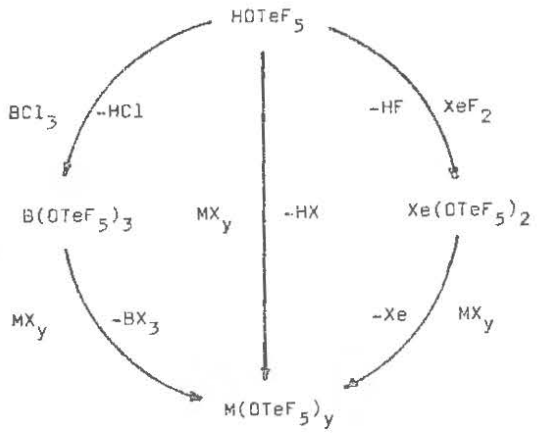
The Chemistry of Highly Electronegative $OTeF_5$ Group

Jayantha Amarasekera Literature Seminar May 6, 1986

After the discovery of pentafluoroorthotelluric acid, $HOTeF_5$, it soon became clear that the chemistry of pentafluoroorthotellurate, $-OTeF_5$ (also called teflate) group, is almost as extensive as that of fluoride [1]. The ability of this ligand to stabilize the highest valency levels of the central atoms to which it is bound is unsurpassed by any other polyatomic ligand. Because of the ligand's size and internal bonding it hardly ever forms bridges, and in this respect it differs from fluorine, although it does share the latter's high electronegativity.

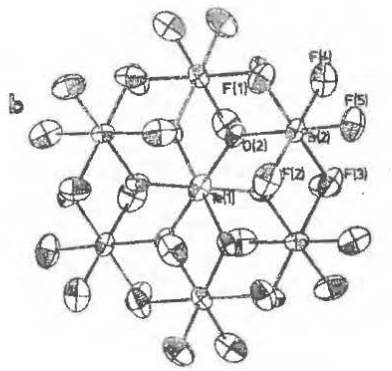
The methods for the preparation of teflate compounds are many. In accord with the high acidity of teflic acid ($HOTeF_5$), proton displacement reactions are frequently performed, affording ionic as well as covalent teflate compounds. A versatile source of the $OTeF_5$ group is $B(OTeF_5)_3$ [2]. The advantage of this reagent is that treatment with fluorides give volatile BF_3 as a byproduct. The xenon derivative, $Xe(OTeF_5)_2$, can be used to introduce the $OTeF_5$ group oxidatively [1], (Scheme 1)



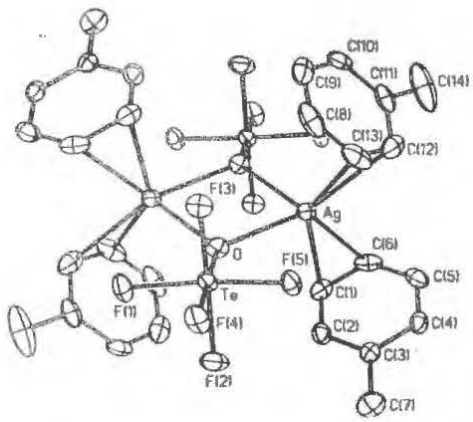
Scheme 1.

The teflate group is capable of stabilizing different oxidation and coordination states, due to its bulkiness and high electronegativity. The anion radius for $OTeF_5$ has been computed from crystallographic data for K^+, Rb^+ and Cs^+ salts. This anion is slightly larger than the iodide ion. Structural studies (group site preference) [3], NMR chemical shifts [4], Mössbauer isomer shifts [5] and chemical reactivity studies [2] indicate the electronegativity of $OTeF_5$ and F are practically equal. As estimated from ^{129}Xe Mössbauer quadrupole splittings the electronegativity of $OTeF_5$ is 3.87 (Pauling scale) compared to 3.98 for F [5]. A rationale for this high electronegativity is certainly the inductive effect of the five fluoride, which additionally promotes ($p\pi - d\pi$) back bonding from oxygen to tellurium. Due to this high electronegativity of teflate group, xenon teflates, $Xe(OTeF_5)_2$, $Xe(OTeF_5)_4$ and $Xe(OTeF_5)_6$ are the most stable xenon compounds known after their fluorides [6].

The elements in the first transition period have a tendency to form tetrahedral teflates. For example, $Ti(OTeF_5)_4$ is a rare example of titanium in a tetrahedral O_4 coordination site [7]. The larger central atoms uranium and tungsten permit relatively simple formation of heavy molecules $U(OTeF_5)_6$ and $W(OTeF_5)_6$ [8]. Some oxo-teflates include $VO(OTeF_5)_3$, $MoO(OTeF)_4$ and $O_2Re(OTeF_5)_4$, the only teflate with a heptavalent central atom [8]. $Mn(CO)_5(OTeF_5)$ can be considered as the first low valent transition metal teflate [9]. Bridging $OTeF_5$ ligands have not been observed or suggested until the very recent discovery of $Ag(OTeF_5)$ [10] and $Au(OTeF_5)_3$ [11].



$Te(OTeF_5)_6$ molecule, projected along the $\bar{3}$ axis:



ORTEP drawing of the centrosymmetric molecule $[AgOTeF_5\cdot(C_6H_5CH_3)_2]_2$ (50% probability ellipsoids, hydrogen atoms omitted).

The properties of many teflate compounds are also similar to fluorides. For example, $As(OTeF_5)_3$ resembles AsF_3 in its ability to form adducts with simple Lewis bases (σ-acidity) and to form complexes with low-valent transition metals (π-acidity) [12]. As in binary fluorides, the teflates can exchange the $OTeF_5^-$ anion between donor and acceptor teflates [13].

The versatility of teflates have prompted the development of other highly electronegative ligands such as $(O)F_4I\text{-}O^-$ [14]. The principle of electronegative ligands can be extended to polydentate ligands. Recently, cis-and trans-$(HO)_2TeF_4$ have been reported and the first derivatives including a xenon compound are available [15]. Sym-$(HO)_3TeF_3$ [16] and $H_2N\text{-}TeF_5$ [17], open up new directions for research. Following the analogy of organo-fluorocarbons, organoteflate chemistry is just now being developed [18]. The promising chemistry of teflate is still very much in its early stages.

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