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THE PREPARATION AND CRYSTAL STRUCTURE OF THE SALT $[C_6F_5NWF_4\text{-}F\text{-}WF_4\text{-}NC_6F_5]^-C_6F_5\overset{+}{N}H_3$

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The reactions of amines with tungsten hexafluoride to yield [W(NR)] species have been well documented and studied by means of ^{19}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}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; $WF_4(NR).MeCN$ and $WF_5(NR)^-\overset{+}{N}RH_3$ (R = H, 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, $[MeN{=}WF_4\text{-}F\text{-}WF_4{=}NMe]^-$, 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 WF_6 with the bulky amine pentafluoroaniline ($C_6F_5NH_2$) a yellow, crystalline solid is formed, which has a mass balance corresponding to the formation of a 3:1 adduct

$$WF_6(xs) + C_6F_5NH_2 \rightarrow 'WF_6.3C_6F_5NH_2'$$

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 $P\bar{1}$. The unit cell is occupied by two formula units of the dimeric species $[C_6F_5N{=}WF_4\text{-}F\text{-}WF_4{=}NC_6F_5]^-\ C_6F_5\overset{+}{N}H_3$, 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 $-NC_6F_5$ moieties. Principal bond distances and angles are: $W\text{-}F_{bridge}$ (average), 2.15(4); $W\text{-}F_{terminal}$ (average), 1.92(3); W-N(average), 1.78(4); N-C(average), 1.45(4)Å; $W_1\text{-}\hat{F}_1\text{-}W_2$, 150.73(1.3)°; $W_3\text{-}\hat{F}_{31}\text{-}W_4$, 169.43(2.0)°.