Synthesis, Chemistry, and Crystal Structures of High-valent Transition-metal Chalcogenide Fluorides and Their Derivatives

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The solid transition-metal chalcogenide fluorides, WF_4S, WF_4Se, and ReF_4S have been prepared in high yield and their chemistry has been examined; *X*-ray crystallography has shown that WF_4S and ReF_4S have fluorine bridged polymeric chain structures whilst $WF_4S{\cdot}MeCN$ is a monomer.

Chalcogenide fluorides of molybdenum, tungsten, and rhenium have been prepared by and isolated from the reaction of the appropriate metal fluoride with Sb_2S_3, Sb_2Se_3, or B_2S_3.[1–4] We have now shown that WF_4S, WF_4Se, and ReF_4S can also be conveniently prepared in stainless steel reactors in high yield by reaction of the hexafluorides with elemental sulphur or selenium at 300 °C. The resultant availability of large quantities of pure materials has permitted investigation of the chemistry of these molecules. We have also determined the first crystal structures of representatives of this class of compound and of one of their adducts.

In a typical preparation sulphur or selenium (2 mmol) was introduced into a prefluorinated stainless steel tube reactor in a nitrogen-filled dry box and, after evacuation, the appropriate hexafluoride (1.5 mmol) was condensed into the tube. The reactor was heated at 300 °C for 20 h. After removal of residual volatile material by pumping the clear crystalline solids, WF_4S (yellow) (**1**), WF_4Se (amber), or ReF_4S (red-brown) (**2**), were removed from the reactor in a dry box where suitable crystals were mounted for *X*-ray studies. Successful structure determinations were made on rectangular platelets of the two sulphur-containing compounds.

Crystal data: (**1**), F_4SW, $M = 291.91$, orthorhombic, $a = 16.934(7)$, $b = 5.514(20)$, $c = 9.460(15)$ Å, $U = 883.32$ Å^3, $Z = 8$, $D_c = 4.387$ g cm^{-3}, space group $Pca2_1$; (**2**), F_4ReS, M

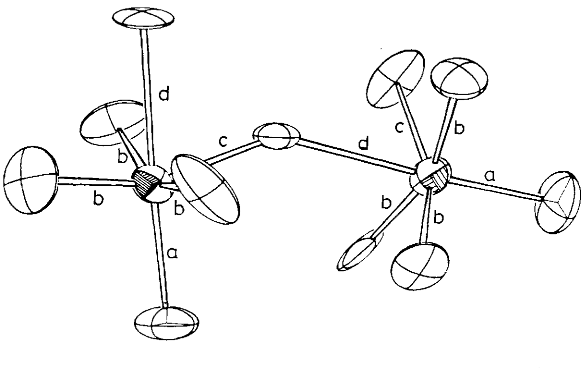

Figure 1. Molecular geometry of WF_4S (**1**). Average bond lengths (Å) with s.d.s (in parentheses), taken from the two non-equivalent molecular units: a = 2.07(2), b = 1.85(3), c = 1.92(3), d = 2.34(3). The W–F–W bridging angles are 163.7(1.9) and 146.0(1.8)°.

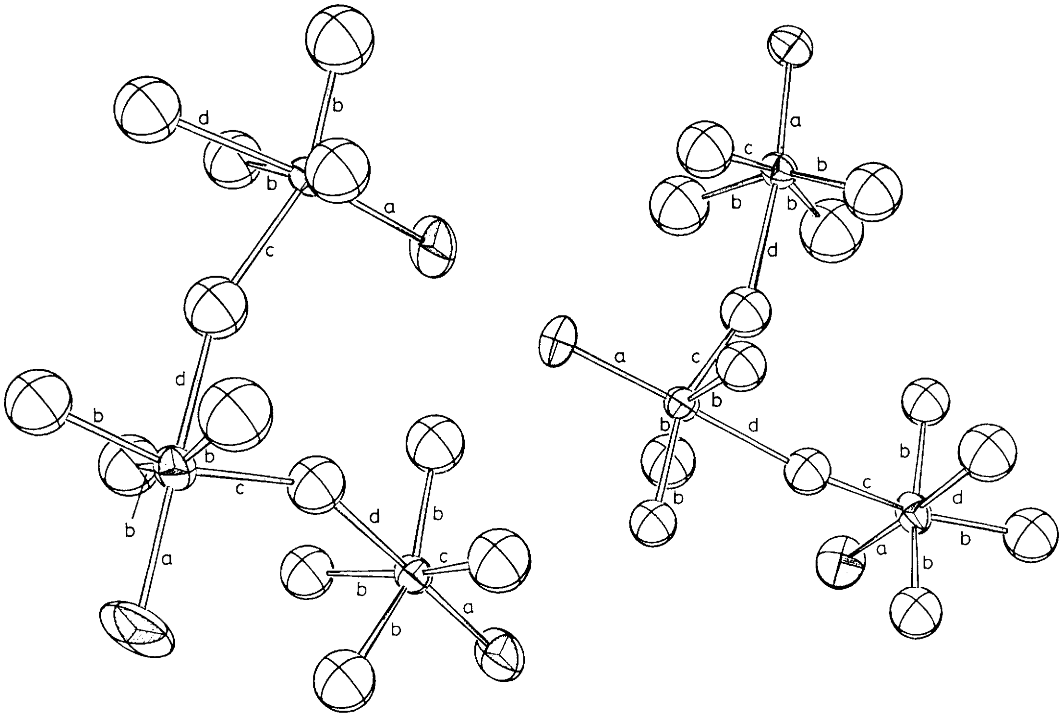

Figure 2. Molecular geometry of ReF_4S. Average bond lengths (Å) with s.d.s (in parentheses), taken from the six non-equivalent molecular units: a = 2.02(2), b = 1.85(4), c = 1.95(4), d = 2.23(4). The Re–F–Re bridging angles range from 146.8(1.8) to 160.5(1.9)°.

= 294.29, orthorhombic, a = 10.893(10), b = 8.278(11), c = 27.663(5) Å, U = 2494.4 Å^3, Z = 24, D_c = 4.700 g cm^{-3}, space group $Pca2_1$. The data, collected by a Stoe Weissenberg diffractometer using Mo-K_α irradiation (graphite monochromator, λ = 0.7107 Å), and corrected for Lorentz, polarization, and absorption effects consist of 598 reflections for (**1**) and 1646 for (**2**). With anisotropic thermal parameters for all atoms in the WF_4S structure a final R of 0.0738 was obtained. Refinement of the rhenium and sulphur atoms anisotropically and the fluorine isotropically yielded a final R of 0.0500 for ReF_4S.†

$WF_4S{\cdot}MeCN$

(**3**)

The crystal structure of (**1**) (Figure 1) contains two WF_5S octahedra in the asymmetric unit linked by *cis*-bridged fluorine atoms into polymeric chains lying parallel to the c axis. The structure of (**2**) (Figure 2) is related but the asymmetric unit consists of six ReF_5S *cis*-linked octahedra and divided equally between two separate chains running parallel to the a axis. Some details of the molecular geometries are given in Figures 1 and 2. Bond lengths are analogous to those found in related structures, with the metal–sulphur distances being slightly shorter than observed in WCl_4S[5] for example. The metal fluorine bridging distances, particularly those *trans* to the sulphur atoms, are significantly longer than the terminal bonds. This *trans* influence has been observed for bonds *trans* to Mo–O multiple bonds[6] and in ReF_4O.[7]

Transition-metal oxide-fluoride structures occur in tetrameric, trimeric, and open-chain forms. The WF_4S and ReF_4S structures are closely related to the *cis*-bridged open chain structures.[7–9]

Preliminary studies of the chemistry of solid transition metal chalcogenide fluorides have shown that the hydrolysis of WF_4Se is similar to that of the thiofluorides,[1,4] yielding HF and H_2Se, that $WF_4S{\cdot}SbF_5$ can be prepared, and that WF_4S and WF_4Se give adducts with MeCN. The adduct $WF_4S{\cdot}SbF_5$ was prepared by reaction of WF_4S with SbF_5 at 30—40 °C as a yellow crystalline solid.

Over long periods solutions of WF_4S in MeCN yield WF_6 and WS_3,[1] but both WF_4S and WF_4Se initially form 1 : 1 adducts. An X-ray single crystal structure of $WF_4S{\cdot}MeCN$ (**3**) has been determined. *Crystal data:* (**3**), $C_2F_4H_3NSW$, M = 332.97, orthorhombic, a = 11.122(1), b = 8.348(1), c = 7.842(10) Å, U = 728.1 Å^3, Z = 4, D_c = 3.037 g cm^{-3}, space group $Pna2_1$ or $Pnam$. The data, collected and corrected in the same manner as described previously, consist of 346 reflections. Unfortunately the data are of limited quality; at the present stage of refinement R is close to 0.10 in either space group, but it is clear that the adduct is monomeric with tungsten octahedrally surrounded by four fluorine atoms in an equatorial plane with the nitrogen atom of the MeCN group *trans* to the sulphur.†

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† The atomic co-ordinates for this work are available on request: for WF_4S and ReF_4S from Prof. Dr. G. Bergerhoff, Institut für Anorganische Chemie, Universität, Gerhard-Domagk-Strasse 1, D-5300 Bonn 1, West Germany; for $WF_4S{\cdot}MeCN$ from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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References

1 M. J. Atherton and J. H. Holloway, *J. Chem. Soc., Chem. Commun.*, 1977, 424.

2 M. J. Atherton and J. H. Holloway, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 121.

3 J. H. Holloway and D. C. Puddick, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 85.

4 J. H. Holloway, D. C. Puddick, G. M. Staunton, and D. Brown, *Inorg. Chim. Acta*, 1982, **64**, L209.

5 M. G. B. Drew and R. Mandyczewsky, *J. Chem. Soc. A*, 1970, 2815.

6 F. A. Cotton, S. M. Moorhouse, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 1603.

7 A. J. Edwards and G. R. Jones, *J. Chem. Soc. A*, 1968, 2511.

8 A. J. Edwards and B. R. Steventon, *J. Chem. Soc. A*, 1968, 2503.

9 A. J. Edwards, G. R. Jones, and B. R. Steventon, *Chem. Commun.*, 1967, 462.