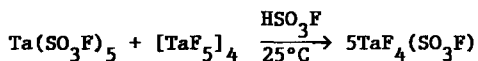


FLUOROSULFATO AND TRIFLUOROMETHYL SULFATO  
DERIVATIVES OF NIOBIUM(V)- AND TANTALUM(V) FLUORIDE

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The title compounds are formally derived from either  $[\text{NbF}_5]_4$  or  $[\text{TaF}_5]_4$  by replacing F by  $\text{SO}_3\text{X}$ , X = F or  $\text{CF}_3$ . They are expected to behave as Lewis acids and to form super acids when dissolved in the parent sulfonic acids or in HF; however, no example in this group seems to have been reported. We want to report the first three representatives of this group.  $\text{TaF}_4(\text{SO}_3\text{F})$  is formed in high yield as a white, hygroscopic solid by the reaction of  $\text{Ta}(\text{SO}_3\text{F})_5$  [1] with  $[\text{TaF}_5]_4$  in  $\text{HSO}_3\text{F}$  according to:



The formation reaction indicates the occurrence of F vs.  $\text{SO}_3\text{F}$  exchange and is capable of yielding other materials of the general composition  $\text{TaF}_n(\text{SO}_3\text{F})_{5-n}$  with n = 1 to 3.  $^{19}\text{F}$  NMR and vibrational spectra show the presence of bidentate, presumably bridging,  $\text{SO}_3\text{F}$  groups and terminal fluorine, suggesting an oligomeric structure. The corresponding  $\text{TaF}_4(\text{SO}_3\text{CF}_3)$  forms as a white solid when  $\text{Ta}(\text{SO}_3\text{F})_5$  dissolved in  $\text{HSO}_3\text{F}$  is reacted with a large excess of trifluoromethylsulfuric acid,  $\text{HSO}_3\text{CF}_3$ . Finally, white, solid,  $\text{NbF}_2(\text{SO}_3\text{F})_3$  forms as the main product when niobium metal is oxidized by bis(fluorosulfuryl) peroxide,  $\text{S}_2\text{O}_6\text{F}_2$ , in  $\text{HSO}_3\text{F}$ . All the materials are characterized by chemical analyses, their vibrational spectra, and, where possible,  $^{19}\text{F}$  NMR spectroscopy.

1 W.V. Cicha and F. Aubke, *J. Am. Chem. Soc.*, in press.