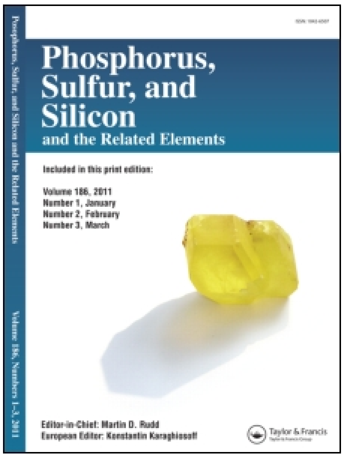

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INORGANIC CHELATE (CARBON-FREE) RINGS IN MONOMERIC AND DIMERIC $[R_xM\{(XPR'_2)(YPR''_2)N\}_y]_n$

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Abstract Structural aspects in inorganic and organometallic derivatives of various tetraorganodichalcogenoimidodiphosphinic acids, $[R_xM\{(XPR'_2)(YPR''_2)N\}_y]_n$ (M = Li, Na, K, Sn, Sb, Te, Co, Ni, Cu, Zn; X = O, S) are discussed, with special attention paid to the formation of inorganic metallocycles.

Keywords: dichalcogenoimidodiphosphinato ligands, inorganic rings, inorganic and organometallic compounds

INTRODUCTION

The tetraorganodichalcogenoimidodiphosphinato anions, $[(XPR_2)(YPR'_2)N]^-$ (X, Y = O, S, Se; R, R' = alkyl, aryl, alkoxy, aroxy), are versatile ligands able to form inorganic (carbon-free) metallacycles. The studies on the coordination chemistry of this type of ligands were mainly concerned to symmetric derivatives containing only phenyl groups and same chalcogens attached to phosphorus atoms[1]. Changes in the organic groups and/or in the chalcogen atoms of the ligand moiety often resulted in unexpected structure modification. Although six-membered $MXYP_2N$ chelate rings are commonly formed through coordination of both chalcogen atoms to the metallic center, in some cases the formation of four-membered or macrocycles was also established by X-ray diffractometry.

MONOMERIC, MONOCYCLIC STRUCTURES

When the tetraorganodichalcogenoimidodiphosphinato anion is coordinated to monovalent inorganic or organometallic centers, *monomeric, monocyclic structures* are generally formed, the phosphorus ligand acting as a monometallic biconnective moiety. Thus, in $Ph_2SbCl_2[(OPPh_2)_2N]$ and $Ph_2SbCl_2[(OPPh_2)(SPPh_2)N]$ the imidodiphosphinato ligand is coordinated through both chalcogen atoms to antimony [Sb(1)-O(1) 2.128(3), Sb(1)-O(2) 2.112(3) Å, and Sb(1)-O(1) 2.113(3), Sb(1)-S(1) 2.614(2) Å, respectively], leading to novel inorganic SbO_2P_2N and $SbOSP_2N$ rings[2]. The $SbOXP_2N$ inorganic rings are non-planar, displaying a twisted boat conformation. In the OPNPX fragment of the ring the magnitude of the phosphorus-oxygen and phosphorus-sulfur bonds suggests a predominant single bond character, while the two phosphorus-nitrogen bonds are equivalent and their lengths suggest a partial double bond character, *i.e.* some π-electron delocalization over the P-N-P fragment.

The molecular structure of $Ph_3Te[(SPPh_2)_2N]$ was described as containing weak cation-anion secondary interactions between tellurium and sulfur (3.264 and 3.451 Å) (Fig. 1), a ionic structure being also consistent with its water solubility[3].

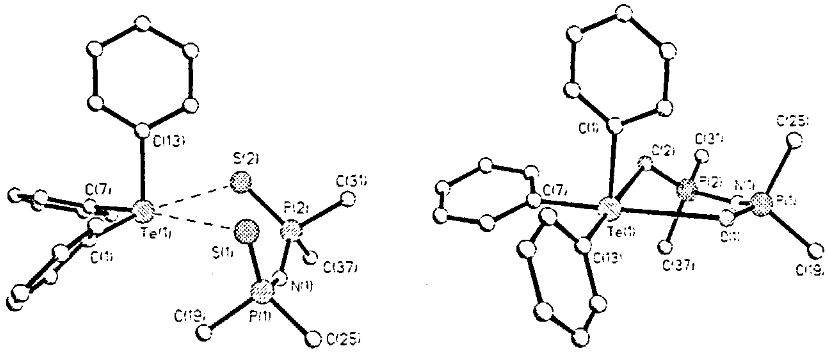

FIGURE 1 The molecular structures of $Ph_3Te[(SPPh_2)_2N]$ and $Ph_3Te[(OPPh_2)_2N]$ (only *ipso* carbons on phosphorus are shown).

For the $Ph_3Te[(OPPh_2)(SPPh_2)N]$ and $Ph_3Te[(OPPh_2)_2N]$ (Fig. 1) analogs[4], the phosphorus-chalcogen and phosphorus-nitrogen bonds seems to have a considerable double bond character and the ligand is best described as chelating the metal atom through weak secondary interactions involving both chalcogen atoms [Te···O(1) 2.926(6) and Te···O(2) 2.654(6) Å, and Te···O 2.77(1) and Te···S 3.282(4) Å, respectively]. The resulting six-membered $TeXYP_2N$ chelate rings may be discussed in terms of a boat, with different degree of distortion. In all three structures the supposed stereochemically active lone pair of tellurium is located *trans* to a carbon atom and completes a distorted octahedral geometry around the central atom.

The mononuclear $(Ph_3P)Cu[(SPPh_2)_2N]$ complex is another example of a monomeric, monocyclic structure[5]. However, a tetranuclear Cu^I complex, $[Cu_4\{(SPPh_2)_2N\}_3][CuCl_2]$, was separated from reaction mixture $Cu^{II}Cl_2$ / $Na[(SPPh_2)_2N]$[6]. In this case the phosphorus ligand coordinates in a trimetallic tetraconnective fashion on each triangular Cu_3 face of a tetrahedral Cu_4 core.

It should be noted here that in the case of $PhTe^{II}$ and Me_3Sn^{IV} derivatives[7,8], the $[(SPPh_2)_2N]^-$ ligand acts as a bimetallic biconnective (bridging) moiety, resulting in a dinuclear structure with a 12-membered $Te_2S_4P_4N_2$ macrocycle, or in a chain polymeric structure $[-SnSPNPS-]_n$.

MONOMERIC, *SPIRO*-BICYCLIC STRUCTURES

When two tetraorganodichalcogenoimidodiphosphinato anions are coordinated to bivalent inorganic or organometallic centers, *monomeric, spiro-bicyclic structures* are generally formed, the phosphorus ligand acting again as a monometallic biconnective moiety.

The molecular structures of various diorganotin derivatives were determiner by X-ray diffractometry: $R_2Sn[(OPPh_2)_2N]_2$ (R = Bu[9], Bz[10]), $R_2Sn[(OPMe_2)(OPPh_2)N]_2$ [R = Me (Fig. 2), Bu, Ph][10], $Me_2Sn[(SPPh_2)_2N]_2$[11], $R_2Sn[(OPPh_2)(SPPh_2)N]_2$ (R = Me, Ph, Bz)[12].

Regardless the nature of the phosphorus ligand and/or of the organic groups attached to tin, all these compounds exhibit in solid

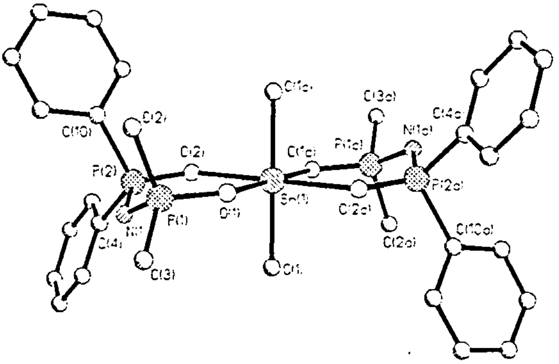

FIGURE 2 The structure of $Me_2Sn[(OPMe_2)(OPPh_2)N]_2$.

state very similar *spiro*-bicyclic structures, with the tin atom as spiro atom. The coordination geometry around the central metal atom is octahedral, with C-Sn-C, X-Sn-X (*trans)* and Y-Sn-Y (*trans*) angles of 180° and a planar SnX_2Y_2 system. Of the two possible isomers, *i.e.* (X *trans* X, Y *trans* Y) and (X *trans* Y), in all cases only the former was observed. The six-membered $SnXYP_2N$ inorganic rings might exhibit various conformations, *i.e.* twisted boat, twisted chair, or even *quasi*-planar.

Monomeric, *spiro*-bicyclic structures are also formed for the inorganic $Zn[(OPPh_2)_2N]_2$[10], $Co[(SPMe_2)(SPR_2)N]_2$ (R = Me[13], Ph[14]), $Ni[(XPPh_2)(SPR_2)N]_2$ (X = S, R = Me, Ph[15]; X = O, R = Me, Ph[10]), and $Cu[(OPPh_2)(SPPh_2)N]_2$[10]. For almost all these compounds the MX_2Y_2 core is tetrahedral and the conformation of the inorganic $MXYP_2N$ ring is twisted boat.

However, two interesting cases should be noted. Thus, in the Ni^{II} series, a surprising example of heterogeometrism was observed. Although most of the monomeric Ni^{II} derivatives are tetrahedral, the

Ni[(SPMe$_2$)(SPPh$_2$)N]$_2$ complex exhibits a square-planar NiS$_4$ core [mean Ni-S 2.239 Å, S-Ni-S 98.3° (endocyclic), 81.1° (exocyclic)] and a ladder structure, with the inorganic NiS$_2$P$_2$N rings folded about the (MeP)S····P(Ph) axis (NiS$_2$P/SP$_2$N dihedral angle of 57.4°) (Fig. 3)[15].

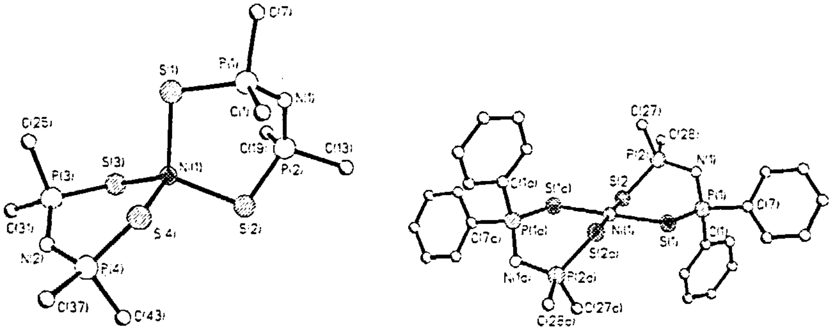

FIGURE 3 The molecular structures of Ni[(SPPh$_2$)$_2$N]$_2$ and Ni[(SPMe$_2$)(SPPh$_2$)N]$_2$ (only *ipso* carbons on phosphorus are shown for the first complex).

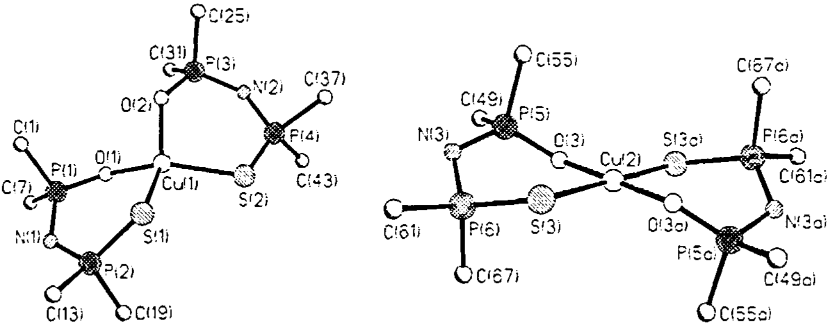

FIGURE 4 Heterogeometrism in the Cu[(OPPh$_2$)(SPPh$_2$)N]$_2$ derivative (only *ipso* carbons on phosphorus are shown).

In the case of the Cu^{II} derivative, Cu[(OPPh$_2$)(SPPh$_2$)N]$_2$, the same unit cell contains both tetrahedral and square-planar isomers

(Fig. 4) in a 2:1 ratio[10]. In both molecules the conformation of the six-membered rings is twisted boat.

It should be noted here that in the case of the $Pd[\{OP(OPh)_2\}\{SP(OPh)_2\}N]_2$ complex, the related phosphorus ligand exhibit a different pattern of coordination, *i.e.* through nitrogen and sulfur atoms, thus leading to a *spiro*-bicyclic structure containing four-membered PdSPN rings[16].

DINUCLEAR STRUCTURES

Both lithium and sodium salts of monothioimidodiphosphinic acids, $Li\{(OPPh_2)(SPMe_2)N\}.2H_2O$ and $Na\{(OPPh_2)(SPPh_2)N\}.2THF$, exhibit dimeric associations, but different structures. In the lithium salt, the ligand bridges two metal atoms only through its oxygen, thus leading to a planar Li_2O_2 ring (Fig. 5)[10].

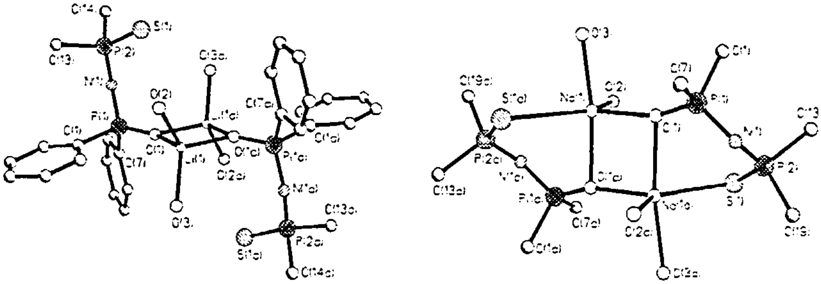

FIGURE 5 Dimer association in $[Li\{(OPPh_2)(SPMe_2)N\}.2H_2O]_2$ and $[Na\{(OPPh_2)(SPPh_2)N\}.2THF]_2$ (only *ipso* carbons on phosphorus and oxygens of the THF molecules are shown for the second compound).

By contrast, in the case of the sodium salt, in addition to the oxygen atoms, the sulfur atoms are also involved in coordination to the metal, thus resulting in a tricyclic system with a central planar four-membered Na_2O_2 ring (Fig. 5). The $NaOSP_2N$ rings are symmetrically folded about the Na(1)······N(1a) and Na(1a)······N(1) axis, respectively, on opposite side relative to the central ring, with a diedral angle between best NaOPN and NaSPN planes of 112.3°. This results in a ladder structure of the whole tricyclic system[17].

A dinuclear structure is also formed in the case of the Ni^{II} complex, $[Ni\{(OPPh_2)_2N\}_2]_2.H_2O$. In this case, three of the phosphorus ligands act as bimetallic triconnective units, while the forth one is monometallic biconnective (Fig. 6). The sixth coordination position on Ni(2) is completed by the oxygen of a water molecule. The result is a fused polycyclic system formed by three six-membered NiO_2P_2N rings and three non-planar four-membered Ni_2O_2 rings[10]. This Ni_2O_9 core is destroyed when the compound is recrystallized from DMFA, when the monomeric, *spiro*-bicyclic $Ni[(OPPh_2)_2N]_2.2DMFA$ is formed (Fig. 6)[10].

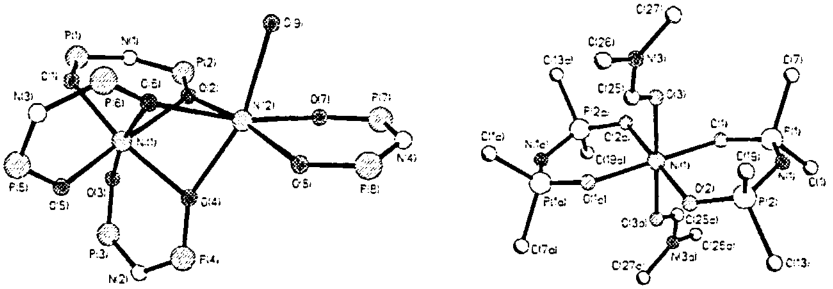

FIGURE 6 The dinuclear $[Ni\{(OPPh_2)_2N\}_2]_2.H_2O$ and its DMFA adduct $Ni[(OPPh_2)_2N]_2.2DMFA$ (only the inorganic skeleton for the first compound, and the *ipso* carbons on phosphorus for the second compound, are shown, respectively).

POLYMERIC STRUCTURES

The potassium salt $K(SPMe_2)_2N$ was found to exhibit a *polymeric structure* due to the unusual coordination pattern of the phosphorus ligand, *i.e.* tetrametallic pentaconnective through four K-S interactions (range 3.189 - 3.365 Å) and one K-N interaction (2.937 Å) (Fig. 7)[11]. In the fused polycyclic skeleton one can distinguish four-membered planar K_2S_2 and KSPN rings, eight-membered $K_2S_2P_2N_2$, $K_2S_3P_2N$ and K_3S_3PN rings.

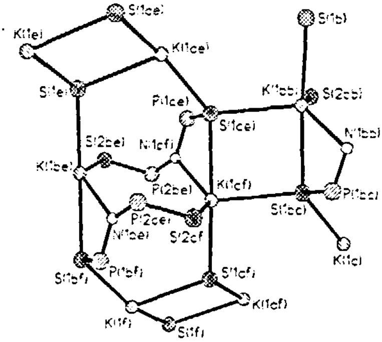

FIGURE 7 Fragment of the polymeric structure of $[K(SPMe_2)_2N]_n$ showing the types of inorganic rings (only the inorganic skeleton is shown).

CONCLUDING REMARKS

The main coordination pattern exhibited by the tetraorganodichalcogenoimidodiphosphinato ligands is monometallic biconnective, leading to six-membered $MXYP_2N$ rings. However, the disponibility of this type of ligand to exhibit other coordination patterns, involving both the chalcogen and the nitrogen atoms and to increase its connectivity, is a source for unusual structures with fused polycyclic systems.

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