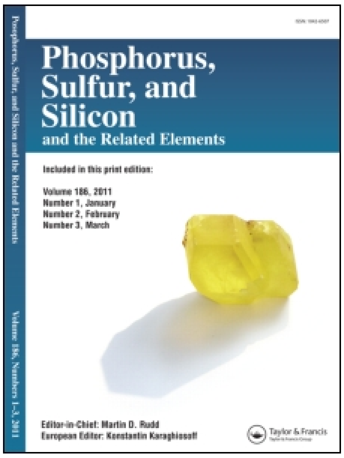

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SYNTHESES AND STRUCTURE OF HEXACOORDINATED SELENIUM (λ^6-SELANE) AND TELLURIUM (λ^6-TELLANE) COMPOUNDS

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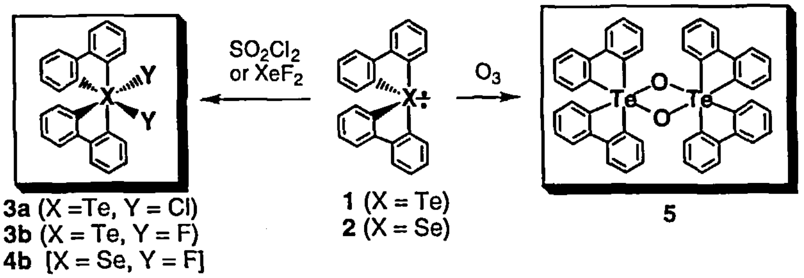
The first isolation of bis(2,2'-biphenylylene)dichloro- and difluoroperchalcogenuranes, [12–Se–6(C4F2)] (λ^6-selane); [12–Te–6(C4X2), X = Cl, F] (λ^6-tellane) and the corresponding tellurane *Te*-oxide dimer [12–Te–6(C4O2)]$_2$, and their crystal and molecular structures are described. Furthermore, on the basis of the difference between the 3c-4e bonds of the dodecet species and that of the decet species a new molecular orbital concept has been proposed on the 3c-4e bond of perchalcogenurane species [12–M–6, M = chalcogen atoms].

Keywords: pertellurane; perselenurane; tellurane *Te*-oxide dimer; X-ray crystallographic analysis; three-center four-electron bond

Organoperselenurane [12–Se–6] and -Telluranes [12–Te–6]

Tellurane **1** and selenurane **2** were reacted with 1 molar equiv of sulfuryl chloride in dry THF at –78 °C, xenon difluoride in dry CH_3CN at –40°C, or ozone in dry CH_2Cl_2 at –78 °C. After the removal of the solvent, the corresponding tetraaryldichloropertellurane (**3a**)[1], tetraaryldifluoro-pertellurane (**3b**)[2], -perselenurane (**4b**) or tetraaryltellurane *Te*-oxide dimer (**5**)[3] were isolated as stable crystals in 50, 54, 54 and 27% yields, respectively, as shown in Scheme 1.

SCHEME 1



Examination of the ^{1}H and ^{13}C NMR spectra of the compounds **3a**, **3b** **4b**, and **5** reveals that the two benzene rings in each biphenylylene groups are in nonequivalent states with 4 doublet and 4 triplet peaks seen in the ^{1}H NMR spectra and a set of 12 peaks in the ^{13}C NMR spectra. Furthermore, only the ^{1}H NMR chemical shift of the 3'-position in these compounds appears at an unusually high field compared with those of the corresponding tellurane **1** and selenurane **2**, when at low temperature the pseudorotation is slower than the NMR time scale[4]. This result indicates that the 3'-proton is shielded by the aromatic ring of the neighboring biphenylylene group. The ^{125}Te signals of **3b** and **4b** appeared as the triplet peaks due to a spin-spin coupling between the tellurium and fluorine nuclei. Furthermore, the ^{19}F signal of **3b** and **4b** appeared with the satellite peaks due to the same spin-spin coupling for the central peak. The ^{13}C NMR signals for each of the 2- and 2'-positions on the biphenylylene groups in the compounds **3b** and **4b** appear at a low field as triplet peaks due to a spin-spin coupling between carbon and fluorine nuclei via the tellurium nucleus. Furthermore, we have succeeded in determining the structures of the products **3a**, **3b**, **4b**, and **5** by X-ray crystallographic analysis. The molecular structures of these compounds for one enantiomer are illustrated by an ORTEP plot in Figure 1.

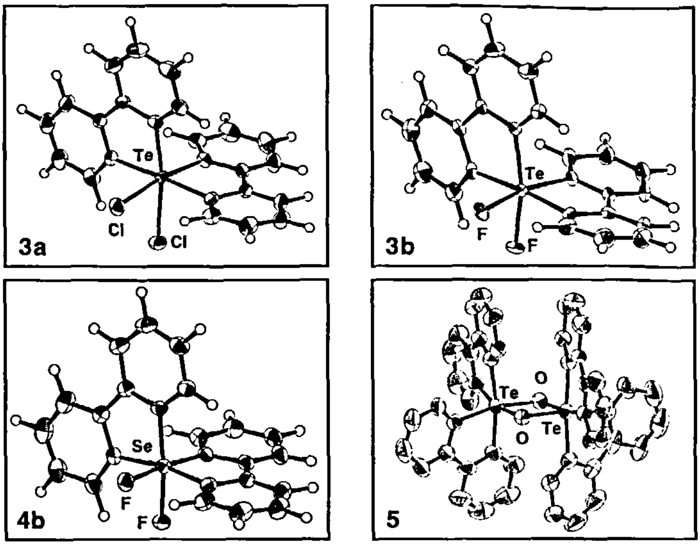


FIGURE 1. ORTEP view of **3a**, **3b**, **4b**, and **5**

Each central chalcogen atoms have a distorted-octahedral coordination geometry with the two halogen or oxygen atoms *cis* to each other.

3c–4e Bonds of Perchalcogenuranes

The dodecet species such as the pertellurane(VI) species are considered to have three sets of 3c–4e bonds which are perpendicular to each other giving an octahedral structure. Strictly speaking, however, the 3c–4e bonds in dodecet species differ from that in decet species such as the tellurane(IV) species. In decet species, the valence s orbital of the central atom is not involved in the 3c–4e bond. On the other hand, in the octahedral dodecet species, the s orbital is empty if only the p orbitals are utilized in description of the three 3c–4e bonds. Actually, the s orbital can be mixed with the nonbonding orbital in the Rundle–Musher 3c–4e model[5]. Namely, the nonbonding orbital splits into bonding and antibonding orbitals. Indeed, the occupancies of the 5s atomic orbitals of tellurium in **3a** and **3b** were calculated to be 1.201 and 1.103, respectively [2]. These values are consistent with the *extended Rundle–*

Musher model description shown in Figure 2. Because of the participation of the s orbital in the three 3c–4e bonds, the bonds in dodecet species are thought to be stronger than the apical hypervalent bonds in decet species. This agrees well with the experimental finding that the chalcogen–carbon bonds in perchalcogenurane species are shorter than the apical chalcogen–carbon bonds in **1**. Hexacoordinated chalcogen species seem to be generally more stable than the corresponding tetracoordinated species.

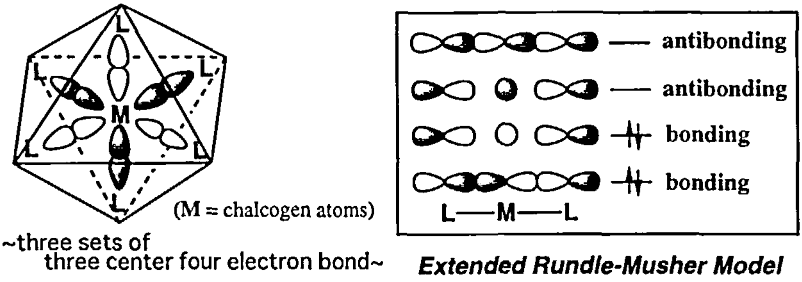


FIGURE 2. Octahedral structure and *Extended Rundle-Musher Model* of 3c–4e bond.

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