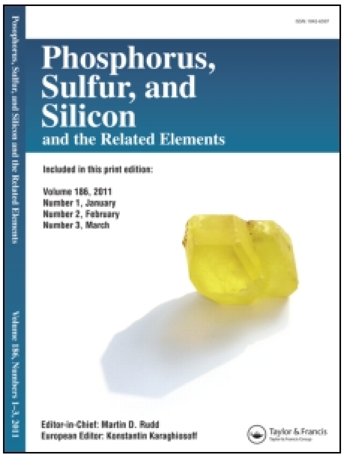

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Formation of Inorganic Quasi-Cyclic Structures Through Secondary Interaction. A Few Cases of Heterogeometrism

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FORMATION OF INORGANIC QUASI-CYCLIC STRUCTURES THROUGH SECONDARY INTERACTION. A FEW CASES OF HETEROGEOMETRISM

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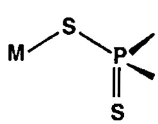
Abstract. Rings formed by secondary interactions are called *quasi-cyclic structures*. Examples are given mainly from the field of dithiophosphorus ligand derivatives of Main Group metals, which may dimerize with formation of quasi-cyclic structures. Intramolecular cyclization and supramolecular association through secondary bonds leading to formation of quasi-cycles, is also cited. In several cases cyclic compounds of the same general formula contain metal atoms in different coordination geometries. The term *heterogeometrism* is suggested to describe this situation. The corresponding compounds are called*heterogeometric analogues.*

***

The phosphor-1,1-dithiolato ligands display a great diversity of coordination patterns;[1] monodentate (monometallic monoconnective) coordination **1** is rare, and bidentate coordination (monometallic biconnective) leads to cyclization (chelate ring formation). In Main Group metal derivatives the cyclization frequently occurs through secondary bonds, **2**, which are characterized by interatomic distances intermediate between the sum of covalent radii and the sum of van der Waals radii.[2] This type of chelating differs from **3** , where the cyclization occurs through dative bonds (of the same order of magnitude as covalent bonds) or from **4**, where symmetrical chelating coordination is achieved through basically covalent bonds. Since the M...S secondary interaction is not an authentic chemical bond, this type of rings are called*quasi-cyclic structures*. They are rather frequent in Main Group metal chemistry.



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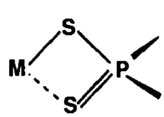

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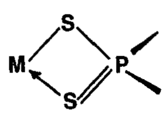

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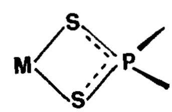

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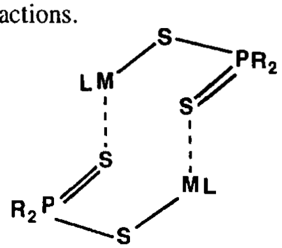
Dimerization of monometallic moieties **1** and **2** leads to formation of quasi-cyclic structures **5**, **6** and **7**, in which the monomers are held together by secondary interactions.



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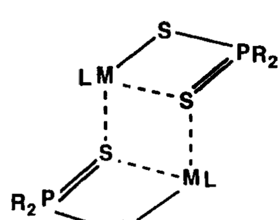

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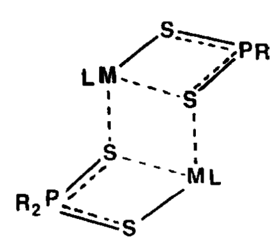

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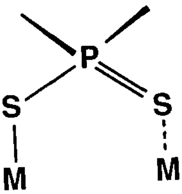
Bridging (bimetallic biconnective) coordination **8** and bimetallic triconnective coordination **9** is thus achieved. When the compound contains a metal-metal bond, the bimetallic biconnective coordination **8** leads to intramolecular cyclization, with formation of a quasi-cyclic structure **10**.



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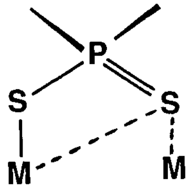

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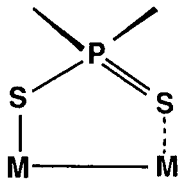

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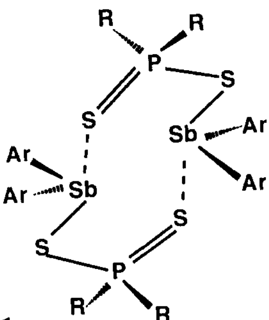
As examples can be cited the compounds of the general formula $R_2SbS_2PR'_2$, which are dimers when R' = Et and R = p-tolyl (structure **11**)[3] and R = R' = Ph (structure **12**).[4] It will be noted that in **11** there are no transannular Sb...S interactions (interatomic distances 3.94 and 4.01 Å) and the metal displays Ψ-trigonal bipyramidal coordination geometry. In **12** the transannular distance of 3.44 Å sugests Sb...S secondary interaction and the metal displays square pyramidal geometry.



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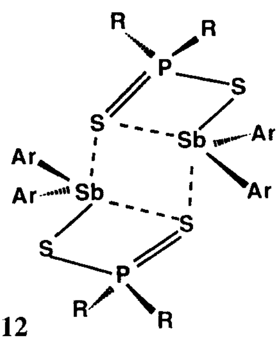
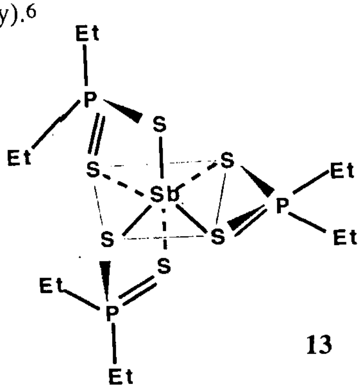


12

Such compounds, of the same general formula, differing only in the nature of peripheric organic substituents (R and R'), which display different coordination geometries are called *heterogeometric analogues*. Other heterogeometric analogues are $Sb(S_2PEt_2)_3$ **13** (distorted octahedral geometry)[5] and $Sb(S_2PPh_2)_3$ **14** (pentagonal pyramidal geometry).[6]



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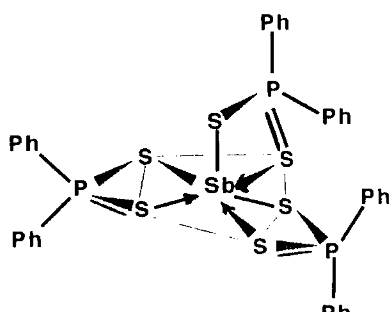

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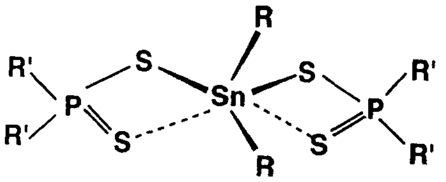
Heterogeometric analogues are also $Ph_2Sn\{S_2P(OEt)_2\}_2$ **15** (bicapped tetrahedron)[7] and $Ph_2Sn\{S_2P(OPr^i)_2\}_2$ **16** (regular octahedral geometry) .[8]



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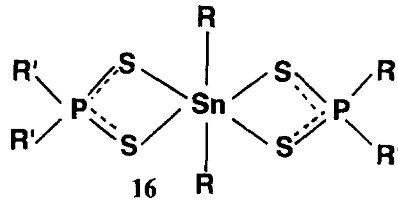

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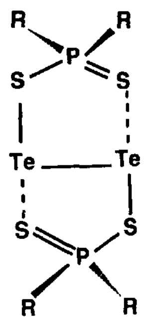
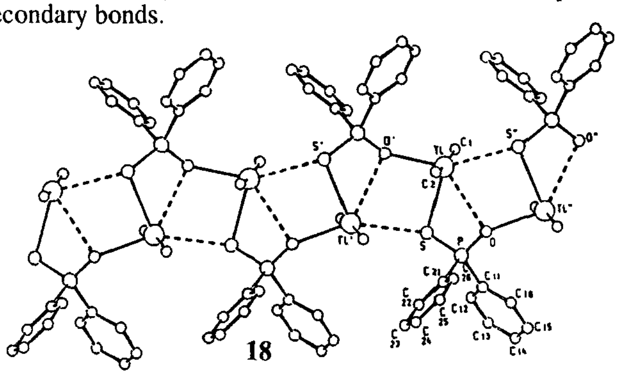
Intramolecular cyclization through secondary bonding and formation of a quasi-bicyclic structure is observed in the tellurium compound $Te(S_2PPh_2)_2$, which is a dimer **17** with a Te-Te bond.[9]

17



Intermolecular association of some main Group metal phosphor-1,1-thiolates leads to formation of polymeric structures, containing quasi-cyclic building units, connected together in a *supramolecular contruction*. Thus, in $Me_2Tl(SOPPh_2)$ the monomeric units form a polymeric chain, **18**, and secondary bonds bewtween the chain segments form four-membered quasicyclic units.[10] In $MeHgSOPPh_2$,[11] $Pb(S_2PPh_2)_2$ [12] and $Pb(S_2PMe_2)_2$ [13] dimeric quasicyclic units are connected in supramolecular structures through secondary bonds.



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