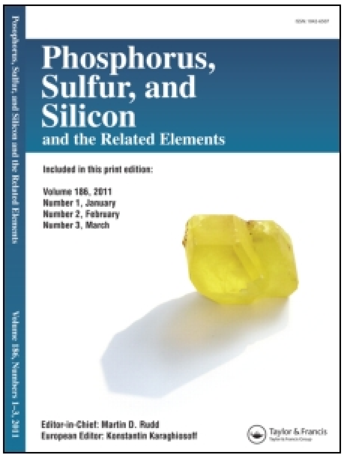
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Coordination Patterns of the Diphenyl-Phosphinodithioato Ligand in Tellurium Compounds

Anca Silvestru

To cite this Article Silvestru, Anca(1998) 'Coordination Patterns of the Diphenyl-Phosphinodithioato Ligand in Tellurium Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 617 — 620

To link to this Article: DOI: 10.1080/10426509808546009

URL: http://dx.doi.org/10.1080/10426509808546009

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus Sulphur and Silicon
Vols. 136, 137 & 138 pp. 617–620
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint
Printed in Malaysia

COORDINATION PATTERNS OF THE DIPHENYLPHOSPHINODITHIOATO LIGAND IN TELLURIUM COMPOUNDS

ANCA SILVESTRU
Chemistry Department, "Babeş-Bolyai" University,
RO-3400 Cluj-Napoca, ROMANIA

Abstract. Solid state monomeric structures with monometallic biconnective (bidentate) diphenylphosphinodithioato groups were found in $Ph_2Te(S_2PPh_2)_2$ (1) or $[Ph_3Te][S_2PPh_2]$ (2), while in the polymeric associations $[Te_2(S_2PPh_2)_2]_n$ (3) and $[PhTeS(S)PPh_2]_n$ (4) bimetallic biconnective (bridging) and monodentate biconnective (bridging) patterns were established by X-ray diffractometry. $[Te(S_2PPh_2)_3]_2$ (5) exhibits an unusual dimeric structure, with both monometallic biconnective and bimetallic triconnective ligand units.

Keywords: diphenylphosphinodithioato ligand, (organo)tellurium compounds

INTRODUCTION

The diphenylphosphinodithioato ligand might exhibit different coordination patterns in tellurium compounds, due both to its either monodentate or bidentate behavior and the tendency of tellurium to achieve large coordination numbers.

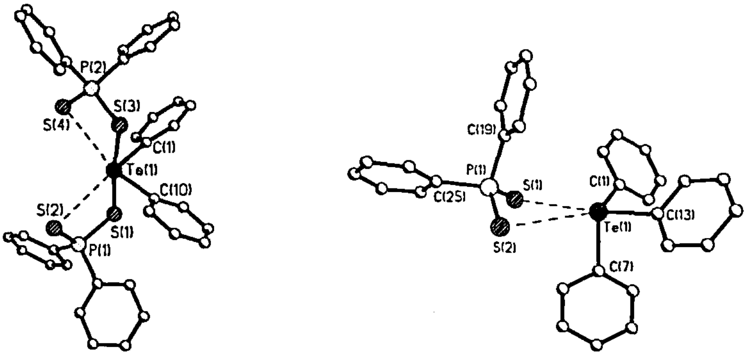
Very often, in compounds containing dithioato ligands, tellurium tends to built 3c-4e bonds, by involving the same *p* orbital in two different bonds[1]. As a result, the bond length becomes longer than the normal tellurium-sulfur covalent distance, characteristic for a 2c-2e bond. In the same time, as a consequence of the 3c-4e system, the strong influence of the organic groups in *trans* to the Te-S bond results in the elongation of this bond, sometimes to a value larger than the sum of the van der Waals radii characteristic for tellurium and sulfur.

MONOMETALLIC BICONNECTIVE

Either in $Ph_2Te(S_2PPh_2)_2$ (Fig. 1a)[2] or in $[Ph_3Te][S_2PPh_2]$ (Fig. 1b)[3] the ligand acts as a monometallic biconnective unit, both sulfur atoms being involved in bonds or interractions to the same tellurium atom. In the first case, the nonequivalent tellurium-sulfur distances reflect an anisobidentate coordination pattern through two covalent Te-S bonds (av. 2.627 Å) and two secondary $Te\cdots S$ interactions (av. 3.301 Å). For $[Ph_3Te][S_2PPh_2]$ both tellurium-sulfur distances (av. 3.493 Å) are much longer than the normal covalent distance suggesting a ionic structure.

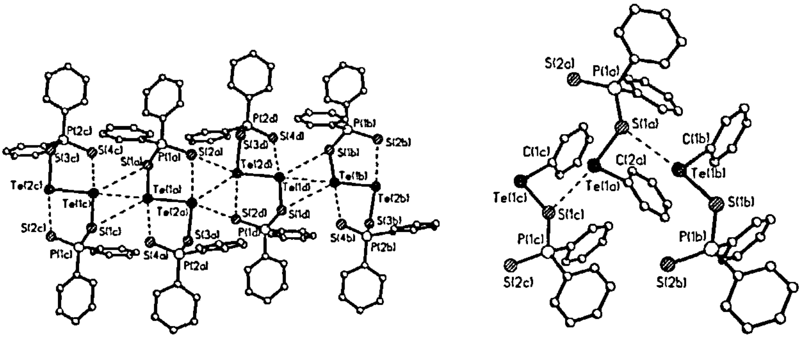
BIMETALLIC BICONNECTIVE

Polymeric associations through bridging Ph_2PS_2 units have been observed in $[Te_2(S_2PPh_2)_2]_n$[4] and $[PhTe(S_2PPh_2)]_n$[5]. In both cases the ligand act bimetallic biconnective, but in the first compound (Fig. 2a) the coordination is realized through both sulfur atoms in a bidentate pattern, while in the second one (Fig. 2b) only one sulfur atom is involved in bonds or interactions to tellurium.



(a) **(b)**

FIGURE 1. Monometallic biconnective coordination pattern in $Ph_2Te(S_2PPh_2)_2$.(**a**) and$[Ph_3Te][S_2PPh_2]$ (**b**).



(a) **(b)**

FIGURE 2. Bimetallic biconnective coordination pattern in $[Te_2(S_2PPh_2)_2]_n$.(**a**) and $[PhTe(S_2PPh_2)]_n$ (**b**).

BIMETALLIC TRICONNECTIVE

In $[Te(S_2PPh_2)_3]_2$[6] an unusual dimeric structure is realized through six ligand units, four of them acting monometallic biconnective, while the other two are bridging the tellurium atoms in a bimetallic triconnective pattern (Fig. 3); one of the two sulfur atoms is involved in coordination to both tellurium atoms. The dimeric molecule has a symmetric structure, but the tellurium atoms are supposed to be in different oxidation states (+2 and +4) in an ionic arrangement, $[TeL_3]^+[TeL_3]^-$, L = Ph_2PS_2. In solution, all six ligands appear to be equivalent, as the NMR spectra (^{1}H, ^{13}C, ^{31}P) suggest, due to a very rapid exchange equilibrium between the two species.

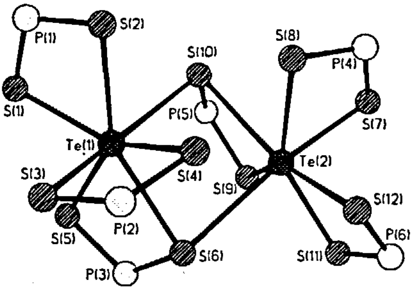


FIGURE 3. Monometallic biconnective and bimetallic triconnective coordination pattern in $[Te(S_2PPh_2)_3]_2$ (for clarity, the phenyl groups attached to phosphorus atoms are not shown).

References

[1.] I. Haiduc, R.B. King, M.G. Newton, *Chem.Rev.*, **94**, 301 (1994).
[2.] A. Silvestru, I. Haiduc, H.J. Breunig, K.H. Ebert, *Polyhedron,* **14**, 1175 (1995).
[3.] A. Silvestru, I. Haiduc, R.A. Toscano, H.J. Breunig, *Polyhedron,* **14**, 2047 (1995).
[4.] M.G. Newton, R.B. King, I. Haiduc, A. Silvestru, *Inorg. Chem.*, **32**, 3795 (1993).
[5.] A. Silvestru, I. Haiduc, K.H. Ebert, H.J. Breunig, *J. Organomet. Chem.*, **482**, 253 (1994).
[6.] A. Silvestru, R.A. Toscano, unpublished results.