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New synthetic route to WSF_4 and its solution-phase structure as determined by tungsten L(III)-edge extended X-ray absorption fine structure studies

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The compound WSF_4 was synthesized in one step by the reaction of WF_6 with $(Me_3Si)_2S$ in solution at ambient temperatures. Solution-phase structural data have been obtained for the first time for it and related tungsten chalcogenide tetrahalides *via* a tungsten L(III)-edge EXAFS (extended X-ray absorption fine structure) study. This demonstrates that WOF_4, $WOCl_4$ and WSF_4 in acetonitrile or dichloromethane solution are monomeric. For WSF_4 analysis of the EXAFS data yielded bond lengths of 2.026(8) (W=S) and 1.863(3) Å (W–F). The W=S bond length is shorter than previously determined, by gas-phase electron diffraction, but is more consistent with that found in related structures.

A large number of fluoride oxides of transition metals are known,[1] they are generally well characterised and a wide range of experimental methods are available for their synthesis. In the solid state most adopt fluoride-bridged structures[2] and it has been suggested[3,4] that the sulfur and selenium analogues are based on similar fluoride-bridged polymeric structures. By comparison the structure of the analogous chlorides appear to be based on distorted chloride-bridged dimeric units.[5,6]

Probably the most studied of these compounds are the chalcogenide tetrahalides of tungsten, *i.e.* WEF_4 (E = S, Se or Te), with the principal synthetic routes being based on high-temperature autoclave methods.[7] However the amount of physical data available is very limited, which may be ascribed to a number of factors including their extreme reactivity to moisture. This lack of data is unfortunate since the combination of traditionally 'hard' and 'soft' ligands on the same high-oxidation-state metal centre makes such species interesting from structural and bonding aspects.

Structural data for the gas-phase tetrahalide sulfide compounds WSX_4 (X = F, Cl or Br) have been obtained from high-temperature electron diffraction studies[8] which concluded that under such experimental conditions they all adopt monomeric square-based pyramidal structures. However examination of the bond lengths obtained reveals an unusual trend for the tungsten–sulfur distance of the tungsten tetrahalide sulfides. The reported W=S bond length decreased from 2.109 Å in $WSBr_4$ to 2.086 Å in $WSCl_4$, as anticipated, but then increased to 2.104 Å in WSF_4. This is clearly not what might be expected on the basis of simple electronegativity arguments,[9] nor is the trend mirrored in the data obtained for the W=O bond lengths in the oxide tetrahalides obtained by electron diffraction (1.684, $WOBr_4$; 1.685, $WOCl_4$; 1.666 Å, WOF_4). However the authors noted that problems were encountered studying WSF_4 primarily due to sample decomposition.[8]

The extreme reactivity of these species is amply demonstrated by the fact that just a single communication of the determination of the crystal structure of WSF_4 exists.[4] This reveals a fluoride-bridged polymeric chain [$d(W{=}S) = 2.07$, $d(W{-}F)_{av} = 1.87$ Å]. It also reports the structure of an acetonitrile adduct ($WSF_4{\cdot}MeCN$) as a monomer with a W=S bond length of 2.034 Å. In both cases the W=S bond distance is significantly shorter than the value derived from the electron diffraction experiments and indeed shorter than the distance in $WSCl_4$. In view of previous successes in the use of solid- and solution-phase EXAFS (extended X-ray absorption fine structure) studies to determine structural parameters for some of the least-stable fluorine-containing species, a re-evaluation of the structure of monomeric WSF_4 was undertaken. We report an extension of a previously published method[10] for the convenient one-step solution-phase synthesis of WSF_4 and our findings regarding the W=S bond length as determined by solution-phase tungsten L(III)-EXAFS studies.

Experimental

Hexamethyldisilathiane and deuteriated acetonitrile and dichloromethane (Aldrich) were used as supplied after degassing by a number of freeze–thaw cycles. Diethyl ether (BDH) was dried by standing over sodium wire for *ca.* 1 d and subsequently refluxed over CaH_2 under a dinitrogen atmosphere. The compound WF_6 (Fluorochem) was used as supplied after verification of its purity by spectroscopic methods. Fluorine NMR spectra were recorded of solutions in heat-sealed prepassivated FEP tubes (outside diameter 4 mm, inside diameter 3 mm) held concentrically in a 5 mm glass NMR tube on a Bruker AC200 spectrometer operating at 188.296 MHz and referenced against $CFCl_3$. All reagents were handled under a nitrogen atmosphere in a dry-box (Belle Technology, UK) or on a glass and PTFE vacuum line.

In a typical reaction a heat-sealed FEP tube fitted with PTFE valve (STD/VC-4 Production Techniques Ltd., Fleet, UK) was evacuated and passivated with WF_6 on a vacuum line. After removing the WF_6 the tube was taken into a dry-box where $(Me_3Si)_2S$ (0.06 g, 0.34 mmol) was dissolved in solvent (acetonitrile or dichloromethane, 0.35 cm^3). The tube was resealed and reconnected to the vacuum line followed by passivation with WF_6 of those parts of the line that had been exposed to the atmosphere. The compound WF_6 (0.1 g, 0.34 mmol) was condensed into the reactor held at 77 K followed by a further 0.15 cm^3 of solvent. On warming to room temperature an immediate reaction ensued which resulted in the formation of a small amount of a dark brown precipitate. After allowing the solid to settle the pale yellow solution was decanted off into a second prefluorinated 4 mm FEP tube and the tube heat sealed. Fluorine NMR spectra of this solution exhibited an intense singlet at δ 86.2 showing tungsten-183 satellite coupling of 33.4 Hz. A weak peak at δ 66.9, also showing tungsten satellites, due to WOF_4 was observed on occasions. A ten-line multiplet centred at δ −157.1 was also observed. This signal is assigned to $SiMe_3F$ on the basis of its chemical shift and the magnitude of the observed coupling constants, 7.4 Hz [$^3J(^1H{-}^{19}F)$] and satellites $^1J(^{29}Si{-}^{19}F) = 272.7$ Hz (4.7%

natural abundance).[11] The compounds WOF_4 and $WOCl_4$ were prepared by standard routes[12,13] and characterised by elemental analysis and spectroscopic methods.

The EXAFS studies were carried out either on solutions of the tungsten chalcogenide tetrahalide dissolved in deuteriated solvents used for recording NMR data or on fresh samples prepared by dissolving a known mass of solid in acetonitrile, diethyl ether or dichloromethane in a dry-box (concentration *ca.* 0.05 mol dm^{-3}). In both cases solutions were transferred to heat-flattened 4 mm FEP tubes (path length *ca.* 1 mm) which were then sealed. The tungsten L(III)-edge EXAFS transmission spectra were recorded at the Daresbury Synchrotron Radiation Source operating at 2 GeV (*ca.* 3.2×10^{-10} J) with an average operating current of 180 mA on station 7.1 using an order-sorting Si(111) monochromator offset to 50% of the rocking curve for harmonic rejection. Several data sets were collected at room temperature in k space and averaged to improve the signal-to-noise ratio. The monochromator was calibrated using a thin tungsten foil. The EXAFS data treatment utilised the programs EX[14] and EXCURV92.[15] The background was removed by fitting the pre-edge by a straight line and subtracting this from the spectrum. The atomic contribution to the oscillatory part of the absorption spectrum was approximated using a polynomial and the optimum fit judged by minimising the intensity of chemically insignificant shells at low r in the Fourier transform. Curve fitting used single-scattering curve-wave theory with phase shifts and back-scattering factors calculated using the X_α option, based on normal *ab initio* methods,[16] within EXCURV92.

Results and Discussion

When hexamethyldisilathiane dissolved in acetonitrile or dichloromethane is added to a solution of tungsten hexafluoride dissolved in the same solvent at low temperature followed by warming to room temperature an immediate reaction ensues. According to fluorine NMR measurements, tungsten tetrafluoride sulfide and trimethylsilyl fluoride are generated as the principal fluorine-containing solution-phase species. In most reactions a variable amount of a dark brown insoluble compound was also formed. A number of separate experiments were performed with slight variations in the solvent and conditions used, however they were generally unsuccessful in completely eliminating this side reaction although it may be minimised by working at low temperature (−30 °C) and with moderately dilute (*ca.* 0.1 mol dm^{-3}) solutions. Solid WSF_4 was isolated by allowing the dark solid to collect at the bottom of the reactor followed by decantation of the solution and subsequent removal of the solvent and volatile trimethylsilyl fluoride resulting in a light yellow solid which is extremely moisture and oxygen sensitive. When exposed to the atmosphere it darkens immediately and H_2S is liberated.

The ^{19}F NMR studies confirm the identity of the tungsten–fluorine product as WSF_4 by comparison with the previously recorded chemical shift of δ 86.9 with respect to $CFCl_3$ and the tungsten-183 coupling constant.[4] An additional weak singlet, also exhibiting tungsten-183 satellites, could occasionally be observed at δ 66.9 corresponding to a small amount of WOF_4, presumably arising from limited hydrolysis. Integration of the signals due to WSF_4 and WOF_4 suggests that typically WOF_4 is present at less than 1%.

The reaction also produced a variable, but small, amount of brown material. The small scale meant it was not possible unambiguously to identify the solid; elemental analysis shows that it contains tungsten and sulfur and it is in all likelihood WS_3. However its apparent complete insolubility in these solvents resulted in facile separation from the desired product and does not pose a problem. This route therefore provides a simple one-step synthesis of WSF_4 in accordance with equation (1).

$$WF_6 + (Me_3Si)_2S \longrightarrow WSF_4 + 2Me_3SiF \quad (1)$$

Attempts to generate WS_2F_2 by increasing the ratio of hexamethyldisilathiane to WF_6 to 2:1 and beyond were unsuccessful, resulting instead in a greater mixture of WSF_4 and the brown compound.

The EXAFS studies were carried out either on fresh samples dissolved in acetonitrile, diethyl ether or dichloromethane or on samples dissolved in deuteriated solvents which were used in NMR measurements. Spectra were recorded in transmission mode out to $k = 15$ Å^{-1} (k = photoelectron wave vector), but due to a poor signal-to-noise ratio the data sets were truncated at $k = 13.5$ Å^{-1}. Several data sets for each compound were collected and averaged and the data multiplied by k^3 to compensate for the fall-off in intensity at higher k. No smoothing or Fourier filtering was applied to the data.

The Fourier transforms of the background-subtracted EXAFS data for WOF_4 and $WOCl_4$ dissolved in dichloromethane exhibit two major peaks. The more intense feature was successfully modelled to the appropriate four halide ligands and the less intense peak to the oxide ligand around the tungsten centre as expected for a monomeric species. In both cases the Fourier transforms also exhibit more-distant weaker features at around 4 Å. These could not be successfully modelled as a second tungsten atom arising from a polymeric structure, and the distances are too great to be due to bridging ligands. However we note that they occur at a similar distance to the solvation spheres that have been observed for metal hexafluorides dissolved in anhydrous HF.[17] Modelling of these more distant features was performed by stepwise addition of further shells containing one and two chlorine atoms which were iterated in the usual way, and the best fits tested for statistical significance. For both compounds the addition of the solvation spheres resulted in a decrease in the R factor whilst the distances of the bonded shells remained essentially invariant. No attempts were made to determine accurately the occupancy numbers and Debye–Waller factors for these non-bonded shells. Checks on the co-ordination numbers of the first two shells were performed by mapping the occupation number of a shell against its Debye–Waller parameter. The distances, and other parameters, determined from these EXAFS analyses are presented in Table 1 where they are compared with the data previously obtained by other techniques.

The Fourier transform of the EXAFS spectrum of WSF_4 in dichloromethane exhibits a single, broad peak centred around 2.0 Å with weaker features at *ca.* 2.9 and 3.6 Å [Fig. 1(*b*)]. Initial modelling of these data was undertaken based on a two-shell model (4 F, 1 S). Both of these contributions are contained within the single broad peak envelope seen in the Fourier transform. However modelling of the data in terms of these two shells alone resulted in a R factor of just under 20%. A considerable contribution to R appears to be due to the presence of the additional features at longer distance. Indeed this is amply demonstrated by removing the contribution to the EXAFS from the more distant shells completely by Fourier filtering (Fourier window 0.2–2.5 Å) followed by iteration which results in a lowering of R to 13% without significant changes to the other parameters. There are a number of possible interpretations of these more distant shells: they could be due to the presence of bridging atoms, sample impurities or solvation shells. The non-Fourier-filtered data set was analysed for each of these possibilities. The distances (*ca.* 2.97 and 3.60 Å) are too great to be due to bridging fluorine atoms and modelling of these features to tungsten atoms at these distances resulted in unacceptably large Debye–Waller factors, thus WSF_4 appears to be monomeric in solution. The second possibility is that these features could arise from an impurity, for example due to sample decomposition. This was investigated by modelling the additional two shells to the most likely non-fluorine-containing impurity WS_3, which is reported

Table 1 Bond distances and EXAFS parameters for the compounds WEX_4 ($E = O$ or S, $X = F$ or Cl)

Compound		Electron diffraction^a	Crystal structure	EXAFS^b							
				Bonded shells			Non-bonded shells				
				Distance/Å	$2\sigma^{2c}$/Å^2	R^d	Distance/Å	$2\sigma^{2c}$/Å^2	VPI/eV	AFAC	R^e (%)
WOF_4	d(W=O)/Å	1.666(7)	2.11(4)^f	1.686(3)	0.002(1)						
	d(W–F)/Å	1.847(2)	1.84(4)^f	1.852(2)	0.004(1)	22.7					
							3.028(7)	0.015(3)			
							3.659(12)	0.014(2)	−4.71	0.86	14.6
WSF_4	d(W=S)/Å	2.104(7)	2.07^g	2.026(8)	0.005(2)						
	d(W–F)/Å	1.847(3)	1.87^g	1.863(3)	0.007(1)	19.7					
							2.969(7)	0.012(1)			
							3.603(7)	0.010(2)	−5.86	0.93	16.7
$WOCl_4$	d(W=O)/Å	1.685(15)	1.81^h	1.691(3)	0.004(1)						
	d(W–Cl)/Å	2.280(3)	2.28^h	2.303(1)	0.006(1)	17.4					
							3.887(15)	0.014(4)			
							4.488(8)	0.010(1)	−6.43	0.93	14.5
$WSCl_4$	d(W=S)/Å	2.086(6)	2.098^i	j							
	d(W–Cl)/Å	2.277(3)	2.299(11)^i	j							

[a] Ref. 8. [b] This work, CD_2Cl_2 solution; standard deviation in parentheses, systematic errors in bond distances arising from data collection and analysis procedures are *ca.* ±0.02 Å. [c] Debye–Waller factor. [d] $R = [\int(\chi^{theor} - \chi^{exptl})k^3dk/\int\chi^{exptl}k^3dk] \times 100\%$ obtained after modelling for shells 1 and 2 only. [e] Final *R* factor obtained after inclusion of non-bonded shells in modelling. [f] Fluoride-bridged tetramer.[3] [g] Fluoride-bridged polymer.[4] [h] Chloride-bridged dimer.[6] [i] Chloride-bridged dimer.[7] [j] Analysis not possible because of low-quality data due to poor sample solubility.

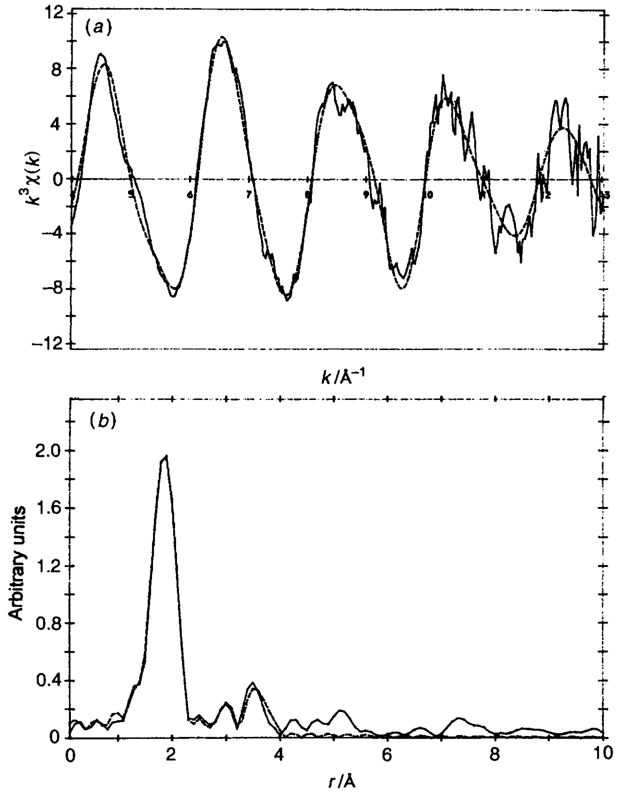

Fig. 1 (*a*) Background-subtracted EXAFS (——, experimental × k^3; - - - -, curved-wave theory × k'^3) for WSF_4 dissolved in CD_2Cl_2 and (*b*) the corresponding Fourier transforms (——, experimental; - - - -, theoretical)

as a product of WSF_4 in extended contact with acetonitrile,[4] by comparison with a previous EXAFS study of tungsten sulfides[18] [WS_3, d(W=S) = 2.41 Å]. However after iteration the model was not able to reproduce the correct distances or co-ordination numbers from the EXAFS data for any known binary tungsten sulfide and thus this possibility was also rejected. This leaves the third hypothesis, that these more distant shells are due to the co-ordination of solvent molecules. For the data recorded in dichloromethane solution we were able to reproduce satisfactorily the additional features observed in the Fourier transform by incorporating shells corresponding to co-ordination spheres containing 1 Cl at 2.97 Å and 2 Cl at 3.60 Å. After iteration this resulted in a decrease in *R* to 16.7% and the parameters given in Table 1. The EXAFS data recorded for acetonitrile solutions of WSF_4 resulted in W=S and W–F distances which are essentially invariant within the precision of the EXAFS technique. Well defined, although slightly less intense, non-bonded shells were also obvious from the Fourier transform of the EXAFS data at 2.86 and 3.48 Å. These are slightly shorter non-bonded distances than those obtained from dichloromethane solution and modelling suggests that they correspond to two and five nitrogen atoms respectively. Again no attempts were made to determine accurately the occupancy numbers and Debye–Waller factors for these non-bonded shells. However we note that the relatively low occupation numbers may be an indication of some form of ordered interaction. Interestingly, incorporation of a single acetonitrile molecule co-ordinated *trans* to the sulfur atom at a similar distance to that observed in the crystal structure of the WSF_4·MeCN adduct (2.25 Å)[5] did not result in a significant improvement to the fit although on the basis of our modelling the possibility of such a species existing in solution cannot be completely discounted.

Two further checks on the modelling of the data were performed. Sequential addition of the shells was tested for statistical significance using the tests of Joyner *et al.*,[19] all the shells passed at the 1% level or better. A check on the primary-shell co-ordination numbers was also undertaken by including in the iteration process the occupancy of the first and second shells (4 F and 1 S) and by mapping the occupation number for each shell against its Debye–Waller factor. A minimum was observed for co-ordination numbers of 4.2 fluorine atoms and 0.86 sulfur atoms. Although the error associated with these values is believed to be ± 10% it has been shown that by careful analysis of EXAFS data[20] it is possible to obtain reasonable confidence in occupancy numbers. We are, therefore, confident that our EXAFS studies show that WOF_4, $WOCl_4$ and WSF_4 all adopt monomeric structures in acetonitrile and dichloromethane solution.

It is instructive to compare the bond lengths derived from the vapour-phase electron diffraction study and those obtained in this work; Table 1 summarises the final parameters obtained from our EXAFS studies. It is obvious that there is good agreement between the two sets of derived W=O and W–X bond lengths for both WOF_4 and $WOCl_4$. For WSF_4 the W–F bond distances obtained from our data [1.863(3) Å] and from electron diffraction [1.847(3) Å] are similar and consistent with values in related tungsten(VI) compounds.[21] However we obtain a significantly shorter W=S bond length [2.026(8) Å compared with 2.104(7) Å by electron diffraction]. In fact the W=S bond length derived from our EXAFS study is more in line with that which may be expected from the observed distances in $WSBr_4$ and $WSCl_4$ and simple electronegativity arguments.[9] The trend to decreasing W=S distances for the lighter, more electronegative halides is also consistent with that observed for the W=O bond distances of the tetrahalide oxides. This is contrary to the findings of the electron diffraction study. We also note that this distance (2.026 Å) is, as expected, now shorter than the W=S distance reported for the crystal structure of $WSF_4 \cdot MeCN$ (2.034 Å) and thus mirrors the behaviour of the W=O distance in WOF_4 (1.66 Å) and its adducts (1.77 Å).[22]

There is therefore a considerable difference between the W=S distance determined in this study and the only other available distance reported for monomeric WSF_4 obtained by the electron diffraction study. As previously noted the latter experiment suffered from a moderately high degree of sample decomposition; the results were interpreted in terms of a sample composition of 23% WOF_4 and 77% WSF_4. This however should have had minimum effect on the derived W=S bond distance since the W=S and W=O distances are quite distinct. There were also reported problems with the vibrational amplitudes obtained during modelling which resulted in these parameters having to be constrained to remain within reasonable limits.[8] However the most important difference between these two sets of experiments was the sample state. The electron diffraction study was carried out on a high-temperature gas-phase species which would be undergoing considerable thermal and vibrational motion.

Conclusion

This work demonstrates that WSF_4 may be prepared by the reaction of $(Me_3Si)_2S$ and WF_6 at or below room temperature in acetonitrile or dichloromethane solution. The identity of the products in solution is confirmed by fluorine NMR studies. Tungsten L(III)-edge EXAFS studies of solutions of WSF_4, WOF_4 and $WOCl_4$ have been made for the first time and demonstrate that these compounds are monomeric in acetonitrile, dichloromethane and diethyl ether solutions. From the EXAFS data a W=S distance of 2.026(8) Å and a W–F distance of 1.863(3) Å is derived for WSF_4 adopting a monomeric structure. This new value for the W=S distance is in line with that expected by comparison with bond distances of other tungsten chalcogen tetrahalides and their adducts.

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