is bonded more strongly to molybdenum than niobium. Support for this is found in the P=S bond lengths, which are shorter (average 2.027 Å) in the present structure than in $MoCl_3O \cdot tppS$ (2.041 Å) [1], compared to 1.951 Å in the free ligand [14]. This is reflected in the IR P=S stretching frequencies. That for the present structure is 580 cm^{-1} compared with 575 cm^{-1} in $MoCl_3O \cdot tppS$ [1] and 638 cm^{-1} in the free ligand. The Raman spectrum shows two P=S stretching frequencies (see earlier).

Neither tppS ligand shows any unexpected departure from the free ligand dimensions. The P–C bond lengths (average 1.79 Å) are shorter than those of the free ligand [13] (average 1.83 Å) but this is typical [1, 15] of the tppS adducts, where average values of 1.80 Å have been recorded. The C–C bond lengths range from 1.34(2) Å to 1.42(2) Å and the phenyl rings show no significant departure from planarity.

The presence of five co-ordinate monomers and six co-ordinate dimers in the same crystal illustrates the small energy difference between the two co-ordination isomers and is presumably brought about by packing considerations. Evidence for this is found in the Nb–S(1)–P–C(n1) (n = 1, 2 or 3) torsion angles, Table III. Rather surprisingly, the values for the dimer (B) approach ideality, and are similar to those found in the non-sterically hindered triphenylphosphine sulphide-iodine adduct [15], whereas those for the monomer (A) deviate by *ca.* 20° from the ideal values, although this is less than for the $MoCl_3O \cdot tppS$ adduct [1] where the deviation is *ca.* 34°. There is a significant difference (5.0(3)°) between the Nb–S(1)–P angles for the two species which can also be attributed to packing effects. That for the dimer (111.5(2)°) is close to the tetrahedral angle and typical of tppS complexes [1, 15] whereas the angle in the monomer is 116.5(2)°. This is probably the result of the close approach of symmetry related C(24A) atoms (Table IV). If the Nb–S–P angle of the monomer were closer to the tetrahedral angle, this approach would be shortened still further. There are other close approaches to C(24A) (Table IV) which presumably preclude the relaxation of the angle strain by rotation about the Nb–S(1) bond.

TABLE IV. Intermolecular Contacts not Involving Hydrogen Atoms, <3.5 Å Involving Carbon, <3.75 Å Involving Heavier Atoms only.

C(35B)...C(33A$^{\mathrm{II}}$)	3.44(2)
C(25A)...C(24A$^{\mathrm{III}}$)	3.44(2)
C(24A)...C(35B$^{\mathrm{III}}$)	3.27(2)
C(24A)...C(24A$^{\mathrm{III}}$)	3.22(2)
S(2A)...S(2A$^{\mathrm{IV}}$)	3.572(6)
Cl(1B)...C(13A$^{\mathrm{V}}$)	3.42(2)
Cl(2B)...Nb(A$^{\mathrm{V}}$)	3.654(4)
Cl(2B)...S(1A$^{\mathrm{V}}$)	3.737(5)
Cl(2B)...Cl(3A$^{\mathrm{V}}$)	3.656(5)
Cl(2B)...Nb(A$^{\mathrm{V}}$)–S(2A$^{\mathrm{V}}$)	173.1(1)
Nb(B)–Cl(2B)...Nb(A$^{\mathrm{V}}$)	139.7(2)
Nb(A)–S(2A)...S(2A$^{\mathrm{IV}}$)	111.1(2)
I	2 − x, 1 − y, −z
II	1 + x, −1 + y, z
III	1 − x, 2 − y, 1 − z
IV	1 − x, 1 − y, 1 − z
V	1 − x, 1 − y, −z

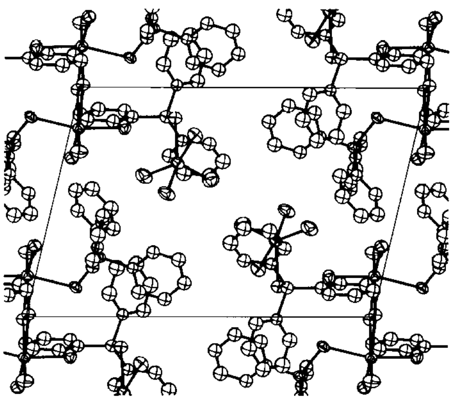

Fig. 3. A view of the packing along *b*.

Figure 3 shows a view of the packing along *b*. This illustrates two further features of the packing. The monomers are aligned such that the sulphido sulphur atoms approach to within 3.572(6) Å. This alignment permits a close approach of 3.654(4) Å between Cl(2B) and Nb(A) which is well within the sum of the van der Waals radii, which we estimate as *ca.* 3.85 Å, and therefore probably indicative of a positive interaction. Further evidence for this is found in the angles subtended at Nb(A$^{\mathrm{V}}$) and Cl(2B), Table IV. This close approach of Cl(2B) to Nb(A$^{\mathrm{V}}$) gives rise to two further contacts between Cl(2B), and S(1A$^{\mathrm{V}}$) (3.737(5) Å) and Cl(3A$^{\mathrm{V}}$) (3.656(6) Å).

Acknowledgement

We thank A. W. Jahans for assistance with the crystallographic investigations.

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