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Chalcogenuranyl Dications Bearing Unusual Bonds and Charges

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ABSTRACT: *A sulfuranyl dication was first prepared from the corresponding tetravalent bis(2,2′-biphenylylene)sulfurane via initial formation of the corresponding hexavalent-persulfurane. The structure of this new dication was found to have a tetracoordinated form as determined by X-ray crystallographic analysis as well as by ^{1}H and ^{13}C NMR spectroscopy. Similarly, selenurane and tellurane dication species were also detected by ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectroscopy. These chalcogenuranyl dications are the isoelectronic analogues of phosphonium salts and silanes.* Heteroatom Chem 13:406–413, 2002; Published online in Wiley Interscience (www.interscience.wiley.com). DOI 10.1002/hc.10089

INTRODUCTION

Herein we report new organo-chalcogenuranyl dications bearing unusual bonds and charges, which have been prepared from tetracoordinated chalcogenuranes [10-X-4(C4), X = S, Se, Te] via hexacoordinated species [12-X-6(C4Y2), X = S, Se, Te, Y = halogen, oxygen], as shown in Chart 1. We also present detailed structures of sulfuranyl dications as determined by X-ray crystallographic analysis and NMR spectroscopy, as well as their reactions.

Hypervalent organic compounds of Group 16 elements have attracted attention for many years [1]. Only a few stable organic hypervalent compounds of group 16 elements are known. Moreover, those having only carbon ligands are not known except for the tellurium derivatives that were prepared in 1952 by Wittig et al. [2]. Telluranes are known to have distorted trigonal bipyramidal structures as determined by X-ray crystallographic analysis [3].

Bis(2,2′-biphenylylene)selenurane was reported by Hellwinkel and coworkers in 1968 [4]; however, tetrakis(pentafluorophenyl)sulfurane was detected by ^{19}F NMR spectroscopy as a sulfurane bearing four carbon ligands [5].

Several years ago, we reported a preparative method for a sulfurane **6** by using trimethysilyl triflate as a condensing agent [6]. The structure of **6**, determined by X-ray crystallographic analysis, indicates that the central sulfur atom has a trigonal bipyramidal structure [10-S-4(C4)] as shown in Scheme 1.

Hexacoordinated Chalcogenuranes

It is well known that hexacoordinated molecules are more stable than the corresponding tetracoordinated species. Hence we tried to prepare higher coordinated chalcogenuranes bearing carbon ligands. The aim of this study was to prepare hexacoordinated chalcogenuranes bearing only carbon ligands, similar to those reported by Akiba and Minoura [7]. We also succeeded in the isolation of

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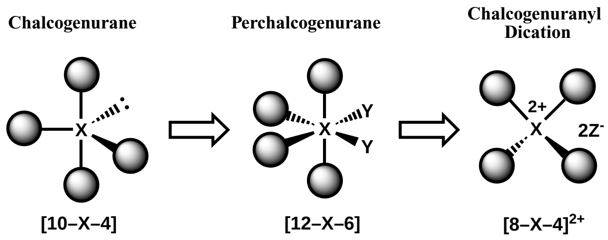
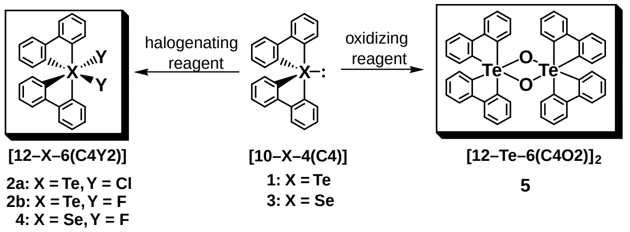


(X = S, Se, Te; Y = F, Cl; Z = BF_4, SbF_6, TfO, DSO_4)

CHART 1 Preparation of perchalcogenuranes and chalcogenuranyl dication species.



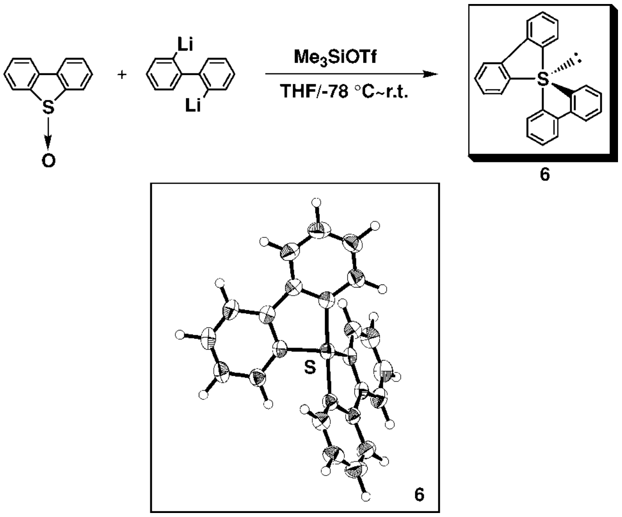
SCHEME 2

hexacoordinated chalcogenuranes bearing only carbon ligands, but this is reported elsewhere [8].

Initially, we intended to prepare stable hexacoordinated chalcogenuranes starting with tetracoordinated chalcogenuranes **1, 3**, and **6** by using appropriate halogenating or oxidizing agents [9]. In fact, both tellurane (**1**) and selenurane (**3**) were readily converted to the corresponding hexacoordinated derivatives **2** and **4** on treatment with halogenating or oxidizing agents. These were obtained as crystalline compounds and their ^{125}Te or ^{77}Se NMR spectra were measured. The structures of these compounds were finally determined by X-ray crystallographic analysis. The halogen or oxygen atoms attached to the central chalcogen elements were formed to occupy cis-positions, and no trans-isomers were obtained. Selective examples of the hexacoordinated selenuranes and telluranes bearing four carbons and two halogen atoms, [12-X-6(C4X2), X = Se, Te] [10] are presented in Scheme 2.

The electronic structures of tetracoordinated molecules [10-X-4] have been well elucidated on the basis of molecular orbital calculations indicating that the central atoms of these molecules are composed of two molecular orbitals, namely a planar equatorial sp^2-orbital and a [3c–4e] bond (3-center 4-electron bond) that is orthogonal to the planar sp^2 equatorial bond. The electronic configuration of the [3c–4e] bond, called the Rundle–Musher model, is illustrated in Fig. 1. The [3c–4e] bond is composed of three bonds, one having bonding orbitals, one nonbonding orbitals, and the third having antibonding orbitals; the four electrons fill the bonding and nonbonding orbitals, respectively. Thus, the molecular structures of tetracoordinated molecules should have trigonal bipyramidal structures (TBP) or decet structures.

Hexacoordinated molecules, on the other hand, should have dodecet structures, namely three equivalent [3c–4e] bonds that are perpendicular to each other; hence the structure of a hexacoordinated species should be octahedral (Oh). However, in the octahedral dodecet species, the s-orbital is empty if only the p-orbitals are utilized in the 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, that is, the nonbonding orbital splits into bonding and antibonding orbitals, as



SCHEME 1

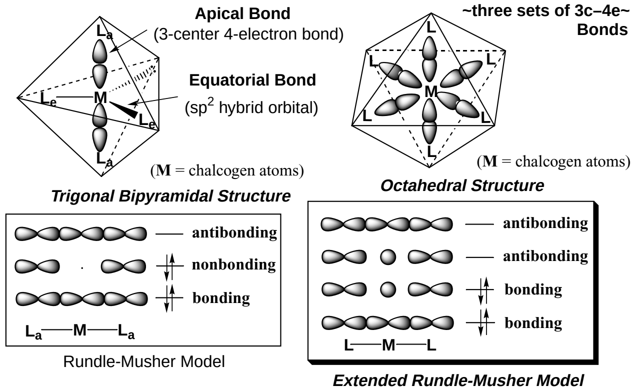


FIGURE 1 Rundle–Musher models of decet and dodecet molecules.

shown in Fig. 1 (we call this an expanded Rundle–Musher model) [11]. Therefore, the corresponding [3c–4e] bond is stronger than that of a decet species.

*First Preparation of Sulfurane Dications $[8\text{-S-}4(C4)]^{2+}$ (**8**)*

As described earlier in the synthesis of hexacoordinated selenuranes and telluranes, we treated sulfurane (**6**) with XeF_2 in CH_2Cl_2/Et_2O at low temperature (−78°C) (Scheme 3). The yellow color of **6** disappeared and a colorless solution was obtained. The ^1H and ^{13}C NMR spectra measured at −70°C in CD_2Cl_2 were nearly identical with those of perselenurane (**4**) and pertellurane (**2**) revealing that the persulfurane (**7**) was actually formed and the configuration of **7** was tentatively assigned as a cis-form. However, in order to isolate the persulfurane (**7**) the temperature of the solution was elevated to room temperature, and yellow precipitates were obtained. This yellow precipitate, compound **8**, was dissolved in CD_3CN and its ^1H, ^{13}C, and ^{19}F NMR spectra were measured at room temperature. The NMR spectra were completely different from those of persulfurane (**7**) at −70°C, as shown in Fig. 2. The ^1H NMR spectrum shows fourpeaks at $\delta = 7.92$ (t, $J = 7.5$ Hz, 4H), 8.22 (d, $J = 7.5$ Hz, 4H), 8.35 (t, $J = 7.5$ Hz, 4H), and 8.57 (d, $J = 7.5$ Hz, 4H); the ^{13}C NMR resonances appear at $\delta = 116.2$, 128.6, 132.5, 136.0, 142.9, and 144.0, respectively. The ^{19}F NMR spectrum of **7** shows only one singlet peak at $\delta = -166.1$. These NMR resonances are not consistent with those of the corresponding persulfurane **7**. Furthermore, on treatment of the yellow precipitate **8** with water, thionin oxide (**9**) was obtained quantitatively.

We assumed that compound **8** is a new sulfur compound, which we designed as a sulfuranyl dication (**8a**). Compound **8a** is a hygroscopic compound, which upon contact with moisture readily converts to the ring-expanded thionin derivative **9**. We therefore tried to synthesize a more stable derivative **8b** by converting compound **7** by the action of $BF_3 \cdot OEt_2$ or SbF_5. Another process for the synthesis of **8b** is the direct reaction of sulfurane (**6**) with XeF_2 in the presence of 2 equiv. of $BF_3 \cdot OEt_2$ at −78°C in CH_2Cl_2. The scheme of preparation of the new organosulfur compounds **8b** and **8c**, bearing a doubly charged sulfur atom, is illustrated in Scheme 4.

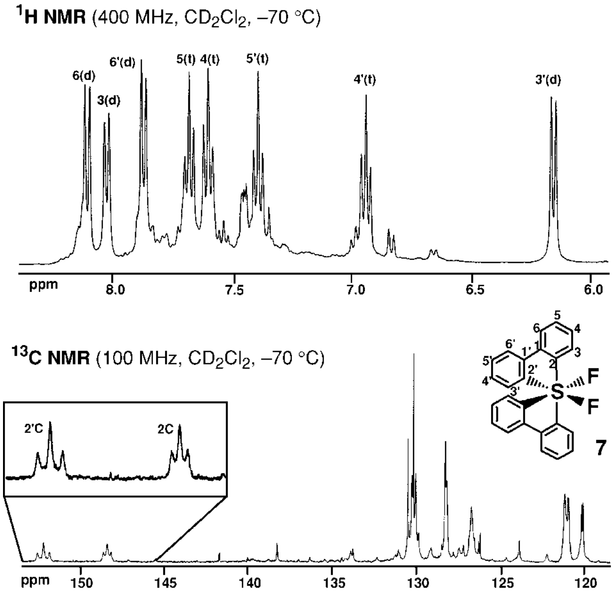
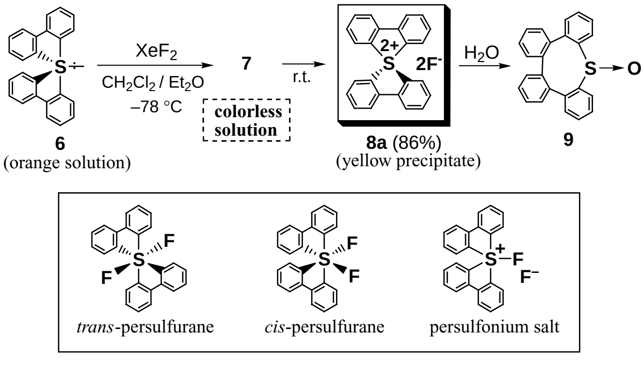


FIGURE 2 ^1H- and ^{13}C NMR spectra of persulfurane (**7**).

A comparison of sulfurane **6** and its dication species **8b** is quite interesting. For a comparison of **6** and **8**, both ^1H and ^{13}C NMR spectra of the two compounds were taken (Fig. 3). The assignment of the peaks was done as per CH-COSY spectrum of **8b**.

Quite unexpectedly, the attempt to synthesize hexacoordinated persulfurane resulted in the formation of a doubly charged dication derivative of sulfurane (**8**). Although assignment of the structure was carried out by NMR spectroscopy, the configuration could be determined correctly only by X-ray



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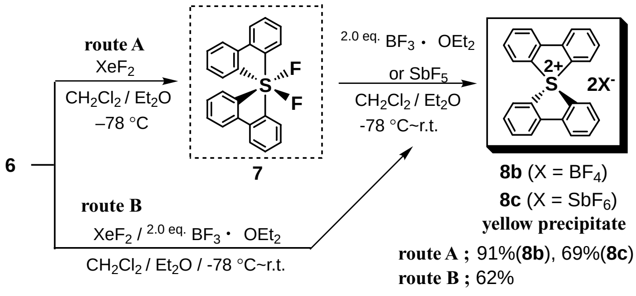


SCHEME 4

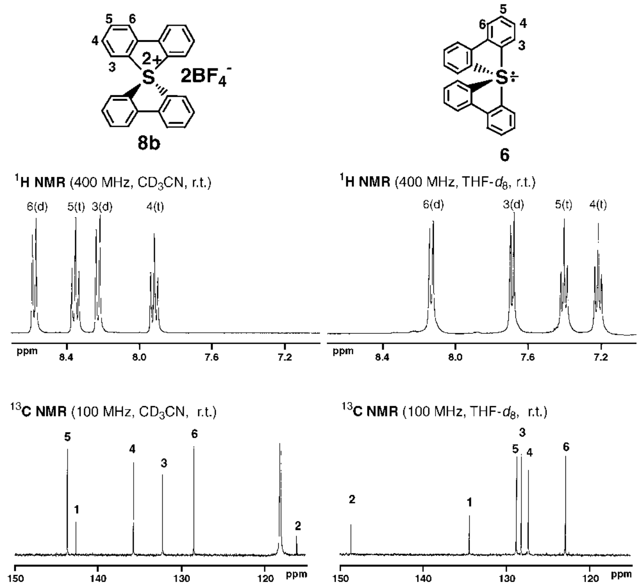


FIGURE 3 ^{1}H- and ^{13}C NMR spectra of sulfurane (**6**) and the sulfuranyl dication (**8b**).

crystallographic analysis. After recrystallization of **8b** and **8c**, golden-yellow colored crystals were obtained, which were used for the X-ray crystallographic analysis of **8b** and **8c**. An ORTEP drawing and representative data of bond lengths and bond angles of **8b** are summarized in Fig. 4 [12].

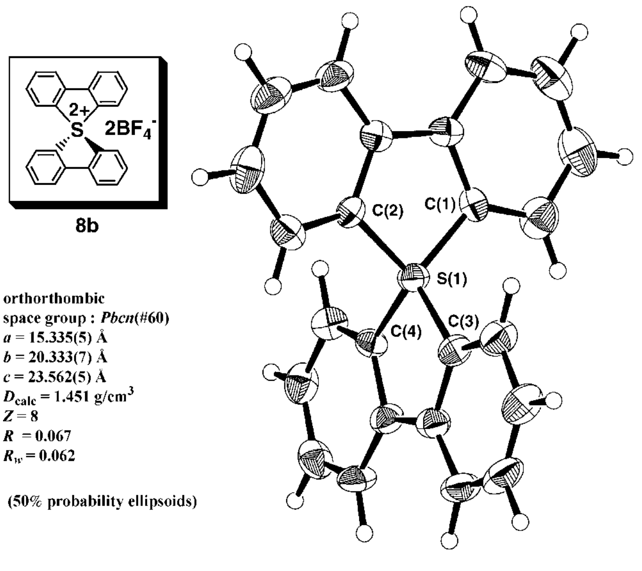


FIGURE 4 An ORTEP drawing of **8b**. For clarity, the counter anions (BF_4^-) are omitted. Selected bond distances (Å) and angles (°) are as follows: S(1)-C(1) = 1.76(1), S(1)-C(2) = 1.76(1), S(1)-C(3) = 1.75(1), S(1)-C(4) = 1.76(1), C(1)-S(1)-C(2) = 95.0(7), C(3)-S(1)-C(4) = 95.6(7), C(1)-S(1)-C(3) = 118.2(7), C(1)-S(1)-C(4) = 117.3(6), C(2)-S(1)-C(3) = 116.2(6).

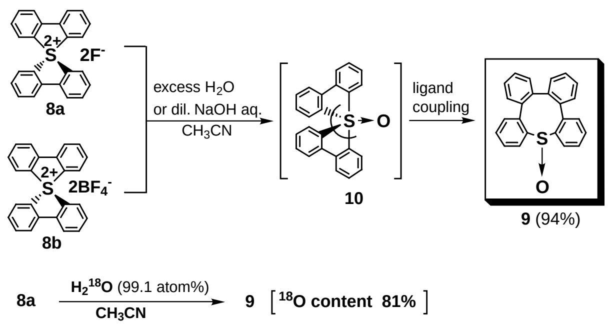
The data indicate that the configuration of the dication **8b** is nearly tetrahedral at the central sulfur atom and that the bond angles and bond lengths are within those of normal tetrahedral sulfur compounds.

Reactivity and Representative Reactions of Sulfurane Dication

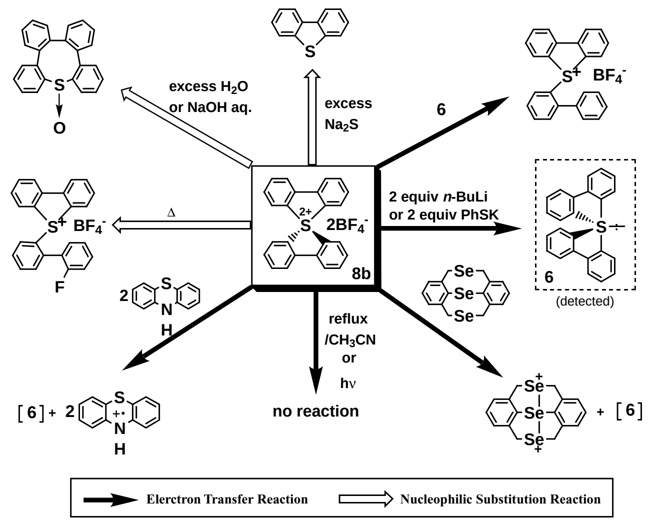
As described previously, during the hydrolysis of each sulfuranyl dication (**8a** or **8b**), a facile ring expansion was observed to give tetrabenzo[*b, d, f, h*]-thionin *S*-oxide (**9**) in quantitative yield. This unusual ring expansion reaction is assumed to take place via an initial formation of the pentacoordinated sulfurane *S*-oxide (**10**) from which an intramolecular ligand coupling reaction finally affords the thionin *S*-oxide (**9**). To confirm this process, we treated **8b** with excess H_2O or dilute aq. NaOH solution to give **9** in 94% yield revealing that this ring expansion reaction may proceed via the formation of sulfurane S-oxide (**10**), which we were unable to identify because of its unstable character. Tracer experiments using ^{18}O-labeled water revealed that the ^{18}O employed in the reaction was found mostly at the sulfinyl oxygen atom of **9**, as shown in Scheme 5.

The reactivity of dication **8** attracted our attention since compound **8b** was thermally and photochemically quite stable if moisture was excluded; it did not decompose under photolysis or even by refluxing in CH_3CN. We performed several experimental reactions of **8b** and the results are illustrated in Scheme 6 [13].

When **8b** was heated in situ at more than its melting point (>130°C), it decomposed to give the corresponding sulfonium salt. Hydroxide anion exerts its action as a nucleophile. On the other hand, thiolate anions seem to work as electron transfer reagents rather than as nucleophiles. For example, when **8b** was treated with function of thiophenolate anion in



SCHEME 5



SCHEME 6

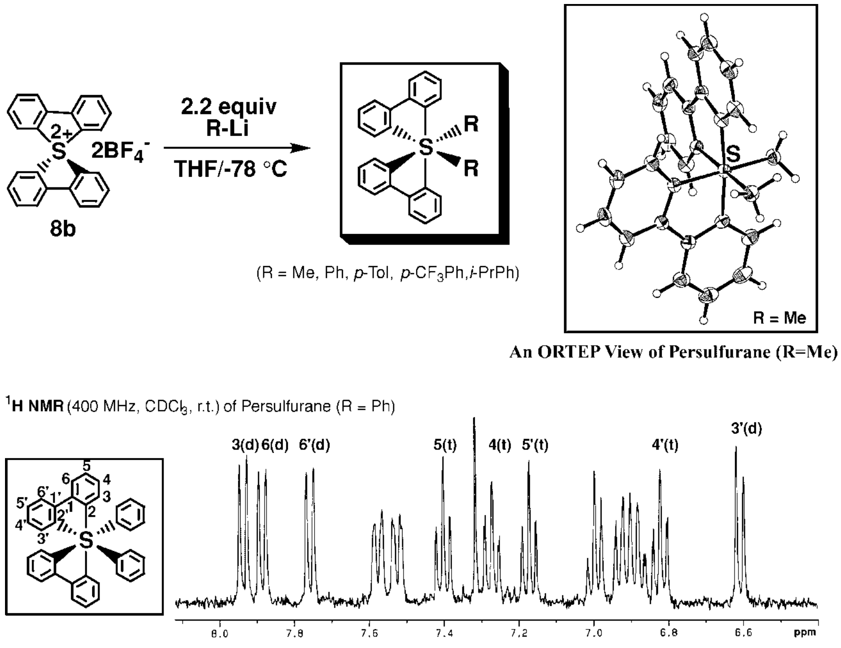
THF, **8b** was converted to **6** quantitatively, together with diphenyl disulfide, indicating that the electron transfer from thiolate anion to **8b** may produce the phenylthiolate radical and sulfurane **6**. Similarly, other electron transfer reagents such as dibenzophenothiazin or 5*H*,7*H*-dibenzo[*b*, *g*][1,5]diselenocine react readily with **8b** to give the phenothiazin cation radical and the diselena dication, together with sulfurane **6** as a reduction product. Butyllithium also works as a reducing agent to give **6** and octane.

Another prominent reaction of the dication **8** is the preparation of hexacoordinated persulfurane bearing only carbon ligands. When an aryllithium or methyllithium was used as a weaker carbon nucleophile instead of BuLi, an addition reaction took place to give hexacoordinated sulfuranes in good to moderate yields. These reactions became interesting and convenient processes for the preparation of hexacoordinated sulfuranes. The structures of hexacoordinated sulfuranes were determined by X-ray crystallographic analyses and by ^{1}H and ^{13}C NMR spectroscopy. The ORTEP drawing of the dimethyl derivative and the ^{1}H NMR spectrum of the diphenyl derivative are shown in Scheme 7 [14].

Molecular Orbital Calculations of the Dication

To elucidate the structure further, the charge distribution and bond order of dication **8b**, we performed the molecular orbital calculations of **8b** using single point ab initio calculations on the basis of the crystal structure coordinates. The calculations were carried out at the RHF/6-31G* level, using Spartan 4.2.1. Atomic charges were calculated by the natural population analysis. The results are summarized graphically in Fig. 5.

The molecular orbital calculations led us to conclude the following: (1) Two positive charges are mostly concentrated at the central sulfur atom, +1.59, while the remaining positive increments are



SCHEME 7

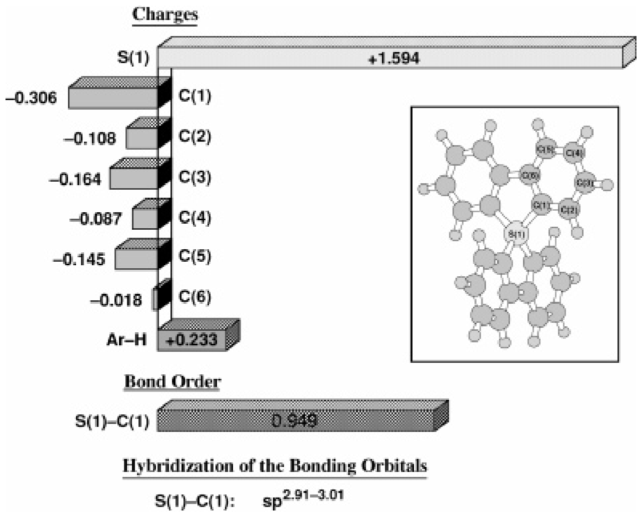


FIGURE 5 MO calculation and charge distribution.

located at the hydrogen atoms in the aromatic ring. (2) Negative charges are distributed among the aromatic carbon atoms, particularly at the carbon atom 1. (3) The bond order of C—S, 0.949 indicates that the C—S bond is roughly a normal single bond. (4) The hybridization of the bonding orbital at the S—C bond is $sp^{2.91-3.01}$, which is nearly representative of a tetrahedral structure.

The sulfuranyl dication should have an isoelectronic structure to the well-known phosphonium salt bearing a mono positive charge and to a silane as a neutral molecule. Both the phosphonium salts and the silanes are known to have tetrahedral structures at the central heteroatoms. To compare the structural similarity and charge distribution, we carried out MO calculations of these three molecular species by ab initio calculations on a SGI O2 work station and Spartan 4.2.1. The structures were initially optimized in D_{2d} symmetry with the RHF/3-21G$^{(*)}$ basis set and were subsequently improved at the RHF/6-31G* level. Atomic charges were calculated by the natural population analysis. The results are summarized in Chart 2.

The following conclusions may be deduced as per the calculation results shown in Chart 2: (1) The isoelectronic three molecules should have an identical configuration at the central atom. (2) The central atoms have nearly the same positive charges, +1.59 (S^{+2}), +1.850 (P^+), +1.960 (Si) and lighter atoms have more positive charges. (3) The negative charges are distributed among the aryl carbon atoms. (4) The hybridization of S—C, P—C, Si—C is nearly the same as the sp^3 configuration at the central heteroatom.

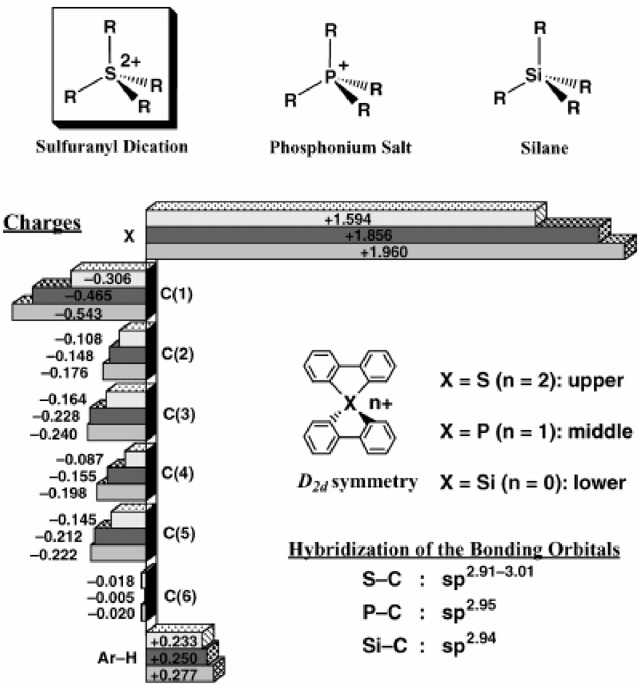


CHART 2 Isoelectronic molecules of sulfuranyl dication.

The existence of a sulfuranyl dication or sulfonium dication has been hypothetically predicted by Olah and coworkers. They calculated the stability of the tetrahydro or tetramethylsulfuranyl dication. As to the structure of the tetrahydrosulfuranyl dication, it may be concluded that on the basis of MO calculations, the tetrahedral structure (*Td*) is more stable than the planar structure (D_{4h}) (Fig. 6) [15].

*Selenurane and Tellurane Dications (**7**)*

Synthesis of tellurane and selenurane dications was carried out in a manner similar to the preparation of a sulfuranyl dication. Telluranyl dications (**11a–d**) were prepared by the method shown in Scheme 8. The starting material was pertellurane (**2a** or **2b**) or tellurane oxide dimer (**5**), which was treated with a suitable Lewis acid or Tf_2O or D_2SO_4 in the

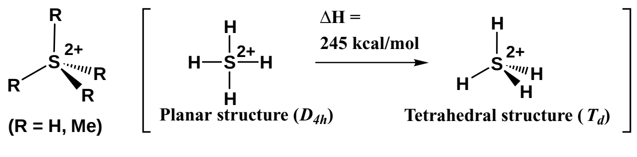
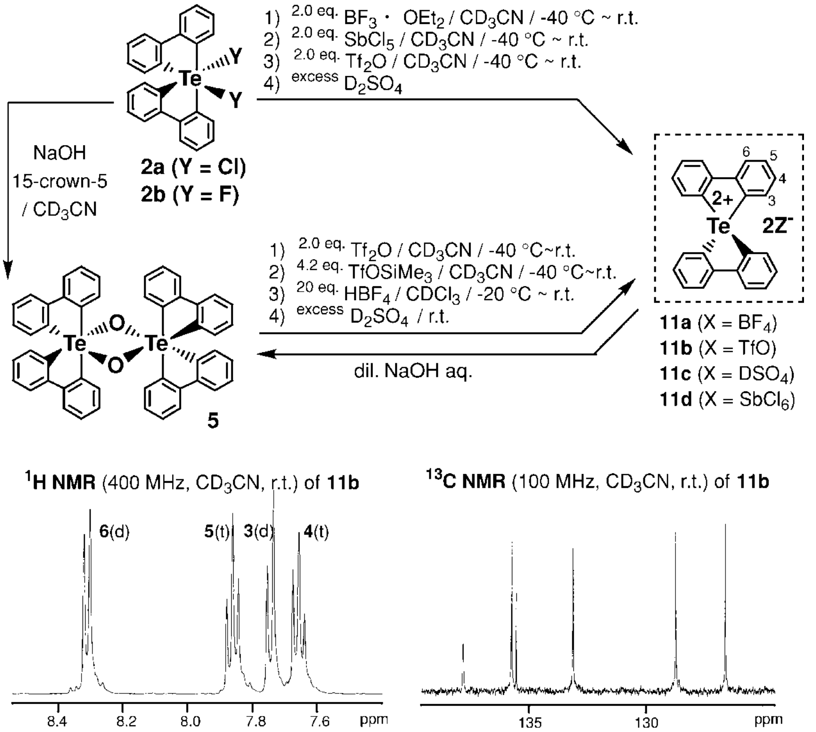


FIGURE 6 Theoretical formation of sulfuranyl dications.



SCHEME 8

range of −40°C to room temperature in CD$_3$CN. The reaction was followed by NMR spectroscopy and the dication (**11b**) was isolated as a crystalline compound having mp 159–161°C. A comparison of the ^{1}H and ^{13}C NMR spectra was consistent with that noted for the sulfuranyl dication **8**. The reaction schemes and the ^{1}H and ^{13}C NMR spectra are shown in Scheme 8. However, the X-ray crystallographic analysis of **11b** indicates that this telluranyl dication has a nearly hexagonal structure although the Te—O bond length (2.425 Å) is between that of a normal Te—O single bond (1.98 Å) and a van der Waals radii of Te—O (3.60 Å) (Fig. 7). This means that the telluranyl dication is actually formed but the attractive force between Te and oxygen atoms works rather strongly to form a hexavalent structure in the solid state (S. Sato, T. Yamashita, T. Ueminami, E. Horn, and N. Furukawa, unpublished results).

Similarly, attempts to prepare selenuranyl dications were made using perselenurane (**4**) with a Lewis acid or an acid anhydride at low temperature (−40°C), (Scheme 9). The reaction was followed directly by ^{1}H and ^{13}C NMR spectroscopy indicating that the dication **12** was actually generated at low temperature. However, when the solution was warmed to room temperature, the original NMR peaks disappeared and new NMR peaks were observed. After isolation, this compound was found to be a ring-opened selenonium salt **14** (S. Sato, H. Arakawa, and N. Furukawa, unpublished results).

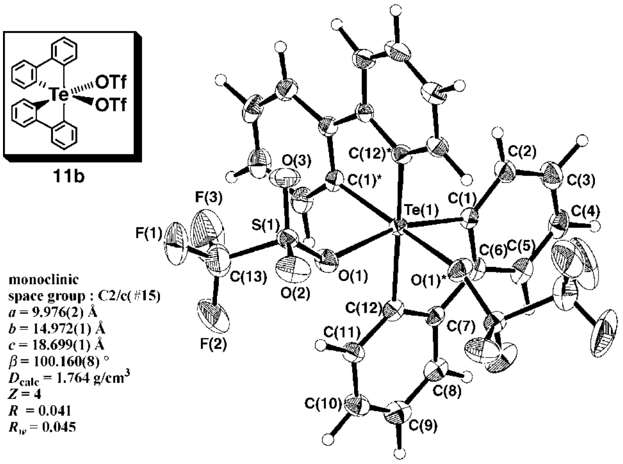
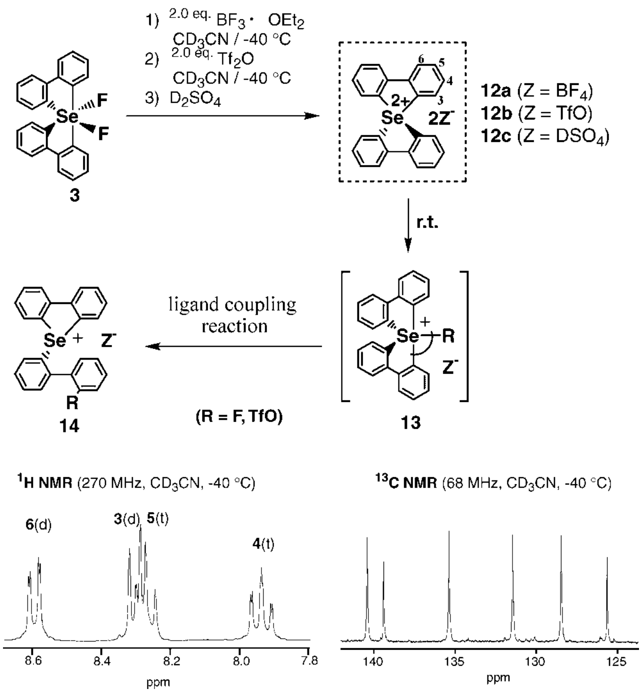


FIGURE 7 ORTEP drawing of **11b**. Selected bond distances (Å) and angles (°) are as follows: Te(1)—O(1) = 2.426(5), Te(1)—C(1) = 2.081(6), Te(1)—C(12) = 2.080(7), O(1)—Te(1)—O(1) = 80.1(3), O(1)—Te(1)—C(12) = 83.9(2), O(1)—Te(1)—C(1) = 89.1(2), C(1) —Te(1)—C(12) = 84.8(3), C(1)—Te(1)—C(1) = 103.3(3), C(1)—Te(1)—C(12) = 104.8(3), O(1)—Te(1)-C(1) = 165.1(2), C(12)—Te(1)—C(12) = 164.7(4), Te(1)—O(1)—S(1) = 140.1(3)



SCHEME 9

CONCLUSION

Hypervalent compounds having a structure of either 10-X-4(C4) or 12-X-6(C6) (where X is a chalcogen element S, Se, or Te) have been prepared and their structures have been elucidated. In this article, we reported the preparation of new organochalcogen compounds, chalcogenuranyl dications that have tetrahedral configurations at the central chalcogen atoms. The stabilities of these new dication species were found to be (at room temperature) in the order S > Te ≫ Se. The sulfur analogue is reasonably stable enough at room temperature, while the tellurium analogue is stable in solution at room temperature; the selenium analogue however, is unstable even in solution, being converted to a selenonium salt.

This stability order among the chalcogenuranyl dications can be explained in terms of the steric rigidity of the dication species that can accommodate extra ligands at the central chalcogen atom. This steric rigidity is balanced with the stability of the valence state; hexavalency should in general be more stable than tetravalency and pentavalency should be the least stable. Some reactions of the sulfuranyl dications have also been reported.

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