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Novel Coordination Pattern of Dithiophosphorus Ligands. Crystal and Molecular Structure of (Diphenylphosphinodithioato)phenyltellurium(II), $PhTeS_2PPh_2$. Supramolecular Association through Monodentate Biconnective Dithiophosphorus Ligands

Anca Silvestru and Ionel Haiduc*

Chemistry Department, Babeş-Bolyai University, RO-3400 Cluj-Napoca, Roumania

Klaus H. Ebert and Hans J. Breunig

Fachbereich 2 Anorganische Chemie, Universität Bremen, Postfach 330440, D-28334 Bremen 33, Germany

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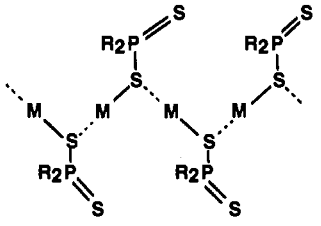
The phosphorodithioato, $(RO)_2PS_2^-$, and phosphinodithioato, $R_2PS_2^-$, ligands exhibit a broad variety of coordination patterns: monodentate, isobidentate (symmetrical), anisobidentate (unsymmetrical), and bridging or, in other terms, monometallic monoconnective, monometallic biconnective, bimetallic biconnective, and triconnective, etc.[1] Except in one case, i.e. monodentate coordination (monometallic monoconnective), the dithio ligand participates with both sulfur atoms in coordination, each forming either primary or secondary bonds. The latter are defined by interatomic distances intermediate between the sum of covalent radii and the sum of van der Waals radii.

We report now a coordination pattern missing from the list of previously identified ones.[1] In the new pattern (**1**)only one sulfur atom of the ligand participates in the formation of the bridge. This novel coordination pattern was discovered in (diphenylphosphinodithioato)phenyltellurium(II), $PhTeS_2PPh_2$ (**1**, M = TePh, R = Ph).



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Organotellurium(II) derivatives of dithiophosphorus ligands are not very common. So far, only the molecular structures of two phosphorodithioato derivatives of the type $RTeS_2P(OMe)_2$, R = 4-$MeOC_6H_4$,[2] and 4-$EtOC_6H_4$,[3] were determined by X-ray diffraction. In both compounds the first sulfur atom of the ligand, attached to tellurium forms single P—S bonds (ca. 2.05 Å), while the second sulfur, doubly bonded to phosphorus (ca. 1.93 A) participates in weak secondary bonds, $P{=}S\cdots Te$ (~3.262 Å and 3.309 Å for R = 4-$MeOC_6H_4$ and 4-$EtOC_6H_4$, respectively.[2,3] As a result, supramolecular polymeric chains (**2**) are formed. Thus, in **1** the dithiophosphorus bridge can be described as monodentate biconnective, while in **2** the coordination of the ligand is bidentate biconnective. A similar coordination (type **2**) was observed for organotellurium(II) methylxanthates, $RTeS_2COMe$, with R = 4-$MeOC_6H_4$[4] and 4-$EtOC_6H_4$,[3] while in tellurium(II) dialkylphosphorodithioates $Te[S_2P(OR)_2]_2$, with R = Me[5] and Et,[6] the essentially monodentate phosphorodithioato ligands participate in an intermolecular association through $P{=}S\cdots Te$ secondary bonds (**3**). Only in the dimeric tellurium(I) phosphinodithioate $Te_2(S_2PPh_2)_2$ the ligands span the Te-Te bond as unsymmetrical bridges (**4**) and the intermolecular assembly is formed through $Te\cdots Te$ secondary bonds, without participation of sulfur.[7]

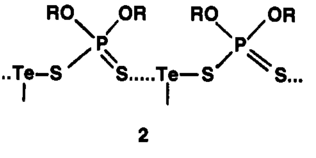

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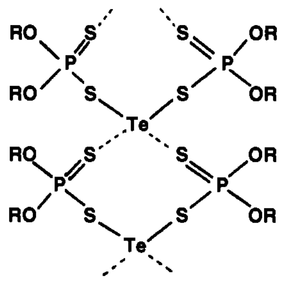
Table 1. Selected Bond Lengths (Å) and Angles (deg) for $PhTeS_2PPh_2$

Te(1a)–S(1ha)	2.406(2)	P(1)–S(2ha)	1.944(2)
Te(1a)···S(1cb)	3.338	P(1)–C(11)	1.809(6)
Te(1a)–C(1)	2.112(5)	P(1)–C(21)	1.817(5)
P(1)–S(1ha)	2.121(2)	Te(1a)···S(2ha) nonbonding	3.989
C(1)–Te(1a)–S(1ha)	98.9(2)	S(2ha)–P(1)–C(21)	113.3(2)
S(1ha)–Te(1a)–S(1cb)	173.1	S(1ha)–P(1)–C(11)	98.4(2)
S(1cb)···Te(1a)–C(1)	87.9	S(1ha)–P(1)–C(21)	106.5(2)
S(1ha)–P(1)–S(2ha)	115.2(1)	C(11)–P(1)–C(21)	107.1(2)
S(2ha)–P(1)–C(11)	115.0(2)	Te(1a)–S(1ha)–P(1)	103.7(1)



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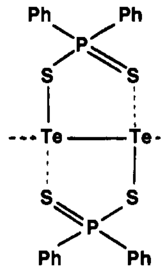

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(Diphenylphosphinodithioato)phenyltellurium(II) $PhTeS_2PPh_2$, was obtained as red prismatic crystals,[8] using a rearrangement reaction between Ph_2Te_2 and the disulfane $Ph_2P(S)S-SP(S)Ph_2$ in refluxing acetonitrile. The compound exhibits a thermochromic behavior, becoming yellow at ca –60 °C.

The molecular structure of $PhTeS_2PPh_2$ was determined by X-ray diffraction analysis.[9] Important bond lengths and angles are listed in Table 1. The structure consists of monomeric $PhTeS_2PPh_2$ units (Figure 1) self-assembled through weak intermolecular

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* Present address for correspondence: Universidad Nacional Autonoma de Mexico, Instituto de Quimica, Ciudad Universitaria, Circuito Exterior, 04510 Mexico, D.F., Mexico.

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(8) Anal. Calcd for $C_{18}H_{15}PS_2Te$: C, 47.58; H, 3.30. Found: C, 47.64; H, 3.22.

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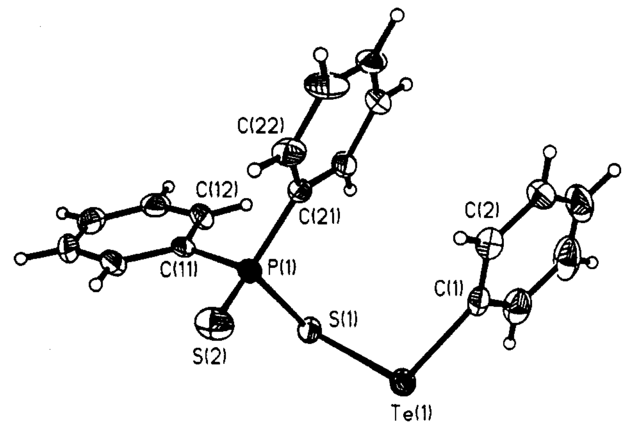

Figure 1. ORTEP drawing of the monomeric unit of $PhTeS_2PPh_2$ with thermal ellipsoids shown at the 50% probability level. Selected bond distances and angles are given in Table 1.

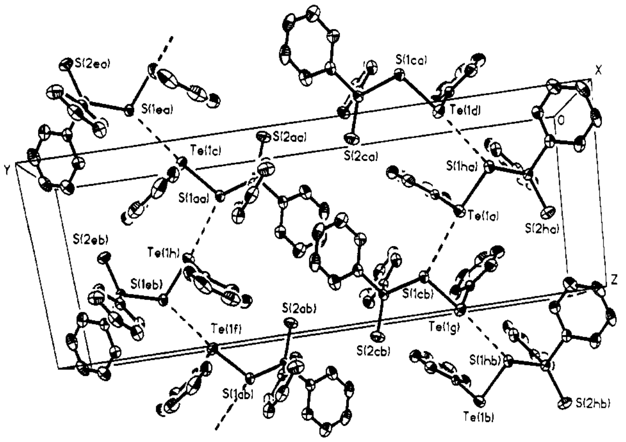

Figure 2. ORTEP view of the unit cell showing the polymeric chains of $PhTeS_2PPh_2$ made up of monomeric units assembled through secondary Te···S bonds.

tellurium–sulfur secondary interactions, leading to single strand polymeric chains as shown in Figure 2. If only the primary bonds are considered, the phosphinodithioato ligand can be described as essentially monodentate, with single P—S (2.121(2) Å) and double P═S (1.944(2) Å) bonds, very close to those observed in the free acid, $Ph_2P(S)SH$, i.e. 2.007(1) and 1.954(1) Å, respectively.[10]

In the crystal of the title compound each tellurium atom has an intermolecular semibonding contact of 3.383 Å, with a sulfur atom belonging to a neighboring molecule. If these weak interactions are considered, the tellurium atom can be regarded as three-coordinate in a T-shaped environment (S–Te···S = 173.1°, C–Te–S = 98.9(2)°, and C–Te···S = 87.9°). The sulfur atom single bonded to phosphorus participates in secondary interactions, while the doubly bonded sulfur is not involved in any inter- or intramolecular bonding with the tellurium atoms. As a result, the supramolecular association in $PhTeS_2PPh_2$ is achieved through monodentate biconnective bridges (**1**) and represents a new, so far unique, coordination pattern of dithiophosphorus ligands. At the present time it is difficult to predict whether this type of coordination will be found in other (main group metal) complexes of other 1,1-dithiolato ligands, including phosphorodithioates, xanthates, dithiocarbamates, etc.

Supplementary Material Available: Tables giving crystal data and details of the structure determination (data collection and solution, and refinement), atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients and hydrogen atom coordinates (8 pages). Ordering information is given on any current masthead page. Tables of structure factors and atomic coordinates and further details on the crystal structure determination of $PhTeS_2PPh_2$ are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissentschaftlich-technische Informations mbH, D-W-7514 Eggenstein-Leopoldshafen 2, Germany, on quoting the deposit number CSD-57232, the names of the authors, and the journal citation.

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(9) Crystal data: $C_{18}H_{15}PS_2Te$, $M = 454.0$, monoclinic, space group $P2_1/c$, $a = 8.658(3)$ Å, $b = 24.270(9)$ Å, $c = 9.237(3)$ Å, $\beta = 112.28(2)°$, $V_{calc} = 1796.3(11)$ Å^3, $Z = 4$, $D_{calc} = 1.6793$ g·cm^{-3}. The data were collected at −100 °C (on the yellow form of the compound) using the Mo Kα ($\lambda = 0.710\,73$ Å) radiation, μ(Mo Kα) = 1.971 mm^{-1}, on a Siemens P4 four-circle diffractometer for 4564 reflections in the 2θ–ω mode, (2θ range from 5.0 to 55.0°) of which 4130 were independent reflections ($R_{int} = 1.04\%$) and 2534 ($F > 6.0\sigma(F)$) were used in the full-matrix least-squares refinement with the SHELXTL PLUS (VMS) program system. Three standard reflections were measured after every 197 reflections. The structure was solved by direct methods for the tellurium atom and difference Fourier synthesis for the positions of the other non-hydrogen atoms and has been refined anisotropically to a final R of 3.7% and $R_w = 4.14\%$.

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