Transition-metal Thiofluorides; Preparation of WSF_4 and Related Anions

By MALCOLM J. ATHERTON and JOHN H. HOLLOWAY
(*Department of Chemistry, University of Leicester, Leicester* LE1 7RH)

Summary ^{19}F N.m.r., i.r., and Raman spectroscopy and mass spectrometry show that WSF_4 is the main product of the reaction of WF_6 with Sb_2S_3; reactions of solutions of $WSCl_4$ in MeCN with XeF_2 give ^{19}F n.m.r. spectra attributable to WSF_4, WSF_3Cl, WSF_2Cl_2, and $WSFCl_3$, and with HF to WSF_4, WSF_5^-, WSF_4Cl^-, $WSF_3Cl_2^-$, $WSFCl_4^-$, and $W_2S_2F_9^-$.

ALTHOUGH tungsten thiohalides are known for chlorine[1-5] and bromine,[3,4] fluorine-containing analogues have not been isolated. The ions WSF_4^+ and $WS_2F_2^+$ have been identified by mass spectrometry,[6] and $WSCl_xF_y^-$ ($x + y = 5$) species have been reported on the basis of ^{19}F n.m.r. studies.[7] We now describe the first preparation and isolation of WSF_4 and the characterization of a number of related molecules and anions.

Stoicheiometric quantities of WF_6 and Sb_2S_3 were heated at 300 °C in a nickel reactor [equation (1)]. After 3 h

$$3WF_6 + Sb_2S_3 \rightarrow 3WSF_4 + 2SbF_3 \qquad (1)$$

short, yellow needles of WSF_4 were found in the cooler part of the reactor.† Smaller quantities of white needles were unambiguously characterized as SbF_3 by mass spectrometry. The yellow needles melt to an amber liquid at 89—90 °C *in vacuo* and, on exposure to direct sunlight, change colour to pale brown. On exposure to the atmosphere, WSF_4 rapidly evolves HF and H_2S.

Both the yellow and pale brown needles appear pale yellow when ground and their i.r. spectra are identical in the region 1800—350 cm^{-1}. The main features of the i.r. spectrum of the solid include strong peaks at 699, 673, and 643 cm^{-1} which can be attributed to ν(M–F) for three distinct terminal fluorines. A tungsten–sulphur bond is clearly evidenced by an intense peak at 577 cm^{-1} and this is confirmed by the presence of a strong peak in the Raman spectrum at 580 cm^{-1}. These values are close to that for ν(W=S) in $WSCl_4$.[4] Tungsten–fluorine bridging-modes at 534 and 514 cm^{-1} complete a picture which suggests that the solid-state structure must be polymeric with fluorine bridges, the most likely arrangement being that of a tetramer like WOF_4.[8]

Investigation of WSF_4 by mass spectrometry reveals that WSF_4^+ is the parent ion and WSF_3^+ the most abundant species. Oxide fluoride species in the mass spectrum originate from traces of WOF_4, which is also evidenced by a small band at 1048 cm^{-1} in the i.r. spectrum and a singlet at δ −66·9 p.p.m. in the ^{19}F n.m.r. spectrum. This may have been formed from Sb_2O_3 impurity in the starting materials.

^{19}F N.m.r. spectra of solutions of WSF_4 in MeCN show only a singlet at δ −85·1 p.p.m. which was assigned to WSF_4. After 14 days at 18 °C, another singlet developed at δ −169·9 p.p.m. Studies of tungsten hexafluoride in MeCN show a singlet in the same position and hence it can be assigned to WF_6. Examination of the solution revealed a slight precipitate, presumably due to the formation of WS_3 [equation (2)].

$$3WSF_4 \rightarrow 2WF_6 + WS_3 \qquad (2)$$

The reaction of $WSCl_4$ with xenon difluoride in MeCN has been followed by ^{19}F n.m.r. spectroscopy. The reactants, in an F.E.P. reactor, were allowed to warm slowly from −196 °C. At *ca.* 0 °C reaction began, the solution changed colour from dark red to pale orange, and small amounts of gas were evolved. Six signals in the region δ −80 to −150 p.p.m. are the main features of the spectrum (Table). Amongst these the signal attributable to WSF_4 and the broad unassigned signal at −144·1 p.p.m. are predominant. Of the signals attributable to WSF_3Cl only the doublet was

---

† Satisfactory elemental analyses were obtained for this compound.

TABLE. ^{19}F N.m.r. parameters for WFS_4 and related anions.

Sample[a]	Solvent[b]	Temp./°C	δ/p.p.m.[c]	Multiplet[d] structure	Coupling constant/Hz	Assignment[e]
WSF_4	MeCN	−19	−85·1	I		WSF_4
WSF_4[f]	MeCN	0	−84·7	I	J_{W-F} 37 ± 2	WSF_4
			−169·9	I		WF_6
$WSCl_4 : XeF_2$[g] (1 : 2)	MeCN–CD_3CN	−28	−84·3	I		WSF_4
			−93·4	I		WSF_2Cl_2
			−109·3	I		Unassigned
			−110·8	II	J_{F-F} 73 ± 2	WSF_3Cl
			−132·3	I		$WSFCl_3$
			−144·1	h		Unassigned
$WSCl_4 : HF$ (1 : 6)	MeCN–CD_3CN	−28	+159·3	IX[i]	J_{F-F} 71 ± 2	$W_2S_2F_9^-$
			+141·2	V	J_{F-F} 72 ± 2	WSF_5^-
			−80·0	II	J_{F-F} 72 ± 2	WSF_5^-
			−83·5	I		WSF_4Cl^-
			−83·7	II	J_{F-F} 70 ± 2	$W_2S_2F_9^-$
			−84·8	I	J_{W-F} 32 ± 3	WSF_4
			−91·1	I		Unassigned[j]
			−109·7	II	J_{F-F} 70 ± 2 J_{W-F} 33 ± 2	$WSF_3Cl_2^-$
			−130·5	I		$WSFCl_4^-$
$WSCl_4 : HF$ (1:12)	MeCN–CD_3CN	25	−79·5	I[k]		WSF_5^-

[a] Spectra recorded immediately after preparation of sample. [b] Concentration *ca.* 0·5 molal in F.E.P. tubes. [c] Spectra run at 94·1 MHz and referenced with respect to external $CFCl_3$. [d] I, Singlet; II, doublet; V, quintet; IX, nonet. [e] Determined with reference to n.m.r. data (refs. 7 and 9 and our unpublished observations). [f] After two weeks at 18 °C. [g] Three weak singlets in the region +60 to +75 p.p.m. not yet assigned. [h] Very broad signal, width at half-height *ca.* 450 Hz. [i] Central five lines identified by intensity ratio 29 : 50 : 65 : 55 : 28. [j] Observed in only one sample; may be due to WSF_2Cl_2. [k] Width at half-height *ca.* 120 Hz.

observed. The expected triplet is almost certainly hidden by the signals due to more dominant species.

Solutions of $WSCl_4$ and anhydrous HF in MeCN were also investigated. The results obtained (Table) substantiate the report of Buslaev *et al.*[7] The lines assigned to uncharged species soon disappear from the spectrum and it appears that the chlorine containing anions slowly decrease in concentration with time whilst the WSF_5^- concentration increases. This behaviour follows the pattern of the $WOCl_4$–HF system in MeCN.[9] With an HF : $WSCl_4$ ratio of *ca.* 12 : 1 the spectrum has a single broad signal at −79·5 p.p.m. This can be assigned to WSF_5^-, its broadness and lack of fine structure being due to rapid exchange at 25 °C. No signal corresponding to the WSF_5^- quintet could be observed due to the presence of the broad resonance of the F.E.P. sample tube.

All tungsten thiofluoride species are extremely sensitive to sources of oxygen and tungsten oxide fluoride anions are readily formed. Details of the ^{19}F n.m.r. spectra of these species can be found in ref. 7 and are not included in the Table.

(*Received*, 7*th April* 1977; *Com.* 337.)

[1] E. F. Smith and V. Oberholtzer, *Z. anorg. Chem.*, 1894, **5**, 68.
[2] K. M. Sharma, S. K. Anand, R. K. Multani, and B. D. Jain, *Chem. and Ind.*, 1969, 1556.
[3] D. Britnell, G. W. A. Fowles, and D. A. Rice, *J.C.S. Dalton*, 1974, 2191.
[4] D. Britnell, G. W. A. Fowles, and R. Mandyczewsky, *Chem. Comm.*, 1970, 608.
[5] N. S. Fortunatov and N. I. Timoshchenko, *Ukrain. khim. Zhur.*, 1969, **35**, 1207.
[6] D. L. Hildenbrand, U.S. Nav. Tech. Inform. Serv. R.D. Rep. No. 757231, 1972.
[7] Y. A. Buslaev, Y. B. Kokymov, and Y. D. Chubar, *Proc. Acad. Sci.* (*U.S.S.R.*), **1973**, **213**, 912.
[8] I. R. Beattie, K. M. S. Livingston, D. J. Reynolds, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1970, 1210.
[9] Y. A. Buslaev, Y. V. Kokunov, and V. A. Bochkareva, *J. Struct. Chem.*, 1972, **13**, 570.