

THE PREPARATION AND CHARACTERISATION OF SOME NEW BINARY FLUORIDES OF ANTIMONY

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Antimony pentafluoride acts as a useful oxidising agent towards many non-metals, giving interesting cations, and in the process is itself reduced. It would be helpful to know what the reduced products are, and under what conditions they are formed. Therefore, SbF_5 and the known $\text{SbF}_5 \cdot \text{SbF}_3^{(1)}$ in AsF_3 solution were reduced by iodine and/or PF_3 giving crystals of the new adducts, $(\text{SbF}_3)_6(\text{SbF}_5)_5$ [Monoclinic, $a = 11.638(1)$, $b = 8.995(1)$, $c = 16.723(3)$ Å, $\beta = 106.81(1)^\circ$, $P2_1/c$]; $(\text{SbF}_3)_5(\text{SbF}_5)_3$ [Orthorhombic, $a = 19.187(9)$, $b = 15.890(2)$, $c = 15.713(3)$ Å, $Pnma$] and $(\text{SbF}_3)_3\text{SbF}_5$ [Monoclinic, $a = 10.895(3)$, $b = 10.941(3)$, $c = 4.772(1)$ Å, $\beta = 96.66(3)^\circ$, $P2_1/m$]. $(\text{SbF}_3)_3\text{SbF}_5$ seemed to be the most reduced adduct, no evidence was obtained for $(\text{SbF}_3)_n(\text{SbF}_5)_m$, $n > 3$, under these conditions. The $(\text{SbF}_3)_6(\text{SbF}_5)_5$ adduct has a Raman spectrum identical to that reported by Gillespie⁽²⁾ and coworkers for an adduct of approximate composition $\text{SbF}_3 \cdot \text{SbF}_5$ and has a very different structure to that of $(\text{SbF}_3)_6(\text{SbF}_5)_5$ reported by Edwards.⁽³⁾ The crystal structures of the new adducts will be discussed and the cations they contain compared with those found in $\text{SbF}_3 \cdot \text{SbF}_5^{(1)}$ and $(\text{SbF}_5)_6(\text{SbF}_5)_5^{(3)}$ (Edward's form).

- 1 R. J. Gillespie, D. R. Slim, and J. E. Vekris, *J. Chem. Soc. Dalton*, 1977, 971.
- 2 T. Birchall, P. A. W. Dean, B. Della Valle, and R. J. Gillespie, *Can. J. Chem.*, 1973, 51, 667. (3) A. J. Edwards and D. R. Slim, *J. Chem. Soc. Chem. Comm.*, 1974, 178.

PREPARATION OF TRANSITION METAL CHALCOGENIDE FLUORIDES

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The species WSF_4 has been observed in solution by reacting WSCl_4 with HF or XeF_2 in dry CH_3CN , and was initially isolated as a solid by reacting WF_6 with Sb_2S_3 at 300 °C.

In this paper new methods for preparing WSF_4 by thermal or room temperature reactions are outlined. The application of these techniques to the preparations of tungsten and molybdenum chalcogenide fluorides as well as thio-fluorides of rhenium, where the metal is formally in an oxidation state of V, VI or VII, are also discussed.