Crystal Structure of Benzyltriphenylphosphonium Pentachlorosulphidotungstate(VI) and a Study of the Vibrational Spectra of Salts containing $[WCl_5Y]^-$ (Y = O or S) Ions

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The salt $[PPh_3(CH_2Ph)][WCl_5S]$ is formed when WCl_4S is treated with $[PPh_3(CH_2Ph)]Cl$ (1 : 1 molar ratio) in CH_2Cl_2 solution. Crystals are monoclinic, space group $P2_1/c$, with a = 10.572(9), b = 18.413(13), c = 14.250(11) Å, and β = 104.20(8)°. The salt consists of discrete $[PPh_3(CH_2Ph)]^+$ and $[WCl_5S]^-$ ions with the W–S bond length being 2.132(13) Å and the W–Cl lengths spanning the range 2.246(17)—2.461(12) Å. The i.r. and Raman spectra of a series of salts containing the $[WCl_5Y]^-$ anion (Y = O or S) have been recorded and are reported, together with an assignment of the a_1 stretching modes.

RECENTLY, a single-crystal *X*-ray study of $[AsPh_4][WCl_5S]$ was published which contained some unusual, unexplained thermal parameters and dimensions in the anion.[1] Numerous other structural studies have been carried out on the 1 : 1 salts $[EPh_4][MX_4Y_nZ_m]$ (E = P or As; M = metal; X, Y, Z are unidentate ligands which may be equivalent, $n = 0$ or 1, $m = 0$ or 1) where the anion has at least C_{4v} symmetry.[2] The species crystallise in the space group $P4/n$ with $Z = 2$, and 17 studies have been reported with a ranging from 12.44 to 13.26 Å and c from 7.44 to 8.46 Å. The E atom of the cation (E = P or As) is in special position (2b) with site symmetry $\bar{4}$ while the central atom of the anion is in special position (2c) with site symmetry 4. This arrangement causes disorder in the anion if it has lower than C_{4v} symmetry. The space-filling characteristics of these 1 : 1 structures containing $[EPh_4]^+$ (E = P or As) are dominated by the large cations and so the anions are accommodated in the gaps between the cations.

We have been attempting to study species of the type $[EPh_4][MCl_nY]$ (Y = O or S, $n = 4$ or 5, M = Mo or W) and in more than one case have detected anion disorder or unusual thermal parameters with species having the space group $P4/n$ {*e.g.* $[PPh_4][MoCl_4(O/S)L]$[3]}. In an effort to alleviate this problem, we synthesised $[PPh_3(CH_2Ph)][WCl_5Y]$ (Y = O or S) in the hope that the less symmetrical cation would yield a lower-symmetry space group and thus give rise to an ordered anion. Unfortunately, of these two species, only crystals of $[PPh_3(CH_2Ph)][WCl_5S]$ were suitable for single-crystal *X*-ray studies. From this study we obtained anion dimensions for $[WCl_5S]^-$ and these we use in a critique of the previously published $[AsPh_4][WCl_5S]$ structure to suggest that some anion disorder passed undetected in the solution of that structure.

EXPERIMENTAL

Preparations were carried out on an all-glass vacuum line. Infrared spectra were obtained from Nujol mulls with a Nicolet 7000 Fourier-transform interferometer. For Raman spectroscopy the samples were sealed under vacuum into a cell. The samples were kept spinning during the course of the measurements which were made with a Spex Ramalog spectrometer equipped with a krypton-ion laser.

The salts were prepared using vacuum-line techniques, by allowing WCl_4O or WCl_4S[4] to react with RCl(1 : 1 molar ratio, R = $PPh_3(CH_2Ph)$, $AsPh_4$, PPh_4, NEt_4, or NMe_4) in dry CH_2Cl_2. Crystals of $[PPh_3(CH_2Ph)][WCl_5S]$ were obtained by recrystallisation from CH_2Cl_2 using the double-ampoule technique. The crystals were pale green needles.

Crystal Data.—$C_{25}H_{22}Cl_5PSW$, M = 746.1, Monoclinic, a = 10.572(9), b = 18.413(13), c = 14.250(11) Å, β = 104.20(8)°, U = 2 689.18 Å^3, D_m (flotation) = 1.78(5) g cm^{-3}, $Z = 4$, D_c = 1.84 g cm^{-3}, $F(000)$ = 1 448, Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) = 28.3 cm^{-1}, space group $P2_1/c$ from systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$.

A crystal with dimensions 0.3 × 0.2 × 0.4 mm was mounted with the (001) planes perpendicular to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. The instrument was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. The stationary-crystal–stationary-counter method was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken for those reflections whose counts were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. Several standard reflections monitored during the course of the experiment showed no significant changes in intensity. Of the 2 502 reflections recorded with $2\theta > 40°$, 1 574 were used in the final refinement. No absorption or extinction corrections were applied. The standard deviations $\sigma(I)$ of the reflections were taken as $[I + 2E + (0.03I)^2]^{\frac{1}{2}}$ where I is the intensity and E is the estimated background of the reflection.

Structure Solution and Refinement.—The structure was determined from Patterson and Fourier syntheses and refined by full-matrix least squares. The tungsten, sulphur, chlorine, and phosphorus atoms were refined anisotropically. The benzene rings were refined as rigid groups with the carbon atoms given individual isotropic thermal parameters. The hydrogen atoms were fixed in trigonal or tetrahedral positions and given a common refined thermal parameter. After refinement by full-matrix least squares R was 0.079. Calculations were carried out using the SHELX 76 programs at the University of London Computer Centre.[5] In the last cycle of refinement, no shift was $> 0.2\sigma$. The weighting scheme used was $\sqrt{w} = 1$ for $F_{obs.} < 70$ and $70/F_{obs.}$ for $F_{obs.} > 70$. Scattering factors and dispersion corrections were taken from ref. 6. In the final difference-

Fourier map there were no significant peaks. The atom positions are given in Table 1. Anion bond lengths and angles are in Table 2 and thermal parameters for the atoms in the anion in Table 3. Structure-factor tables, hydrogen-atom positions, thermal parameters for the cation, and cation dimensions are given in Supplementary Publication No. SUP 23134 (12 pp.).*

TABLE 1

Final positional parameters ($\times 10^4$) for $[PPh_3(CH_2Ph)][WCl_5S]$ with estimated standard deviations in parentheses

Atom	x	y	z
W	3 246(2)	1 679(1)	224(1)
Cl(1)	1 639(13)	784(6)	−128(9)
Cl(2)	1 800(12)	2 452(7)	690(10)
Cl(3)	4 938(11)	2 485(6)	836(8)
Cl(4)	3 669(12)	1 226(7)	1 896(8)
Cl(5)	4 751(16)	849(9)	58(12)
P	7 713(9)	1 744(6)	4 120(6)
S	2 857(14)	2 094(8)	−1 216(9)
C(1)	7 383(24)	2 673(10)	3 919(19)
C(2)	8 322(24)	3 202(10)	4 279(19)
C(3)	8 058(24)	3 930(10)	4 039(19)
C(4)	6 856(24)	4 130(10)	3 440(19)
C(5)	5 918(24)	3 601(10)	3 080(19)
C(6)	6 181(24)	2 872(10)	3 320(19)
C(11)	8 402(22)	1 419(14)	3 212(15)
C(12)	7 625(22)	1 127(14)	2 361(15)
C(13)	8 191(22)	898(14)	1 625(15)
C(14)	9 535(22)	961(14)	1 739(15)
C(15)	10 313(22)	1 253(14)	2 590(15)
C(16)	9 947(22)	1 482(14)	3 326(15)
C(21)	6 197(33)	1 284(18)	4 111(25)
C(22)	6 452(24)	531(10)	4 512(16)
C(23)	6 546(24)	−56(10)	3 914(16)
C(24)	6 786(24)	−751(10)	4 305(16)
C(25)	6 933(24)	−859(10)	5 295(16)
C(26)	6 839(24)	−273(10)	5 893(16)
C(27)	6 599(24)	423(10)	5 501(16)
C(31)	8 739(21)	1 581(13)	5 278(13)
C(32)	8 551(21)	1 990(13)	6 057(13)
C(33)	9 200(21)	1 801(13)	7 001(13)
C(34)	10 037(21)	1 204(13)	7 165(13)
C(35)	10 225(21)	795(13)	6 386(13)
C(36)	9 576(21)	984(13)	5 443(13)

TABLE 2

Bond lengths (Å) and angles (°) for the anion $[WCl_5S]^-$ in $[PPh_3(CH_2Ph)][WCl_5S]$ with estimated standard deviations in parentheses

W–Cl(1)	2.344(12)	Cl(2)–W–Cl(3)	90.1(4)
W–Cl(2)	2.317(14)	Cl(2)–W–Cl(4)	84.3(5)
W–Cl(3)	2.310(11)	Cl(2)–W–Cl(5)	169.2(6)
W–Cl(4)	2.461(12)	Cl(2)–W–S	93.7(5)
W–Cl(5)	2.246(17)	Cl(3)–W–Cl(4)	85.2(4)
W–S	2.132(13)	Cl(3)–W–Cl(5)	89.2(5)
Cl(1)–W–Cl(2)	89.3(5)	Cl(3)–W–S	95.1(5)
Cl(1)–W–Cl(3)	170.3(4)	Cl(4)–W–Cl(5)	84.9(5)
Cl(1)–W–Cl(4)	85.0(4)	Cl(4)–W–S	178.0(5)
Cl(1)–W–Cl(5)	89.7(5)	Cl(5)–W–S	97.1(6)
Cl(1)–W–S	94.7(5)		

TABLE 3

Final thermal parameters ($10^3 \times$ Å^2) for $[WCl_5S]^-$ with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W	63(2)	46(2)	53(2)	6(1)	3(2)	−7(1)
S	93(10)	80(9)	55(8)	17(7)	6(7)	−22(9)
Cl(1)	85(9)	51(7)	72(8)	0(8)	−4(7)	−21(7)
Cl(2)	72(9)	58(8)	95(10)	−2(7)	13(7)	16(7)
Cl(3)	62(8)	62(8)	74(8)	8(6)	7(6)	−28(6)
Cl(4)	69(8)	89(9)	53(7)	17(7)	−3(6)	−22(7)
Cl(5)	122(13)	99(11)	97(10)	9(9)	30(9)	34(10)

RESULTS AND DISCUSSION

Description of the Structure of $[PPh_3(CH_2Ph)][WCl_5S]$.—Few structures containing the $[PPh_3(CH_2Ph)]^+$ cation have been published. Accordingly, we initially describe the structure of $[PPh_3(CH_2Ph)][WCl_5S]$ and then compare it with that of one of the few salts containing the $[PPh_3(CH_2Ph)]^+$ ion, namely $[PPh_3(CH_2Ph)][UCl_6]$. This comparison reveals that, as for the $[EPh_4][MX_4Y_nZ_m]$ salts, the space-filling characteristics of the cation dominate the structure.

The unit cell of $[PPh_3(CH_2Ph)][WCl_5S]$ and the atom-numbering scheme are shown in Figure 1. All the atoms are in general positions, in contrast to the 1 : 1 salts formed by $[EPh_4]^+$ that have space group $P4/n$.

The W–S distance [2.132(13) Å] is comparable to that observed in WCl_4S [2.098(8) Å] [7] and a number of its adducts [2.07(1) Å in $2WCl_4S{\cdot}MeSCH_2CH_2SMe$,[8] 2.10(1) Å in $WCl_4S{\cdot}WCl_2OS{\cdot}MeOCH_2CH_2OMe$[9]]. The length of the W–S bond suggests the presence of a doubly bonded W=S unit and thus some lengthening of the *trans* W–Cl [Cl(4)] bond compared to the other W–Cl distances is to be expected. This lengthening is observed, since the W–Cl(4) distance [2.461(12) Å] is longer than the average of the equatorial W–Cl bond lengths (2.304 Å). The presence of the W=S unit also causes in increase above 90° of the S–W–$Cl_{eq.}$ angles (average 95.1°). The W atom is 0.21 Å above the plane of the four equatorial chlorine atoms in the direction of the sulphur atom. This contrasts with the related distance of 0.45 Å observed in WCl_4S when of course there is no strongly bonded *trans* atom.

The four equatorial W–Cl distances span a wide range. The average distance (2.304 Å) is similar to the W–Cl terminal bonds observed in WCl_4S [2.267(12), 2.273(12), and 2.291(13) Å],[7] $2WCl_4S{\cdot}MeSCH_2CH_2SMe$ [2.29(1)—2.34(1) Å],[8] and $WCl_4S{\cdot}WCl_2OS{\cdot}MeOCH_2CH_2OMe$ [2.31(1)—2.32(1) Å].[9] The W–Cl(5) distance [2.246(17) Å] is shorter than all the others and examination of the intermolecular contact distances reveals that Cl(5) approaches across the centre of symmetry (at $\frac{1}{2}$,0,0) the Cl(5) atom of another anion [3.18(2) Å]. Thus, it seems this relatively short W–Cl distance is a consequence of packing forces. This postulation is supported by the size of the S–W–Cl(5) angle [97.1(6)°] when compared to the other S–W–Cl(eq.) angles (average 94.5°). Thus, it appears that the S–W–Cl(5) angle is enlarged to increase the Cl(5) ··· Cl(5^I)† contact distance while an increase in the W–Cl(5) distance decreases the Cl(5) ··· Cl(5^I) distance, since the W–Cl(5) ··· Cl(5^I) angle is 141°. It is not clear, however, why this short Cl ··· Cl contact is not increased by expansion of the unit cell or by adoption of a different form of packing for the anions, particularly as both effects are observed in the isomorphous structure of

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

† Superscript I refers to the equivalent position $1 - x, -y, -z$.

$[PPh_3(CH_2Ph)][UCl_6]$.[10] The co-ordinates of the atoms of the $[PPh_3(CH_2Ph)]^+$ cations in the two structures are very similar, as are those of the two metal ions. However, comparison of the unit cells of $[PPh_3(CH_2Ph)][UCl_6]$ (Figure 2) and $[PPh_3(CH_2Ph)][WCl_5S]$ (Figure 1)

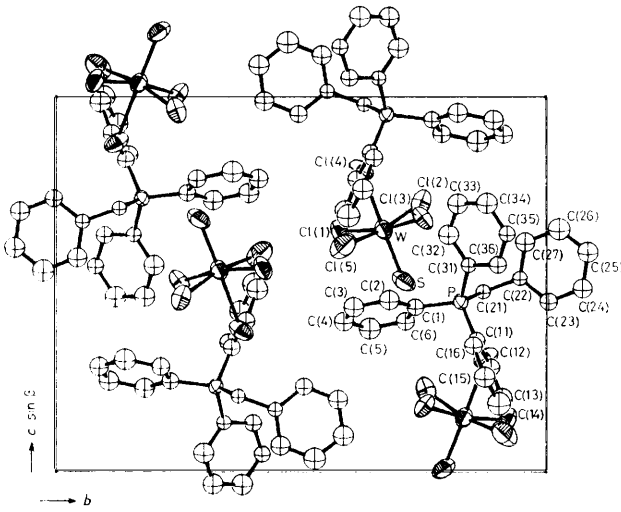

FIGURE 1 Unit cell of $[PPh_3(CH_2Ph)][WCl_5S]$ showing the atom-numbering scheme

reveals that the orientations of the anions in the two structures differ. This results in a large dissimilarity in the anion · · · anion closest contact distances across the centre of symmetry {3.96 Å in $[PPh_3(CH_2Ph)][UCl_6]$, 3.18(2) Å in $[PPh_3(CH_2Ph)][WCl_5S]$}. It would seem that in the tungsten salt the $Cl(5) \cdots Cl(5^I)$ contact

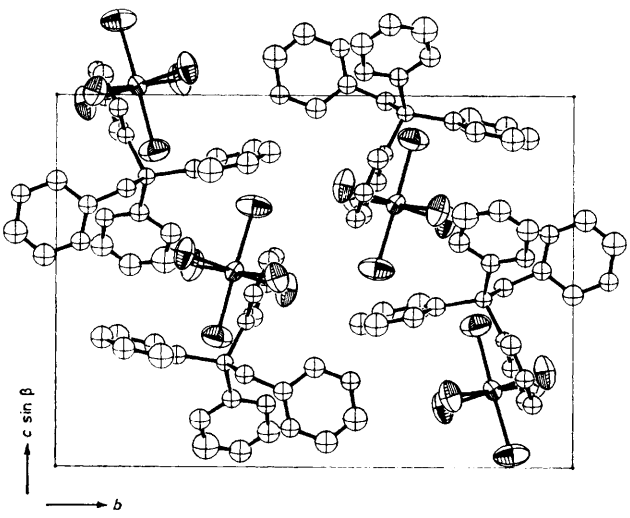

FIGURE 2 Unit cell of $[PPh_3(CH_2Ph)][UCl_6]$

distance could easily be increased by rotating the anion to the relative orientations found in the $[UCl_6]^-$ salt or by expanding the unit cell. It is surprising that neither of these two possibilities is adopted but that the contact distance is increased to some small extent by shortening of the W–Cl(5) distance. Even this bond shortening leaves the contact distance well within the sum of the van der Waals radii (3.50 Å) and, thus, there must be severe strain in the structure, compensated for in other ways. Possibly, the compensation arises through the efficiency of the packing which in turn leads to a favourable lattice enthalpy. Examination of anion–cation contact distances reveals that all six atoms of the co-ordination sphere of the tungsten atom are close to hydrogen atoms on the cations (range 2.82—3.18 Å).

Comparison of the Structures of $[PPh_3(CH_2Ph)][WCl_5S]$ *and* $[AsPh_4][WCl_5S]$.—As was stated earlier, unusual thermal parameters for the sulphur atoms are contained in the report of the structure of $[AsPh_4][WCl_5S]$ [$U_{11} = U_{22} = 0.174(4)$, $U_{33} = 0.034(3)$ Å^2].[1] For the sulphur atom in $[PPh_3(CH_2Ph)][WCl_5S]$ no such unusual parameters were observed. Three further differences are apparent in the geometry around the $[WCl_5S]^-$ anion in $[PPh_3(CH_2Ph)][WCl_5S]$ and $[AsPh_4][WCl_5S]$. In the latter compound the W–S bond is longer [2.173(6) compared to 2.132(13) Å], the W–Cl(ax.) bond is shorter [2.353(5) compared to 2.461(12) Å], and the tungsten atom is closer to the plane of the four equatorial chlorine atoms (0.11 compared to 0.21 Å). We believe our determination to be more accurate for, as stated earlier, the W–S distance is directly comparable to those observed in a whole range of WCl_4S adducts. The difference between the W–Cl(eq.) and W–Cl(ax.) bond lengths in our determination is of the expected magnitude, as is the distance of the tungsten atom from the Cl(eq.) plane. In our view there are two possible reasons for the peculiar parameters observed for $[AsPh_4][WCl_5S]$. The first possibility is that the axial sulphur and chlorine atoms are disordered so as to give unequal proportions of each in the two sites. The second is that the sulphur atom is displaced by a small distance off the four-fold axis and thus is disordered over four sites. The first proposition would obviously result in a lengthening of the W–S bond and a shortening in the W–Cl(ax.) bond but it would not account for the unusual thermal parameters. Such thermal parameters could be a result of our second postulate, that is the positioning of the sulphur atom off the four-fold axis.

The packing of cations of the type $[EPh_4]^+$ (E = P or As) in *P4/n* structures has been shown to be very efficient and so it is likely that disorder may occur within large anions when they attempt to arrange themselves in the available space of the cation array. The interionic distance [Cl(ax.) · · · S] of 3.28 Å in $[AsPh_4][WCl_5S]$ is well within the sum of the van der Waals radii. Displacement of the sulphur atom off the *c* axis would obviously increase this non-bonded distance. If the axial chlorine atom were also placed off the axis a further increase in the Cl(ax.) · · · S distance would result. We believe the reason why this does not occur lies in a consideration of the Cl(ax.) · · · H and S · · · H non-bonded contact distances. An analogous situation is found in the salt $[PPh_4][NbCl_6]$ [11] where there is a wide disparity in the Nb–Cl(ax.) distances [Nb–Cl(1) 2.33, Nb–Cl(2) 2.27

Å] and the atom Cl(2) has unusual thermal parameters [$U_{11} = U_{22} = 0.177(4)$, $U_{33} = 0.035(3)$ Å^2]. The authors state that when corrected for thermal vibration the Nb–Cl(2) distance becomes 2.31 Å but they also suggest that Cl(2) may be positioned off the four-fold axis. Examination of the closest axial Cl · · · H contact distances [Cl(1) · · · H 2.97, Cl(2) · · · H 3.94 Å] reveals that Cl(1) may be constrained to its four-fold position by Cl · · · H interactions whereas Cl(2) is not. Similarly, in [$AsPh_4$][WCl_5S], it is Cl · · · H interactions that hold the Cl(ax.) on the four-fold axis. The reports on [PPh_4][$NbCl_6$] and [$AsPh_4$][WCl_5S] were made by the same research group. The report on the niobium compound was made after that of the tungsten compound, thus it is likely that the authors would now present a slightly different interpretation of the results in their first paper. The Cl(ax.) · · · S distance could also be increased by an expansion of the *c* axis. However, as the *c* distance is already 7.80 Å, a relatively large value for this set of compounds,[2] and an increase to 8.3 Å would be required to make the Cl(ax.) · · · S distance greater than the sum of the van der Waals radii, this increase is unlikely to be feasible whilst retaining the same mode of cation packing. Support for this last statement derives from a consideration of the structures of [PPh_4][$NbCl_6$] and [PPh_4][$NbBr_6$].[12] The former belongs to the space group $P4/n$ whilst the latter has the lower symmetry of $C2/c$. This suggests that [$NbCl_6$]$^-$ is able to fit into the available space in the $P4/n$ system, albeit with some distortion, whilst the larger [$NbBr_6$]$^-$ is not.

On the basis of these arguments, we conclude that the most likely cause of the unusual thermal parameters observed in [$AsPh_4$][WCl_5S] and [PPh_4][$NbCl_6$] is disorder of one of the axial atoms over four sites and constraint of the second axial atom to its position on the axis by non-bonded interactions with hydrogen atoms. In this way the maximum packing efficiency of cations is maintained in the [EPh_4][$MX_4Y_nZ_m$] series of salts having $P4/n$ symmetry.

Infrared and Raman Spectra of [WCl_5Y]$^-$ (Y = O *or* S).—For anions [MX_5Y]$^{n-}$, having C_{4v} symmetry, 15 normal modes are to be expected which span the representation (1). Of these vibrations, only the a_1 and *e* modes are i.r. active while all are Raman active. The vibrations which occur at highest energy, and therefore are most easily detected and assigned, are the five stretching modes ν(M=Y) a_1, ν(M–$X_{ax.}$) a_1, ν(M–$X_{eq.}$) a_1, b_1, and *e* and the deformation mode of the doubly bonded fragment δ(W=Y) *e*.

$$\Gamma_{vib.} = 4a_1 + 2b_1 + b_2 + 4e \qquad (1)$$

A range of salts containing [WCl_5O]$^-$ and [WCl_5S]$^-$ has been prepared and characterised by satisfactory elemental analyses.[3] The i.r. and Raman spectra of these salts have been recorded, and the essential features are given in Table 4. As is expected for these anions having C_{4v} symmetry, the tungsten–chlorine stretching regions of the salts showed marked similarities and we were able to make tentative assignments of some of the common bands.

Tungsten–chlorine vibrations. The symmetric in-phase breathing mode of the four equatorial chlorine atoms (a_1) occurs as a strong band in the Raman spectra of most of the salts around 380 cm^{-1}. A corresponding weak band is found at a slightly lower frequency in the i.r. spectra. Similar results have been reported for [PPh_4][WCl_5O] where $\nu_{sym.}$(W–Cl_4) (a_1) was assigned to a band at 387 cm^{-1} in the Raman spectrum and to a weak feature at 382 cm^{-1} in the i.r. spectrum.[13] The axial vibration ν(W–$Cl_{ax.}$) is tentatively assigned to a band around 360 cm^{-1} in the spectra of [WCl_5S]$^-$ salts and around 350 cm^{-1} in the [WCl_5O]$^-$ salts. This is at a lower wavenumber than the symmetric equatorial ($WCl_{eq.}$) stretch which agrees with the finding that W–$Cl_{ax.}$ is longer than the mean W–$Cl_{eq.}$ in [$PPh_3(CH_2Ph)$][WCl_5S]. The relatively large difference in ν(W–$Cl_{ax.}$) between [WCl_5S]$^-$ and [WCl_5O]$^-$ could be explained by a larger *trans* effect of the oxygen atom although no structural evidence is available to support this theory. The asymmetric ν(W–$Cl_{eq.}$) (*e*) mode is assigned to an i.r. band (which sometimes appears split) in the range 317—333 cm^{-1}. This band is either weak or not observed in the Raman spectra, analogous to the case previously reported for [PPh_4][WCl_5O].[13] The splitting of the doubly degenerate $\nu_{asym.}$(W–$Cl_{eq.}$) mode may be caused by the lack of perfect C_{4v} symmetry in the [WCl_5Y]$^-$ ion such as that found in [$PPh_3(CH_2Ph)$][WCl_5S].

Tungsten–sulphur or -oxygen modes. The ν(W=Y) stretching vibration has been assigned to the highest non-cation band observed in the spectrum of each salt.

TABLE 4

Infrared and Raman spectra (cm^{-1}) of some [WCl_5Y]$^-$ (Y = O or S) anions

	ν(W=Y)		$\nu_{sym.}$(W–Cl_4) (a_1)		ν(W–$Cl_{ax.}$)		$\nu_{asym.}$(W–Cl_4) (*e*)		δ(W–Y)	
Compound	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.
[$PPh_3(CH_2Ph)$][WCl_5S]	522m	*a*	384s	384		364w	328w	330, 317s	150m	155s
[$AsPh_4$][WCl_5S]	524	520s		*c*	361m	358w		318s		
	b	526s [d]		340 [d]		320 [d,e]		320 [d,e]		
[PPh_4][WCl_5S]	527	*a*		383w	364m	363 (sh)		321s		
[NEt_4][WCl_5S]	519s	518s	380s	377w	364m	363s		329s, 317s	156w	155s
[NMe_4][WCl_5S]	*b*	520s		379w				320s		
[$PPh_3(CH_2Ph)$][WCl_5O]	952w	952s	375s	373m				330s	247m	247s
[$AsPh_4$][WCl_5O]	*b*	954s	382s	379w	345w	350 (sh)		330s	244m	243s
[PPh_4][WCl_5O]	957s	956s	387s	383w	350w			333s	248m	244s
[NEt_4][WCl_5O]	959w	958s	375s	372m				333s	249m	245s

[a] Obscured by cation band. [b] Not measured. [c] Cation band seen at 340 cm^{-1}. [d] From ref. 1. [e] Assigned to same absorption.

The position and intensity of the ν(W=O) stretching frequency (952—958 cm^{-1}) agrees with previously reported values.[13] The ν(W=S) stretching mode was observed in the range 518—520 cm^{-1}. For salts containing a phosphonium cation this mode was obscured in the i.r. spectra by the carbon–phosphorus stretch. However, in the Raman spectra of $[PPh_3(CH_2Ph)][WCl_5S]$ where the phosphorus–carbon stretch is inactive, ν(W=S) was observed at 522 cm^{-1}.

It is interesting to compare the position of the ν(W=S) stretch for a range of tungsten compounds. In the neutral species WCl_4S, ν(W=S) occurs at 560 cm^{-1} in the Raman spectrum and at 559 cm^{-1} in the i.r. spectrum, while in the tetrahedral $[WS_4]^{2-}$ ion, ν(W=S) occurs at 479 cm^{-1}.[14] The values reported here for ν(W=S) are intermediate between the two sets of previously published data, as is to be expected considering the variation in charge and co-ordination number.

The deformation mode δ(W=O) has been assigned to the common band observed in the spectra of $[WCl_5O]^-$ (around 242 cm^{-1}) and not seen in the spectra of $[WCl_5S]^-$.

The equivalent δ(W=S) is to be expected at a much lower frequency and we tentatively assign this to a band observed at 155 cm^{-1} in the spectra of the $[PPh_3(CH_2Ph)]^+$ and $[NEt_4]^+$ salts of $[WCl_5S]^-$. Included in Table 4 are two sets of spectroscopic data for $[AsPh_4][WCl_5S]$. We examined the published data [1] and found it varied from that which we had obtained for a range of $[WCl_5S]^-$ salts and so we synthesised $[AsPh_4][WCl_5S]$ and obtained results at variance with those previously published but in agreement with our other measurements on $[WCl_5S]^-$.

Conclusions.—We have shown by a comparison of the structures of $[AsPh_4][WCl_5S]$ and $[PPh_3(CH_2Ph)][WCl_5S]$ that the species $[EPh_4]X$ (E = As or P, X = Cl or Br) which are frequently used to produce salts for study by single-crystal X-ray techniques have to be used with caution, for if the resulting anion has a six-co-ordinate metal and is moderately large, disorder may occur. Also, by a comparison of the spectra of various $[WCl_5Y]^-$ (Y = O or S) containing species, data for the W–S vibrations have been obtained. Various splittings of the $\nu_{asym.}(W-Cl_4)$ mode were observed but these cannot be definitely assigned to the existence of less than four-fold symmetry for the $W-Cl_4$(eq.) unit for, although it occurs in the spectrum of $[PPh_3(CH_2Ph)][WCl_5S]$, it is not observed in the isomorphous oxygen analogue.

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