Volume 32

Number 18

September 1, 1993

Inorganic Chemistry

Communications

A Unique Supramolecular Structure of *catena*-Poly[bis(μ-diphenylphosphinodithioato)ditellurium(I)(*Te*—*Te*)], $[Te_2(S_2PPh_2)_2]_n$, Containing Te–Te···Te–Te··· Chains

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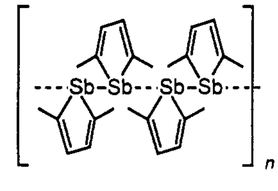
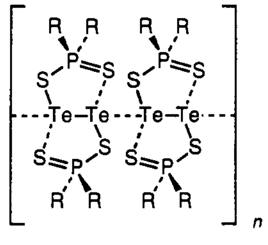
Received May 4, 1993

One of the interesting properties of distibines R_2Sb–SbR_2 is the deep color of certain such derivatives with relatively compact R groups. For example, crystals of 2,2′,5,5′-tetramethylbistibole (I) reflect iridescent purple-blue light and appear red to transmitted light, but they melt reversibly to a pale yellow oil at 99 °C.[1] X-ray diffraction studies on crystalline I indicate the presence of an antimony chain Sb–Sb···Sb–Sb··· in which the short Sb–Sb distances are 2.835 Å and the long Sb···Sb distances are 3.625 Å. Extended Hückel molecular orbital calculations[2] suggest that the presence of this chain is responsible for the thermochromic properties of I. This communication reports the first example of a tellurium complex, namely $\{Te_2(S_2PPh_2)_2]_n$ (II: R = Ph), with a similr type of Te–Te···Te–Te··· chain.



I



II

For the preparation of II (R = phenyl) a mixture of tellurium dioxide (0.31 g, 2 mmol) and diphenylphosphinodithioic acid (2.0 g, 8 mmol) in 50 mL of acetone was boiled under reflux for 2 h. The reaction mixture was filtered hot to remove unreacted TeO_2. Concentration of the filtrate gave 0.3 g (40% yield) of dark red $[Te_2(S_2PPh_2)_2]_n$, mp 165 °C. Anal. Calcd for $C_{24}H_{21}P_2S_4Te_2$: C, 38.2; H, 2.7. Found: C, 39.2; H, 2.8. The formation of $[Te_2(S_2PPh_2)_2]_n$ from tellurium dioxide and Ph_2PS_2H formally involves reduction of Te(IV) to Te(I) possibly by the following sequence of reactions with a Te(II) intermediate:

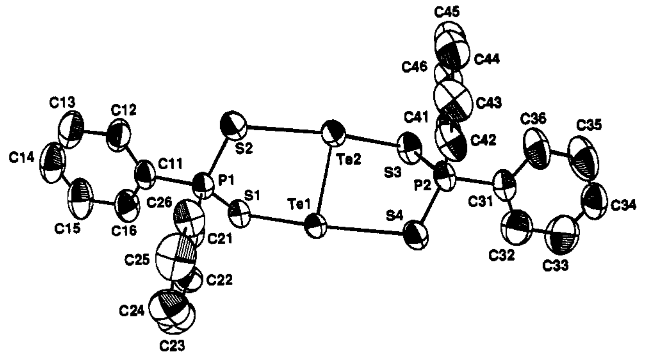


Figure 1. ORTEP diagram for one monomeric unit of II (R = phenyl). The benzene of solvation is omitted for clarity.

$$Te^{IV}O_2 + 4Ph_2P(S)SH \rightarrow Te^{II}(S_2PPh_2)_2 + 2Ph_2P(S)S\text{–}SP(S)Ph_2 \quad (1a)$$

$$2Te^{II}(S_2PPh_2)_2 \xrightarrow{\Delta} Te^{I}_2(S_2PPh_2)_2 + Ph_2P(S)S\text{–}SP(S)Ph_2 \quad (1b)$$

A sample of $[Te_2(S_2PPh_2)_2]_n$ for X-ray diffraction (Figures 1 and 2) was obtained as dark red needles by crystallization from benzene. Cell dimensions were determined as a = 11.669 (1) Å, b = 17.577(2) Å, c = 16.008(1) Å, and β = 91.30° in the monoclinic space group $P2_1/n$. A benzene of solvation was discovered in the diffraction analysis. The feature of particular interest in the structure of $[Te_2(S_2PPh_2)_2]_n$ (II: R = phenyl) is the presence of the zigzag Te–Te···Te–Te··· chain with alternating short (2.723 Å) and long (3.514 and 3.668 Å) tellurium–tellurium distances and alternating Te–Te···Te angles of 157.4 and 138.8° in the direction of the a axis (Figure 2). The presence of these tellurium chains may explain the needlelike habitus of the crystals. The short Te–Te distance in the $Te_2(S_2PPh_2)_2$ units is slightly longer but compares well with the Te–Te bonds previously found

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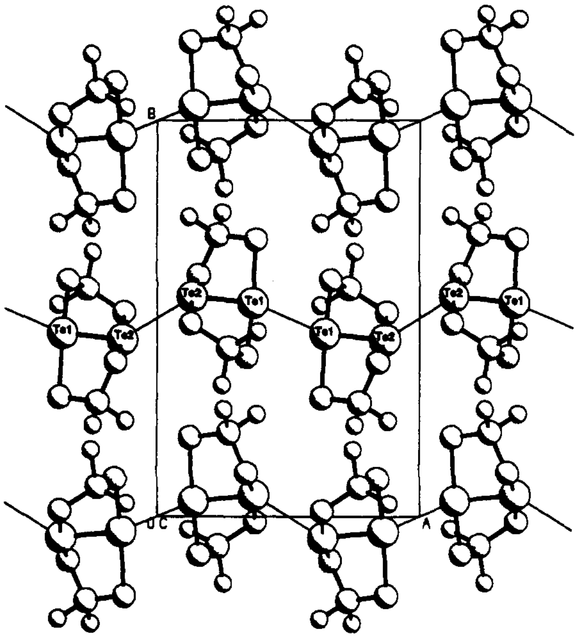

Figure 2. PLUTO diagram showing the unit cell packing. The largest circles represent tellurium atoms. The supramolecular semibonding Te···Te interactions are indicated as thin bonds connecting the monomolecular units. All carbons have been omitted for clarity except those carbon atoms directly attached to phosphorus.

in diorganoditellurides such as PhTe–TePh (2.712 Å),[3] Me$_2$NC(O)Te–TeC(O)NMe$_2$ (2.665 Å),[4] and 5,6:11,12-bis(ditelluro)tetracene (2.673 Å).[5] The long Te···Te distances connecting individual Te$_2$(S$_2$PPh$_2$)$_2$ units are longer than the covalent Te–Te bond distance but shorter than the sum of the van der Waals radii (4.40 Å), thus indicating semibonding interactions.[6]

In the Te$_2$(S$_2$PPh$_2$)$_2$ units the diphenylphosphinodithioato ligand displays a small difference in the phosphorus–sulfur bond lengths, thus suggesting the presence of essentially single P—S bonds (2.066 Å) and double P=S bonds (1.983 Å). Much larger differences (and therefore dissymmetry) are observed in the tellurium–sulfur interatomic distances: the short Te–S bond lengths (2.471 and 2.493 Å) associated with the long P–S bonds are normal covalent bonds in agreement with the sum of the covalent radii of tellurium and sulfur (2.38 Å). The long Te···S bond distances (2.989 and 3.066 Å) are longer than the Te–S covalent bond but significantly shorter than the sum of the van der Waals radii (4.20 Å). This leads to a much more unsymmetrical coordination of the phosphinodithioato ligand than in the similar metal–metal doubly bridged gold compound Au$_2$[S$_2$P(OPr^i)$_2$]$_2$ in which the two Au–S bonds in the five-membered Au$_2$S$_2$P rings are practically equal (2.30, 2.28, 2.27, and 2.29 Å).[7] Similarly, in the molybdenum compound, Mo$_2$(S$_2$PEt$_2$)$_4$, the S$_2$PEt$_2$ ligand is symmetrically bridging with practically equal Mo–S bond lengths (2.498, 2.499, 2.505, and 2.518 Å).[8]

Acknowledgment. I.H. gratefully acknowledges the support from the National Science Foundation for a visit at the University of Georgia, which made this work possible.

Supplementary Material Available: Tables of experimental crystallographic experimental details, positional parameters and their estimated standard deviations, bond distances in Å, bond angles in deg, torsion angles in deg, and general displacement parameter expressions (10 pages). Ordering information is given on any current masthead page.

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