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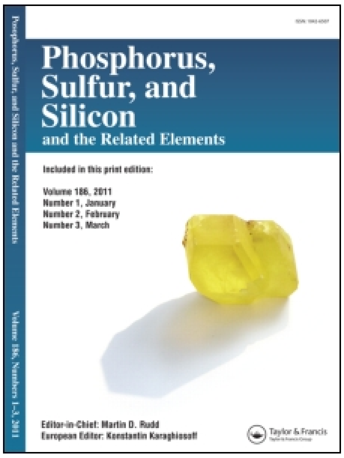

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TELLURONIUM SALTS INVOLVING HYPERVALENT TELLURIUM-TELLURIUM INTERACTIONS

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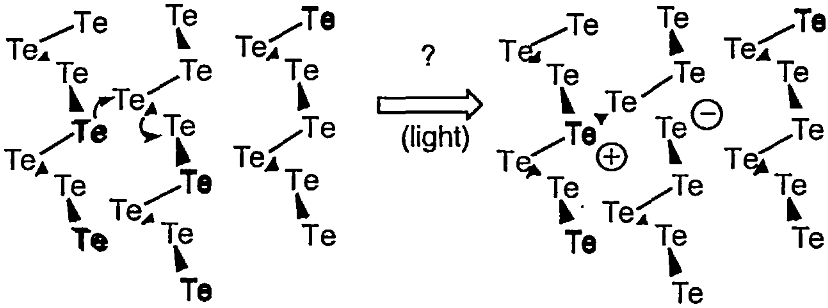
Interactions of telluronium cations with soft nucleophiles are discussed.

Keywords: tellurium, hypervalency, secondary interactions

Residual charges of amorphous Se/Te alloys from the *Xerox* process may be due to persistent charge separation by formation of chalcogenonium cations and chalcogenolate anions in the solid sate, as depicted in Fig. 1:

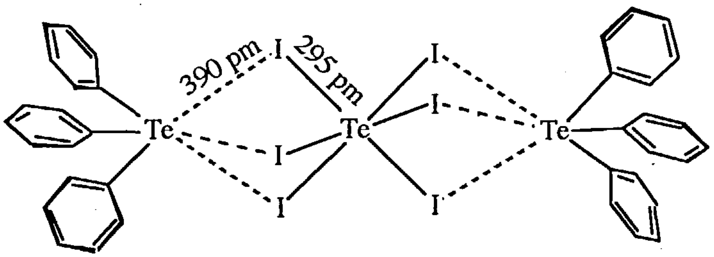
FIGURE 1.



Such charge separation in Se/Te alloys should be metastable with respect to thermal reactions (collapsing of the ion pairs) leading to "classical" chalcogene chains implying only dicoordinate selenium and tellurium. Our idea is, that apart from collapsing, "onium" and "ate" functions might interact with each other in a nonclassical way leading to structural moieties related to *Böttchers* hypervalent polytellurides [1]. To gain insight into the question of existence, structure and properties of yet unknown homonuclear chalcogenonium chalcogenolates, we decided to construct organic model compounds that will allow to study ways of interaction of telluronium cations with tellurolate anions: the anions will be nucleophiles that may attack the formally charged three-coordinated telluronium center or - alternatively- one of the two-coordinated Te atoms in α- or β-position from the telluronium function. Such a nucleophilic Te->Te attack would be related to the (formal) formation of nonclassical polytellurides from the classical chain-like ones. The most simple "nonclassical polytelluride", the linear Te_3^{4-} ion, derived from addition of Te^{2-} to Te_2^{2-}, is experimentally not (yet) available. Generally, the attack of nucleophiles at tellurium centers seems to preferred to the one at atoms in α- or β-position.

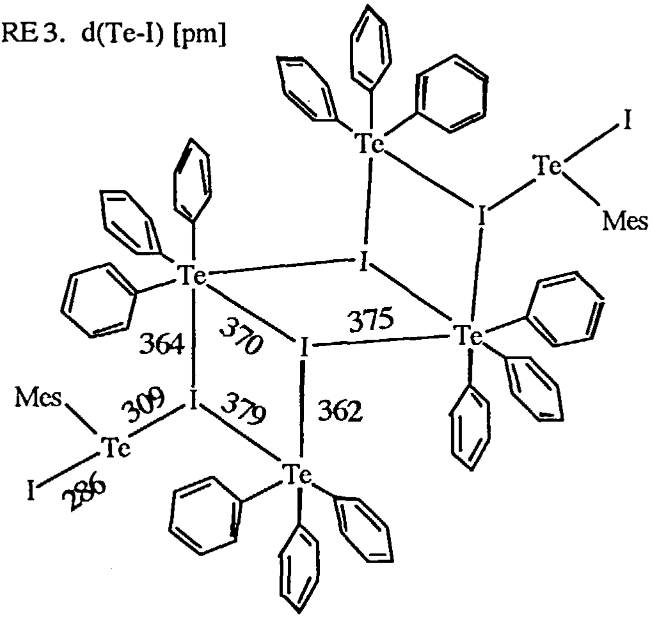
Comparing the organic telluronium ion Ph_3Te^+ and the cationic TeI_3^+ moiety, iodide ions prefer to attack the latter one. Nucleophlic (I^--> TeI_3^+) attacks lead to the stable salt $(Ph_3Te)_2TeI_6$ with cation-anion Te$\cdots$I contacts of 389.7 pm, as shown in Fig. 2:.

FIGURE 2. $(Ph_3Te)_2TeI_6$, brown prisms



When iodide ions as soft nucleophiles are allowed decide between competing R_3Te^+ and RTeI electrophiles, they prefer to attack the latter one; i. e. formally uncharged dicoodinated tellurium atoms with one Te-I bond are stronger electrophiles toward "soft" iodide ions than triorganotelluronium cations (Fig 3: structure of $[(Ph_3Te)_4(I)_2(MesTeI)_2])$.

FIGURE 3. d(Te-I) [pm]

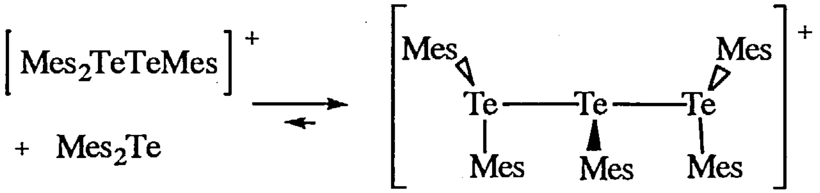


Compared with R_3Te^+ the weaker Te-I bonds of TeI_3^+ and of RTeI are more susceptible to the (n->σ*) attack by nucleophiles because of their low-lying σ* energy levels.

Recently, telluronium tellurolates and selenolates were prepared and isolated for the first time by reactions of triphenyltelluronium chloride with the corresponding sodium tellurolate of selenolate at low temperature [2]. In the dimeric structures of Ph_3Te^+ TeR^- salts, weak Te->Te interactions from bridging tellurolate donors with accepting triphenyltelluronium cations leads to homonuclear contacts between pyramidal (3-Te-8) and hypervalent square pyramidal (5-Te-12) tellurium atoms. However, these hypervalent Te-Te interactions are much weaker than those within *Böttchers* nonclassical polytellurides.

Compared with R_3Te^+ cations, the first ditelluronium cation $Mes_3Te_2^+$ (Mes = $[2,4,6\text{-}(CH_3)_3]C_6H_2$) is more susceptable to (n->σ^*) attack of nucleophiles because of its low-lying (Te-Te bond) σ^* energy level. Surprisingly, the cation $Mes_3Te_2^+$, however, behaves as iodine-like electrophile not by its formally charged *telluronium*-Te atom, but by its "*dicoordinated*" Te atom adjacent to the telluronium center [3].

This "inverse electrophilicity" (α-atom > *onium* center) is reflected by the different extent of cation-anion interactions of $Mes_3Te_2^+$ cation with fluorine atoms of the SbF_6^- counteranions in solid $[Mes_3Te_2^+ SbF_6^-]_2$: $d(Te^{II}\cdots F) << d(Te^{IV}\cdots F)$!



Mes_2Te adds as nucleophile to $Mes_3Te_2^+$ furnishing the novel cation $Mes_5Te_3^+$. The way of formation of $Mes_5Te_3^+ SbF_6^-$, its NMR spectra (kinetic lability in solution) and its solid state structure (nearly linear Te_3-chain, hypervalent central Te atom) show clearly the narrow relationship between "nonclassical" tellurium chains and more familiar polyiodides.

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