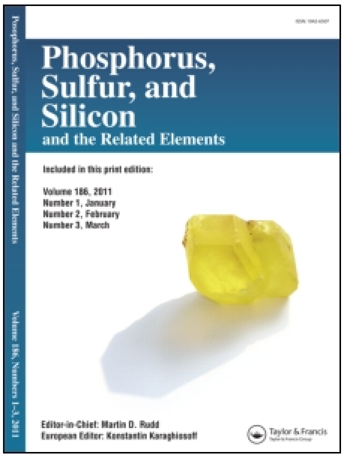

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Organotellurium(IV) Compounds Containing Symmetric Imidobis(Diphenylphosphinechalcogenide) Ligands

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The following compounds $[C_4H_8Te(Ph_2(S)PNP(S)Ph_2)_2]$ (**1**), $[C_4H_8TeI(Ph_2(S)PNP(S)Ph_2)]$ (**2**), $[C_8H_8TeI(Ph_2(S)PNP(S)Ph_2)]$ (**3**), $[C_4H_8TeI(Ph_2(Se)PNP(Se)Ph_2)]$ (**4**), and $[(C_4H_8TeOTeC_4H_8)_2(Ph_2(O)PNP(O)Ph_2)_2][I, I_3]$ (**5**) were isolated from the reaction of $C_4H_8TeI_2$ or $C_8H_8TeI_2$ with the appropriate $M[Ph_2(X)PNP(X)Ph_2]$ (M= K or Na; X= O, S and Se) salt. The compounds have been characterized by IR, multielemental NMR spectroscopy, positive-ion FAB mass spectrometry and elemental analysis. Compounds **1**, **3**, **4** and **5** were also characterized by single-crystal X-ray diffraction analysis. The sulfur and selenium ligands display an asymmetrical chelating coordination mode on interaction with the tellurium center, while two oxygen ligands behave as bridges between two C_4H_8Te-O-TeC_4H_8 units, leading to a 16-membered ring.

Keywords: Tellurium(IV); Imidodiphosphinechalcogenide ligands; Metallacycles

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INTRODUCTION

We became interested in the chemistry of organotellurium(IV) compounds in conjunction with our studies on the coordination chemistry of heavy main group elements using imidobis(diphenylphophinechalcogenide) ligands. The $[Ph_2(X)PNP(X')Ph_2]^-$ (X/X' = O/O, S/S, Se/Se, O/S, S/Se) ligands are ideally suitable for studying the influence of distinct donor atom sets on the geometry of metal complexes. They are excellent chelating agents, which offer the opportunity to vary the both donor atoms. In addition, they possess a high degree of ring flexibility and ring bite, as evidenced by the large number of reported six-membered metallacycles, some of them with unusual structures [1-3]. Derivatives with these ligands also exhibit a variety of bonding modes[4].

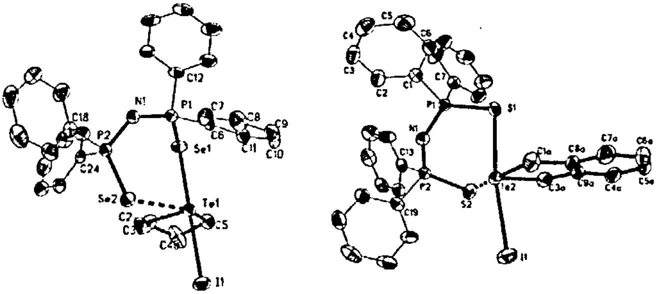
The synthesis and the structural analysis of organotellurium derivatives with the symmetric oxygen, sulfur and selenium imidodiphosphinates were undertaken to study the changes produced by the employment of ligands with relative unrestricted bite lengths and angles in comparison with the structures of related organotellurium(IV) compounds containing 1,1-dithioligand [5-8].The present paper described the results presented in the 9th Inorganic Rings Systems Symposium (IRIS IX) and previous papers [9].

RESULTS AND DISCUSSION

The starting materials and the organotellurium (IV) derivatives were obtained as described before[9]. The compounds display strong tendencies to undergo reductive elimination, as it was observed in related organotellurim(IV)[5-8, 10]. The obtained organotellurium(IV) derivatives were characterized by microanalysis, multielement NMR, IR, and positive ion FAB mass spectroscopy. The crystal and molecular structure of $[C_4H_8Te(Ph_2(S)PNP(S)Ph_2)_2]$ (**1**), $[C_8H_8TeI(Ph_2(S)PNP(S)Ph_2)]$ (**3**), $[C_4H_8TeI(Ph_2(Se)PNP(Se)Ph_2)]$ (**4**), and $[(C_4H_8TeOTeC_4H_8)_2(Ph_2(O)PNP(O)Ph_2)_2][I, I_3]$ (**5**) were determined by single-crystal X-ray diffraction analysis. Suitable crystals of $[C_4H_8TeI(Ph_2(S)PNP(S)Ph_2)]$ (**2**) for this study were obtained recently.

The solid state structures are built of discrete molecules. None intermolecular interaction is observed. The coordination geometry at tellurium can be described as the sawhorse structure typical of tellurium(IV) compounds in which the lone-pair of electrons is supposed to occupy an equatorial position in a distorted trigonal bipyramid. The carbon atoms are occupied the equatorial positions with the average C–Te–C angle and Te–C bond length being 85.07° and 2.134 Å.

The sulfur and selenium ligands in derivatives **1**, **3** and **4** display an asymmetrical chelating coordination mode on interaction with the tellurium center. The molecular structures and the atomic labeling schemes of **3** and **4** are illustrated in the ORTEP plot of Figure 1.



3 **4**

FIGURE 1 ORTEP plot of 3 and 4 with Te···S/Se interactions.

The short Te–S bond distances cover the range 2.53 to 2.57 Å, comparable with the values reported for related R_2TeXL structures[5-8]. The short Te–Se bond length is 2.721(1) Å. The strong-bonded sulfur atoms from two different ligands are occupying the axial positions in **1**. In the RTeIL derivatives (**3** and **4**), the axial positions are occupied by one of the strong-bonded donor atoms and the iodine atoms. The I–Te–Se axial angle (177.51(3)°) is considerably larger than the I–Te–S angle (171.8(1)°), while the S–Te–S axial angle is shorter (170.59(5)°). The long Te···S lengths range from 3.282(2) to 3.451(2) Å and the Te···Se distance is 3.4650(12) Å. The corresponding normalized Pauling partial bond orders[10] of these long bond distances are within the range of 0.16 to 0.27 (0.19 for the Te···Se length). They are still compatible with their being part of the coordination sphere and hence aniso-bonded. Including the two aniso-bonded sulfur atoms, the environment about Te becomes distorted octahedral for **1**. The weak-bonded donor atom rather than the lone pair, occupy the third equatorial position of the TBP structure in **3** and **4**.

The TeS_2P_2N and $TeSe_2P_2N$ chelate rings are arranged in a very distorted boat conformation with one phosphorus and one donor atom at the apices. The ring bond lengths are consistent with some localization of the bonding, i.e. the bond lengths alternate through the six-membered ring.

The molecular structure of $[(C_4H_8TeOTeC_4H_8)_2(Ph_2(O)PNP(O)Ph_2)_2][I, I_3]$ (**5**) is shown in Figure 2.

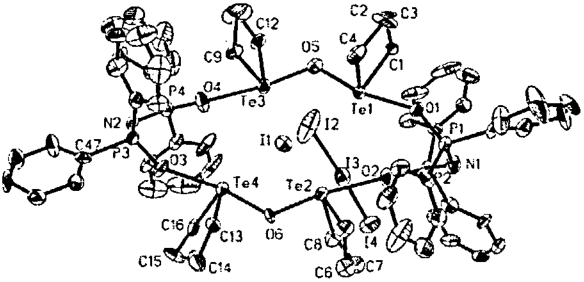


FIGURE 2 ORTEP plot of **5** (thermal ellipsoids at 30%)

In these unexpected derivatives two oxygen ligands behave as bridges between two $C_4H_8Te–O–TeC_4H_8$ units. This compound is probably formed from two ligands and $[C_4H_8TeI]_2O$. The later 1,1-oxydiiodide may be obtained from $C_4H_8TeI_2$ and alkali in the reaction media, as the analogous 1,1-oxydibromide[11] was synthesized. The alkali comes from the freshly prepared ligand salt. The $[(C_4H_8TeOTeC_4H_8)_2(Ph_2(O)PNP(O)Ph_2)_2]$ cation has two contraions, the I^- and I_3^-, located above and below the 16-membered ring with Te···I1 and Te···I2 interaction lengths ranging from 3.532(2) to 3.902(3) Å.

CONCLUSION

Despite the use of more flexible ligands than those 1,1-dithioligands studied before, the coordination mode is still anisobidentate. The bite angles and lengths are larger so that the angles about Te are less distorted. None intermolecular interaction was observed.

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