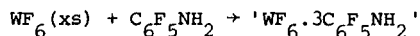


THE PREPARATION AND CRYSTAL STRUCTURE OF THE SALT  $[\text{C}_6\text{F}_5\text{NWF}_4\text{-F-WF}_4\text{-NC}_6\text{F}_5]^- \text{C}_6\text{F}_5\text{NH}_3^+$

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The reactions of amines with tungsten hexafluoride to yield  $[\text{W}(\text{NR})]$  species have been well documented and studied by means of  $^{19}\text{F}$  n.m.r., but, to date, have not yielded crystal structures. Kokunov *et al.* (Koord. Khim., 1975, 1(8), pp. 1100-5) first postulated the formation of imido-tungsten fluoride species from  $^{19}\text{F}$  n.m.r. data, obtained from acetonitrile (MeCN) solutions of hexafluoride and amine mixtures. The data established the formation of both neutral and anionic species;  $\text{WF}_4(\text{NR})\cdot\text{MeCN}$  and  $\text{WF}_5(\text{NR})^-\text{NRH}_3^+$  ( $\text{R} = \text{H}, \text{Bu}^t$ ). More detailed work by Chambers *et al.* (J. Chem. Res. (M), 1977, pp. 1846-73) supported this idea, and also indicated the formation of an anionic, dimeric species,  $[\text{MeN}=\text{WF}_4\text{-F-WF}_4\text{=NMe}]^-$ , with linear C-N-W-F-W-N-C framework. However, to date, no crystal structures of this type of compound have been obtained. By treating  $\text{WF}_6$  with the bulky amine pentafluoroaniline ( $\text{C}_6\text{F}_5\text{NH}_2$ ) a yellow, crystalline solid is formed, which has a mass balance corresponding to the formation of a 3:1 adduct



The solid dissolves readily in MeCN, anhydrous HF and is less soluble in trifluoroacetic acid (TFA). Crystals grown from TFA proved suitable for X-ray studies, and were found to be triclinic, space group  $\text{P}\bar{1}$ . The unit cell is occupied by two formula units of the dimeric species  $[\text{C}_6\text{F}_5\text{N}=\text{WF}_4\text{-F-WF}_4\text{=NC}_6\text{F}_5]^- \text{C}_6\text{F}_5\text{NH}_3^+$ , each with a near linear C-N-W chain but with a slightly differing geometry about the bridging fluorine. Terminal fluorine atoms bonded to tungsten are bent away from the bulky  $-\text{NC}_6\text{F}_5$  moieties. Principal bond distances and angles are: W-F<sub>bridge</sub> (average), 2.15(4); W-F<sub>terminal</sub> (average), 1.92(3); W-N (average), 1.78(4); N-C (average), 1.45(4) Å;  $\text{W}_1-\overset{\circ}{\text{F}}_1-\text{W}_2$ , 150.73(1.3)°;  $\text{W}_3-\overset{\circ}{\text{F}}_{31}-\text{W}_4$ , 169.43(2.0)°.