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Conjugate superacids over a large Lewis acid concentration range: a study of the fluoride–fluorosulfates of Nb, Ta and Sb

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The importance of very strong acids (superacids) in organic synthesis has been thoroughly demonstrated, where they have been used to generate and stabilize a variety of carbocations, and have served as catalysts in the industrial production of organic compounds such as hydrochlorofluorocarbons and hydrofluorocarbons. We discuss here the highly acidic properties of recently developed conjugate superacid systems of the type HSO_3F–$MF_{5-x}(SO_3F)_x$ (M = Nb or Ta; x = 1–5) [1,2], as well as the comparable systems HSO_3F–$SbF_{5-x}(SO_3F)_x$ (x = 0–2), where we have isolated from solutions of magic acid, HSO_3F–SbF_5 with 50–80 mol% SbF_5, single crystals of $[H_3O][Sb_2F_{11}]$. The structure is shown in Fig. 1.

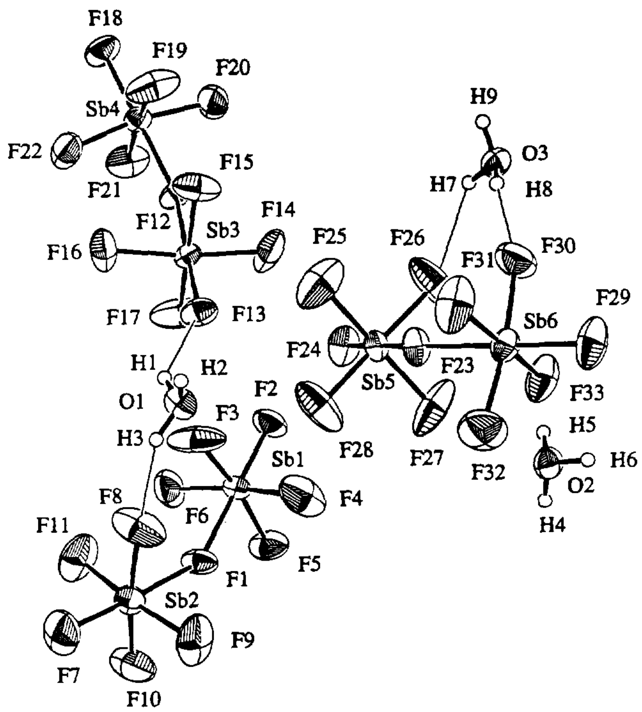

Fig. 1. ORTEP drawing of $[H_3O][Sb_2F_{11}]$.

Table 1
Conductivity maxima in HSO_3F

Lewis acid	Concentration (mol%)	Conductivity (Ω^{-1} cm^{-1})
SbF_5	19.3–19.7	0.034
$TaF_3(SO_3F)_2$	17.7	0.011
$NbF_3(SO_3F)_2$	19.4	0.0056
$TaF_4(SO_3F)$	22.2–22.6	0.0037
$NbF_4(SO_3F)$	22.3	0.0031

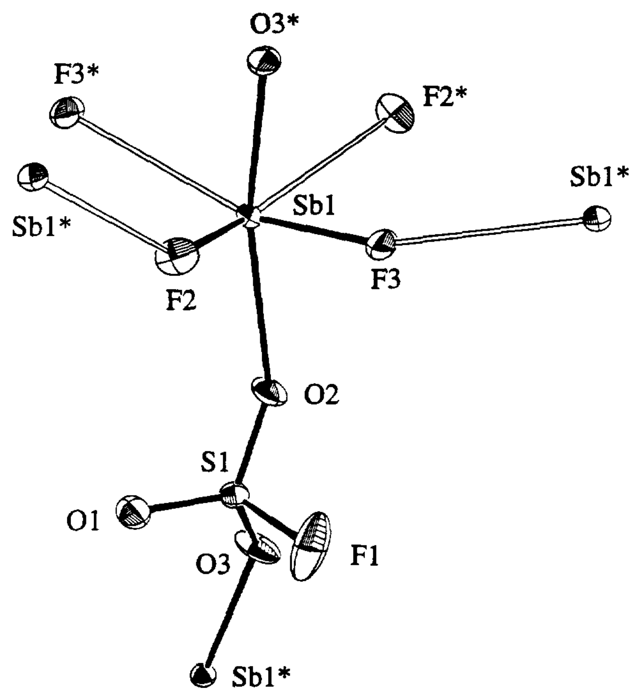

Fig. 2. ORTEP drawing of $SbF_2(SO_3F)$.

At very low Lewis acid concentrations (< 0.05 mol kg^{-1}) in HSO_3F, the Hammett acidity of $Ta(SO_3F)_5$

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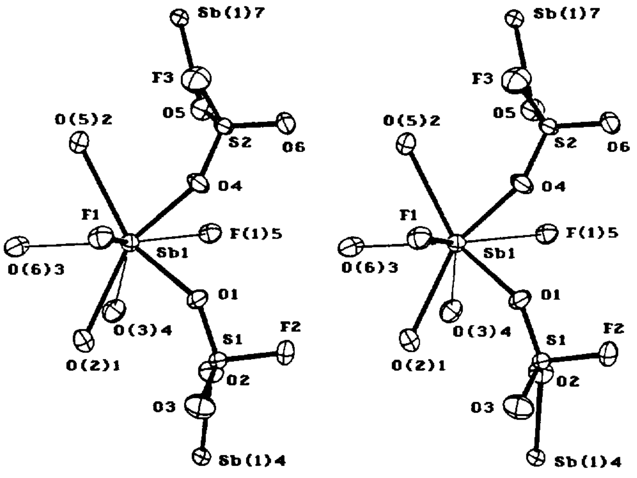

Fig. 3. Stereoview of $SbF(SO_3F)_2$.

(generated in situ) is lower than that of SbF_5. At higher concentrations, the $-H_0$ value of the former exceeds that of SbF_5, and beyond a concentration of ca. 1 M, $Ta(SO_3F)_5$ displays an acidity approximately at par with the strongest conjugate acid system HSO_3F–$3SO_3$–SbF_5, to give a $-H_0$ value of ca. 19 at a concentration of 4 M. Each of the four novel materials $MF_{5-x}(SO_3F)_x$ (M = Nb or Ta; x = 1 or 2) can be isolated in pure form as a colorless, viscous liquid. All four Lewis acids display conductivities comparable to that of HSO_3F, which increase slightly with temperature and suggest ionic dissociation of oligomers into conducting fragments. All four are found to be miscible with HSO_3F at any mole ratio. This allows specific electrical conductivity measurements in HSO_3F for each species over the entire concentration range. At low concentrations (ca. 0.1 mol%), their relative order of conductivities is $TaF_3(SO_3F)_2 > NbF_3(SO_3F)_2 > TaF_4(SO_3F) > NbF_4(SO_3F)$. Conductometric titration shows all four species to be weak acids in HSO_3F at these low concentrations. In this concentration range, conductivity is primarily due to the $H_2SO_3F^+$ ion and the proton jump mechanism is active. On further addition of Lewis acid to HSO_3F, the conductivities increase sharply and reach maximum at similar Lewis acid/HSO_3F ratios of ca. 20 mol% and then fall off as the Lewis acid concentration increases. Data on the conductivity maxima are listed in Table 1 alongside analogous data for SbF_5.

It hence appears that the five conjugate superacid systems studied here are highly conducting and strongly ionizing media over the entire concentration range.

In contrast to the fluoride–fluorosulfates of antimony(V), which are viscous non-stoichiometric phases [3,4], the antimony(III) fluoride–fluorosulfates $SbF_2(SO_3F)$ and $SbF(SO_3F)_2$ are well-defined crystalline solids. They form in the reaction of Sb with HSO_3F or as initial products when Sb is oxidized by $S_2O_6F_2$. Their complex polymeric structures are shown in Figs. 2 and 3. Details will be published shortly [5].

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