

## SYNTHESIS AND CRYSTAL STRUCTURES OF HIGH-VALENT TRANSITION-METAL CHALCOGENIDE FLUORIDES AND THEIR DERIVATIVES

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Chalcogenide fluorides of molybdenum, tungsten and rhenium have been prepared by and isolated from the reaction of the appropriate metal fluoride with either  $Sb_2S_3$ ,  $Sb_2Se_3$  or  $B_2S_3$ .<sup>1-4</sup> We have now shown that  $WSF_4$ ,  $WSeF_4$  and  $ReSF_4$  can also be very 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 for the first time.

The adduct  $WSF_4 \cdot SbF_5$  was prepared by reaction of  $WSF_4$  with  $SbF_5$  at 30-40°C. After removal of excess of  $SbF_5$  under dynamic vacuum at room temperature, yellow crystals of the adduct remained.

$WSF_4$  and  $WSeF_4$  react with acetonitrile at room temperature to give 1:1 adducts. A single-crystal structure of  $WSF_4 \cdot CH_3CN$  has been determined. In contrast to the polymeric structure of  $WSF_4$ ,  $WSF_4 \cdot CH_3CN$  contains monomeric molecules of the adduct. Tungsten is octahedrally surrounded by four fluorine atoms in an equatorial plane, a sulphur atom, and the nitrogen atom of the acetonitrile group trans to the sulphur.

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