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Account

Thiophosphorus and related ligands in coordination, organometallic and supramolecular chemistry. A personal account

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Dedicated to Professor Herbert W. Roesky on his 65th anniversary, with great admiration for his contributions to modern inorganic chemistry.

Abstract

The results obtained in the investigation of sulfur containing ligands (dithiophosphates, -phosphinates and -phosphonates, monothiophosphinates, dithioarsinates and dichalcogenoimidodiphosphinates) in a broad international cooperation, are concisely presented. Oxo- and thio-organophosphorus and -organoarsenic anions are versatile ligands in metal and organometallic derivatives, with molecular monomeric, cyclic or supramolecular structures, at the interface between the traditional branches of inorganic chemistry: coordination, organometallic and inorganic ring chemistry.

Keywords: Dithiophosphates; Dithiophosphinates; Dithioarsinates; Dichalcogenoimidodiphosphinates; Supramolecular; Self-assembly

1. Introduction

Thiophosphorus ligands, including dithiophosphates and -phosphinates, dithioimidodiphosphinates and mixed thio-oxo analogues, as well as dithioarsinates, have been in the center of interest in our laboratory for many years. These compounds are versatile ligands, displaying a broad variety of coordination patterns leading to a great diversity of molecular and supramolecular structures. Many of their metal derivatives are soluble in organic solvents and can be extracted from aqueous solutions, serving in separation procedures. In addition, their metal compounds are useful as lubricant additives and received considerable interest in the literature.

I will present here our contributions to the field, achieved by my research group in a continuous struggle with many difficulties, under nonstimulating economic conditions, often influenced by political factors which are hard to understand from the outside world. The publications of other authors active in the area are covered in several reviews cited in the appropriate place of this text and are included only when necessary to underscore some of the aspects of the work presented.

Our involvement in sulfur-containing ligands has an interesting history. As an undergraduate student (between 1954–1959) I discovered (in the literature) and became fascinated with inorganic rings; at that time sulfur nitride, borazine, metaphosphates and cyclophosphazenes (still called phosphonitriles) were regarded as parts of the chemistry of individual elements (sulfur, boron, silicon, phosphorus) and not as a part of a self-consistent chapter of inorganic chemistry. Several excellent monographs reflected this view [1–5]. My book '*Introduction to the Chemistry of Inorganic Rings*' published first in Romanian, in 1960, one year after I graduated with a BSc degree [6a], translated into Polish [6b] and then much expanded into an English two volume monograph published in 1970 [7], along with a book by H. Garcia-Fernandez [8], were the first to present an integrated view of inorganic ring chemistry, a field which could be comparable and competitive with the chemistry of organic homo- and heterocycles. These were followed by others [9–12] and after the organiza-

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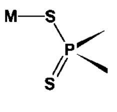
tion of the 1st International Symposium on Inorganic Ring Chemistry in 1975, followed by a regular series of ‘IRIS Symposia’, the new field was accepted as a self-consistent chapter of inorganic chemistry [13].

In 1960 there was no possibility of pursuing my interest in Romania, as all inorganic chemistry carried out in the country was aqueous coordination chemistry, and nobody was involved in any inorganic ring chemistry or organometallic chemistry research. The only possible place at the time, under the existing political conditions, was the former Soviet Union, so I went for a PhD to Moscow, where I worked with the famous organosilicon chemist K.A. Andrianov and received my ‘candidate degree’ (equivalent to PhD) with a thesis on cyclic silicon–nitrogen compounds [14]. In the meantime, the political conditions temporarily relaxed somewhat in my country, and a new opening to the West allowed me to get a Fulbright grant and to work as a post-doc in the USA with the great American chemist Henry Gilman at the University of Iowa, in Ames, IA, during 1966–1968. This was followed by a new post-doc experience, with R. Bruce King, in Athens, Georgia, during 1971–1972 [14]. I returned home, to the ‘Babes-Bolyai’ University in Cluj-Napoca, Romania, full of youthful enthusiasm and with newly gained experience in organolithium, organosilicon, metal carbonyl and transition metal organometallic chemistry. However, continuing this line of research was impossible. In a centrally planned economy the imported reagents had to be ordered much in advance and were received more than a year later (if ever), there were no facilities for inert atmosphere research and everything was difficult. We had to prepare almost any starting materials, certainly the organometallic derivatives, even those which are normally commercially available, like the organotins. Sometimes we devised convenient methods for such reagents, e.g. phenylarsenic chlorides (without realizing at the time that these are chemical warfare agents) [15] or organoantimony chlorides [16]. Still, I did not give up the idea of working in inorganic ring chemistry. The work which could be done should fulfil two conditions: (a) to require no inert atmosphere, (b) to use reagents readily available in the country. The dithiophosphates fulfilled these conditions, since phosphorus pentasulfide was available from an insecticide factory (‘Sinteza’ Oradea) and their anions, $(RO)_2PS_2^-$, were known to form four-membered chelate rings with many metals. This set the stage for inorganic (carbon-free) chelate ring chemistry, a field which offers rich opportunities [17]. My interest in inorganic rings remained vivid, and occasionally I dealt with rings other than chelates (metallacycles), in reviews about the nomenclature of inorganic homo- and heterocycles [18,19], inorganic heterocycles as ligands [20], interconversion reactions of inorganic heterocycles [21], the coverage of inorganic rings in *Chemical Abstracts* [22] and application of graph theory [23] or in the crystal structure investigation of some cyclosilazanes [24] and cyclosilazoxanes [25] prepared earlier. Theoretical investigations on inorganic rings were continued in our group (cyclodisilazanes [26], cyclodiphosphazanes [27]) and included studies about inorganic (carbon-free) fullerene-like molecules [28].

The dithiophosphorus ligands can exhibit various coordination patterns, mainly monodentate (**1**) (rare), bidentate chelating (**2**) and bridging (**3**). The last two can lead to inorganic ring formation.



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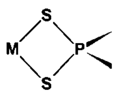

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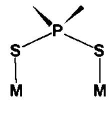

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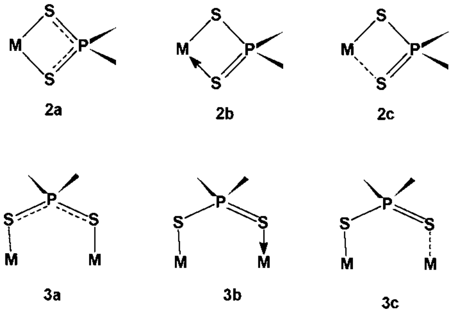
In fact, the coordination patterns of dithiophosphorus ligands are more diversified, since the S–P–S group can behave as isobidentate (symmetrical) or anisobidentate (unsymmetrical), both in chelating and bridging situations (Scheme 1) [29–33].



Scheme 1.

In my work on sulfur-containing ligands I had some excellent coworkers and students, some of which became my colleagues. I would like to mention the names (in alphabetical order) of those who during many years were my companions in the investigation of sulfur-containing ligands: Maria Curtui, who did the solvent extraction work; Rodica Micu-Semeniuc, who started the work on transition metal dithiophosphates and their adducts; Ioan Silaghi-Dumitrescu, a born computer expert, who did the theoretical work; Luminitsa Silaghi-Dumitrescu, who was brave enough to struggle with the dithioarsinates without getting poisoned and to obtain interesting results; Cristian Silvestru, a top-notch synthetician, who was very successful with dithiophosphinates and dichalcogeno–imidodiphosphinates; Anca Silvestru, who had a lot of good luck with the unpredictable chemistry of the tellurium compounds. The names of other coworkers, who spent less time in our laboratory, can be found in the cited references.

In our work we had the privilege of collaboration with a number of foreign colleagues, who did the crystal structures and some spectroscopic characteriza tion (e.g. mass spectra, Mössbauer) of our compounds (again in alphabetical order): H.J. Breunig (Bremen, Germany); A.R. Barron (Houston, TX); F. Caruso (Rome, Italy); J.S. Casas, A. Castiñeiras, A. Sánchez (Santiago de Compostella, Spain); E.E. Castellano (Sao Carlos, Brazil); Raymundo Cea-Olivares (Mexico City, Mexico); J.E. Drake (Windsor, Ontario, Canada), Frank T. Edelmann (Magdeburg, Germany); Mark J. Fink (New Orleans, LA); Marcel Gielen (Brussels, Belgium); Lai Yoong Goh (Singapore); R. Bruce King, G. Newton (Athens, GA); K.C. Molloy (Bath, UK); Josef Novosad (Brno, Czech Republic); K.H. Pannell (El Paso, TX); H.W. Roesky, Mathias Noltemeyer (Göttingen, Germany); M.J. Rozales-Hoz (Mexico City, Mexico); D.B. Sowerby (Nottingham, UK); Ulf Thewalt (Ulm, Germany); J. Weiss (Heidelberg, Germany); the late J.J. Zuckerman (Norman, OK) and Julio Zukerman-Schpector (Sao Paulo, Brazil). With some of them we developed a long standing collaboration and friendship which I am proud of. Thus, an 'invisible college' was created around sulfur-containing ligands, without administration and bureaucracy, based only upon human bonds and co-operation, in spite of the difficulties of the cold war. We made full use of the new opportunities after 1990, when the walls finally collapsed. I am grateful to all these colleagues, whose contribution was essential for the results reported in our joint publications and greatly influenced the quality of these works.

Much of the synthetic work reported here was done in the labs of the 'Babes-Bolyai' University and the X-ray diffraction studies were performed in foreign laboratories. Some preparations were carried out by this author or his coworkers in foreign labs, during visiting periods supported by various fellowships and travel grants (European Community, NATO, Humboldt, DAAD and national agencies) for which we are also grateful.

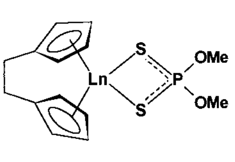
2. Metal dithiophosphates

When we first became involved, the chemistry of dithiophosphato ligands dealt mostly with homoleptic transition metal complexes, $[M\{S_2P(OR)_2\}_n]$ and their adducts with various bases, $[M\{S_2P(OR)_2\}_n]\cdot D$ (D = donor, e.g. amine) [34].

We prepared some nickel bis(dialkyldithiophosphate) adducts with diamines [35–38] and other bases [39–41] and the first crystal structure determinations of the diamine adduct tetramethylethylenediamine-bis(*O*,*O*′-diethyldithiophosphato)nickel(II), $[Ni\{S_2P(OEt)_2\}_2]\cdot Me_2NCH_2CH_2NMe_2$ [42] and *N*,*N*′-diphenylethylenediamine - bis(*O*,*O*′ - diethyldithiophosphato)nickel(II) $[Ni\{S_2P(OEt)_2\}_2]\cdot PhHNCH_2CH_2NHPh$ [43] marked the beginning of a fruitful collaboration with Bryan Sowerby (University of Nottingham, UK).

The structure of mercury(II) bis(isopropyldithiophosphate), $Hg[S_2P(OPr^i)_2]_2$, was reinvestigated recently and interpreted in terms of supramolecular organization [44].

A few organolanthanide dithiophosphates were investigated in collaboration with F.T. Edelmann. Thus, *ansa*-metallocene derivatives, $Me_4C_2(C_5H_4)_2LnS_2P(OMe)_2$ (Ln = Sm, Yb) (**4**) were prepared by the reaction of divalent organolanthanide compounds $Me_4C_2(C_5H_4)_2Ln$ with the disulfides $(RO)_2P(S)S-SP(S)(OR)_2$ [45] and a unique triple bridging coordination mode (**5**) with participation of the alkoxy groups was found in the dimeric organosamarium derivative $[(C_5Me_5)Sm\{S_2P(OMe)_2\}_2]_2$ [46].



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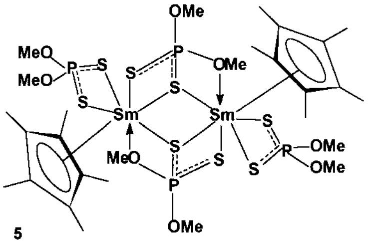

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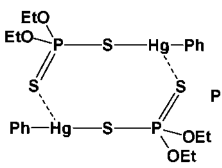
As our interest for Main Group organometallic derivatives increased, the studies of transition metal dithiophosphates were reduced to a minimum.

3. Organometallic dithiophosphates

Only ethylmercury [47], some organothallium [48] and manganese carbonyl [49] dithiophosphates were known as organometallic derivatives before 1970. We prepared and characterized several arylmercury derivatives, $RHg-S(S)P(OR')_2$ (R = Ph, R′ = Me, Et, Ph) [50] and extended the series to organolead dithiophosphates, $Ph_nPb\{S_2P(OR')_2\}_{4-n}$ ($n = 3$, R′ = Me, Et, Pr, Pr^i, Bu; R = 2, R′ = Me, Et, Ph) [51]. We did not have the chance to obtain a crystal structure, but later it has been shown by others [52] that the organomercury dithiophosphates are cyclic dimers (**6**) with unsymmetrically bridging ligands (e.g. $[PhHgS_2P(OEt)_2]_2$), whereas in the triphenyllead diethyldithiophosphate (**7**) the ligand is monodentate [53].



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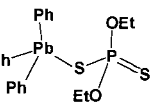

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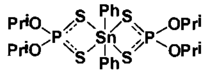
An important step in our work was the collaboration with J.J. Zuckerman in the study of organotin dithiophosphates. Many derivatives were prepared and characterized by multiple spectroscopic methods, including Mössbauer spectroscopy, and some representative compounds were analysed by single crystal X-ray diffraction [54–57]. This lead to the identification of a monodentate coordination of the ligand in $Ph_3Sn-S(S)P(OEt)_2$ [55] and of a symmetric (isobidentate) coordination of diisopropyldithiophosphato ligand in the diphenyltin derivative, $Ph_2Sn\{S_2P(OPr^i)_2\}_2$ containing octahedrally coordinated tin (**8**) [56], differing from the asymmetric (anisobidentate) coordination of diethyldithiophosphate in an analogous diphenyltin derivative, $Ph_2Sn\{S_2P(OEt)_2\}_2$, which contains bicapped tetrahedrally coordinated tin (**9**) [58].



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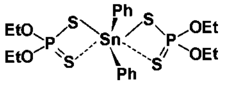

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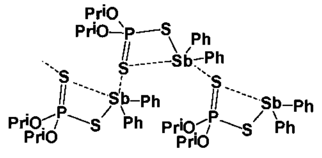
Among diphenylantimony(III) dialkyldithiophosphates, $Ph_2SbS_2P(OR)_2$, the crystal structure of the isopropyl derivative (**10**, R = *iso*-Pr) has been determined.



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The compound is a supramolecular chain-like polymer, formed by intermolecular association through Sb···S secondary bonds (3.172 and 3.266 Å vs. primary Sb–S 2.531 and 2.555 Å) [59].

4. Dithiophosphinates

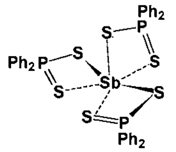
Dithiophosphinates are compounds containing direct P–C bonds and generate the $R_2PS_2^-$ anions. Generally, they are not commercially available and their preparation is a little cumbersome. Therefore, they are much less investigated than the readily available dithiophosphates. Their coordination chemistry is expected to be similar (which is not always true), but they are more stable. We used dialkyl- and diphenyldithiophosphinate anions as ligands in a series of compounds. Again we concentrated more on organometallic derivatives, since before 1970 only some compounds containing organoaluminum, -gallium, -indium [60], -thallium [61] and -tin [62] coordination centers were known, with no X-ray crystal structure reported.

Monodentate coordination, which is rare among dithiophosphorus ligands, was established in triphenylgermanium derivatives, $Ph_3Ge-S(S)PR_2$ (R = Me, Ph), which consist of discrete molecules in the crystal [63] (unlike organolead analogues — cited below).

A series of organotin dialkyl- and diphenyldithiophosphinates, $R_nSn(S_2PR'_2)_{4-n}$ ($n = 2$, 3; R = Me, Bu, Bz, Ph, Cy; R′ = Me, Et, Ph) have been prepared and characterized by spectroscopic and diffractometric methods [64–66]. The crystal structures of $Me_2Sn(S_2PEt_2)_2$ [65] and *cis*-$Cl_2Sn(S_2PPh_2)_2$ [67] were determined; the dimethyltin(IV) compound contains anisobidentate ligands, but in the dichlorotin(IV) derivative the ligand is basically isobidentate. A unique macrocyclic structure of tetrameric trimethyltin(IV) diphenylphosphinate, $[Me_3SnO_2PPh_2]_4$, containing a 16-membered $Sn_4O_8P_4$ inorganic ring [68] was not repeated in triorganotin dithiophosphinates, which seem to be all monomeric.

A series of interesting supramolecular structures were established for lead(II) dithiophosphinates, $Pb(S_2PMe_2)_2$ [69] and $Pb(S_2PPh_2)_2$ [70]. The phenyllead dialkyldithiophosphinates, $Ph_nPb(S_2PR_2)_{4-n}$, (R = Me, Et, Ph) tend to disproportionate and were studied in solution by NMR spectroscopy [71]. In spite of this, other authors were able to obtain crystalline $Ph_2Pb(S_2PPh_2)_2$ and to determine its crystal structure by X-ray diffraction [72] and we found that triphenyllead dimethyldithiophosphinate, $Ph_3PbS_2PMe_2$, forms supramolecular arrays in the solid state through Pb···S secondary bonds ([73].

The first interesting result obtained during our studies on dithiophosphinates was the finding that antimony(III) tris(diphenyldithiophosphinate), $Sb(S_2PPh_2)_3$, displays a very rare pentagonal pyramidal coordination geometry (**11**) [74,75]. This differs from the structure of antimony(III) tris(dithiophosphates), $Sb\{S_2P(OR)_2\}_3$, (R = Me and *iso*-Pr) [76] which are octahedral complexes (**12**) according to X-ray single crystal structure determinations.



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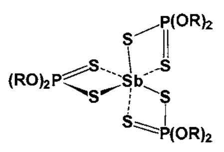

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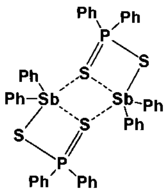
Comparative X-ray diffraction studies of antimony(III) and indium(III) dithiophosphinates, $M(S_2PR_2)_3$ (M = Sb, R = Et; M = In, R = Me and Ph) were carried out in order to asses the role of the lone pairs localised at the metal in determining the coordination geometry [77].

Another interesting finding was the dimeric nature (**13**) of diphenylantimony(III) dialkyldithiophosphinates, $[Ph_2Sb-S(S)PR'_2]_2$, formed through secondary Sb···S bonds (e.g. 3.474 Å vs. primary Sb–S 2.490 Å in $[Ph_2Sb-S(S)PPh_2]_2$) [78,79]. This type of rings, formed through secondary bonds were called ‘quasi-cyclic structures’ [80]. The dimer formation contrasts with the structure of $Me_2Sb-S(S)PMe_2$, which is a supramolecular polymeric array, also formed through Sb···S secondary bonds (3.158 Å vs. primary Sb–S 2.555 Å) [81]. Another dimer, $[(p\text{-}MeC_6H_4)_2Sb-S(S)PEt_2]_2$, differs from the previous ones in that transannular Sb···S interactions are absent (**14**) [82]. The trimethylantimony(V) derivative, $Me_3Sb(S_2PPh_2)_2$, is a monomeric compound (**15**), with a bicapped trigonal bipyramidal geometry [83].



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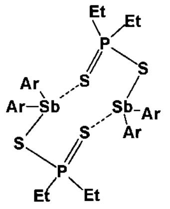

Ar = p-tol

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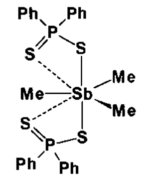

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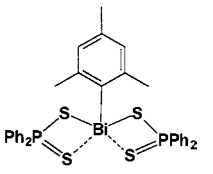
A dimeric association was also observed in a phenoxarsin-10-yl diorganodithiophosphinate, which is the first dimeric organoarsenic(III) 1,1-dithiolate associated through As···S secondary bonding [84].

The bismuth(III) compounds, $Bi(S_2PPh_2)_3$, [75] and $Bi(S_2PMe_2)_3$ [85] are dimers formed through Bi···S secondary bonds with pentagonal bipyramidal coordination geometry of bismuth, whereas $Bi(S_2PEt_2)_3{\cdot}C_6H_6$ is a distorted octahedral monomer, containing a BiS_6 polyhedron lying almost midway between the octahedral and trigonal prismatic coordination geometry [86].

Mesitylbismuth(III) bis(diphenyldithiophosphinate), $MesBi(S_2PPh_2)_2$, is a monomer (**16**), containing five-coordinate bismuth in a distorted square pyramidal geometry and anisobidentate ligands [87].



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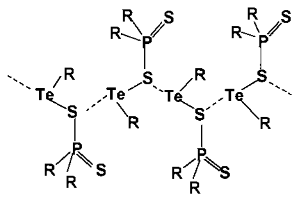
The tellurium compounds also provided some interesting results. Thus, phenyltellurium diphenyldithiophosphinate, $PhTe-S(S)PPh_2$, has a supramolecular structure based upon Te···S secondary bond (3.422 Å vs. primary 2.401 Å) intermolecular association, in which the ligand displays a novel coordination pattern, as illustrated in (**17**) [88,89]. An interesting structure (**18**) was found for $Te_2(S_2PPh_2)_2$, obtained from TeO_2 and $Ph_2P(S)SH$; the compound contains a Te–Te bond (2.723 Å), two five-membered quasi-cyclic Te_2S_2P units and the molecules are associated through Te···Te secondary bonds (3.514 and 3.668 Å) into supramolecular chains [90].



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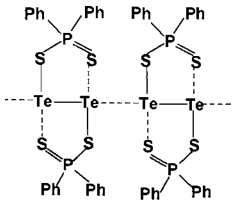

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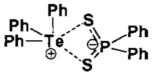
Diphenyltellurium dialkyldithiophosphinates, $Ph_2Te(S_2PR_2)_2$ (R = Me, Et), readily disproportionate into $TePh_2$ and $[R_2P(S)S]_2$, but $Ph_2Te(S_2PPh_2)_2$ could be isolated and its crystal structure has been determined. The compound is monomeric and the ligands are anisobidenate [91]. The coordination geometry of tellurium is ψ-trigonal bipyramidal, with presumably a lone pair in the vacant equatorial site.

Triphenyltelluronium diphenyldithiophosphinate, $[Ph_3Te]^+[S_2PPh_2]^-$, is a quasicyclic ion pair (**19**) with weak Te···S secondary interactions (3.331 and 3.655 Å) [92].



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The stereochemistry of organotellurium dithiophosphinates contributes significantly to the rich structural diversity of tellurium complexes with sulfur ligands [93].

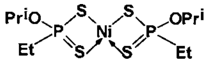
A study on the amine adducts of nickel(II) diphenyldithiophosphinate with substituted ethylenediamines [94] was our early incursion in the transition metal chemistry of dithiophosphinato ligands. More interesting was the cleavage of bis(thiophosphinyl) disulfanes, $R_2P(S)-S-S-P(S)R_2$ (R = Et, Ph), by low-valent transition metal compounds. Thus, the palladium dimer $Pd_2(dcpe)_2$ (dcpe = 1,2-bis(dicyclohexyl)-phosphinoethane) lead to ionic dithiophosphinato chelate complexes $[(dcpe)Pd(S_2PR_2)][S_2PR_2]$ (R = Et, Ph) and dimeric $[Pd(S_2PEt_2)_2]_2$ [95a]. The facile cleavage of bis(diphenylthiophosphinyl) disulfane, $Ph_2P(S)-S-S-P(S)Ph_2$, with dimeric cyclopentadienylchromium tricarbonyl, $[CpCr(CO)_3]_2$, gave purplish–brown $CpCr(CO)_2(S_2PPh_2)$ and blue $CpCr(S_2PPh_2)_2$ [95b]. The structures of some of these products were confirmed by X-ray diffraction.

5. Dithiophosphonates

Dithiophosphonates are hybrid ligands, $R(R'O)PS_2^-$, of intermediate composition between dithiophosphates $(R'O)_2PS_2^-$ and dithiophosphinates, $R_2PS_2^-$.

The extension of the work to dithiophosphonates and an X-ray crystal structure determination (performed at the University of Nottingham) of bis(*O*-isopropyl-ethyldithiophosphonato)nickel(II), $[Ni\{S_2P(OPr^i)Et\}_2]$

[96] produced an interesting result: unsymmetrical (anisobidentate) coordination of the dithio ligand, with distinct P–S (2.031 and 1.900 Å) and Ni–S (2.115 and 2.262 Å) bond lengths, as shown in (**20**), in contrast with all transition metal dithiophosphate complexes, or palladium(II) and platinum(II) dithiophosphonates, $[M\{S_2P(OEt)Ph\}_2]$ (M = Pd, Pt) which are symmetrically (isobidentate) chelated (**21**) [97].



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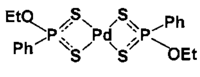
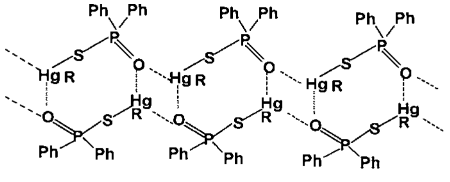


21

Although dithiophosphonates can be interesting ligands, we limited our further work to spectroscopic and magnetic studies of some copper(II) and chromium(III) complexes [98], the study of infrared spectra of methyl(*O*-methyl)dithiophosphonic acid (multiplicity of some bands due to different conformers) [99], and ESR and IR studies of some oxovanadium dithiophosphonates [100]. Some more work with these ligands is currently in progress.

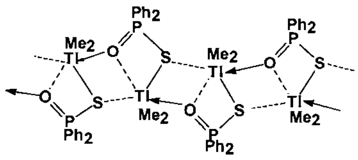
6. Monothiophosphinates

As a natural extension of studies on dithiophosphato and -phosphinato ligands was the investigation of monothiophosphinates. These reagents are apparently more stable and easier to prepare and handle than monothiophosphates, and we concentrated our interest upon them. Some of the work was done during my stay in Santiago de Compostela (Spain), with the group of Professor S.J. Casas. Thus, interesting associated supramolecular structures were identified by X-ray diffraction in monocrystals of $[MeHg(SOPPh_2)]_n$ (**22**) [101] and $[Me_2Tl(SOPPh_2)]_n$ (**23**) [102].



R = Me

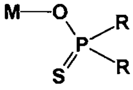
22



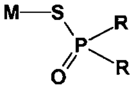
23

The reaction of $GaBu^t_3$ with diphenylthiophosphinic acid gave two isomers (head-to-head and head-to-tail) of dimeric $[Bu^t_2Ga–O(S)PPh_2]_2$ [103].

The monothiophosphinato groups are ambident ligands, able to form primary bonds either through sulfur or oxygen (**24a** and **24b**). Primary bonding through sulfur was observed in the 'soft' metal derivatives, e.g. mercury, thallium, lead, whereas germanium and tin are bonded to oxygen.



24a



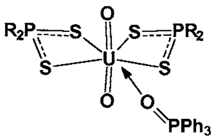
24b

The germanium compound, $Ph_3Ge–O(S)PPh_2$ [104], was found to be monomeric, and contains a Ge–O bond. Some organotin derivatives, i.e. $[Ph_2Sn\{O(S)PPh_2\}_2]$ [104], $Me_2Sn\{O(S)PEt_2\}_2$ [105], $Me_2Sn\{O(S)PPh_2\}_2$ [106], have also been prepared and structurally characterized by X-ray diffraction, with the identification of some more examples of supramolecular structural organization. Thus, $Me_2Sn\{O(S)PEt_2\}_2$ is a monomeric, molecular compound, whereas $Me_2Sn\{O(S)PPh_2\}_2$ contains a chain-like supramolecular array formed through oxygen–tin dative bonds.

Diphenylantimony(III) diphenylmonothiophosphinate, $Ph_2Sb–O(S)PPh_2$, and its dioxo analogue, $Ph_2SbO_2PPh_2$, were both found by X-ray crystallography to have chain-like polymeric structures, with bridging ligands and pseudotrigonal bipyramidal geometry [107]. A series of trimethylantimony bis(monothiophosphinates), $Me_3Sb\{O(S)PR_2\}_2$ (R = Me, Et, Ph), were synthesized and the X-ray crystal structure determination of $Me_3Sb\{O(S)PPh_2\}_2$ revealed monodentate coordination of the ligand through Sb–O bonds (2.114 Å) in a trigonal bipyramidal geometry [108].

7. Solvent extraction studies

Dialkyldithiophosphates are known as potent extraction reagents. With my coworker Maria Curtui, we initiated a program of investigating the possible use of these reagents for the solvent extraction of uranium [109–119], thorium [120–123] and Rare Earths [121,124,125]. Since uranium is more oxophilic than thiophilic, we did not expect to improve the industrial extraction methods of uranium based upon tributylphosphate, but since the country had a nuclear energy program this allowed us to get some financing, including an International Atomic Energy Agency contract [126,127], which was extremely useful for the aquisition of some equipment and chemicals. In the process, we isolated some dioxouranium dithiophosphate and dithiophosphinate triphenylphosphine oxide adducts, $UO_2(S_2PR_2)_2{\cdot}OPPh_3$ (R = alkyl or alkoxy) [128], and the structure (**25**) suggested on the basis of spectroscopic data, was later confirmed by another laboratory with the aid of single crystal X-ray diffraction [129].



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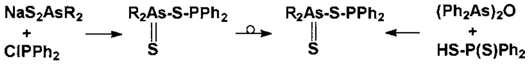
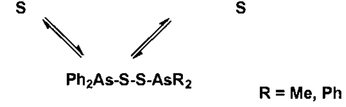
8. Dithioarsinates and other arsenic–sulfur compounds

The initial plans of comparing dithioarsinates with dithiophosph(in)ates grew into a larger area of investigations on chalcogeno–organoarsenic compounds [130]. Within this program, carried by my former student, Luminitsa Silaghi-Dumitrescu, the coordination and self-assembly in the crystal structure of $K[Me_2AsS_2]\cdot 2H_2O$ was established by X-ray diffraction (carried out at Nottingham) [131]. A number of dimethyl- and diphenyldithioarsinates of Main Group metals [Sn(IV), Pb(II), As(III), Sb(III), Bi(III)] were synthesized [132] and the crystal structure of $In(S_2AsR_2)_3$ (R = Me, Ph) was determined [133]. A series of organosilicon, -germanium, -lead, [134], and -tin [135,136] derivatives of dimethyl- and diphenyldithioarsinic acids, $Ph_{4-n}M(S_2AsR_2)_n$ (M = Si, Ge, Sn, Pb; $n = 1$ and 2, R = Me, Ph) were prepared and the crystal structure of $Me_2Sn(S_2AsMe_2)_2$ was established by X-ray diffraction [136].

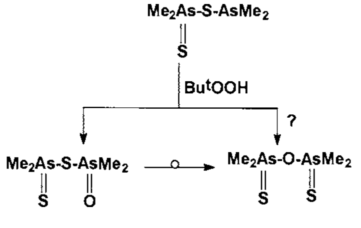
Antimony(III) and phenylantimony(III) dimethyldithioarsinates were synthesized and the crystal structure of $Ph_2Sb{-}S(S)AsMe_2$, revealed the first coordination polymer associated via bridging dimethyldithioarsinate ligands involving Sb···S secondary bonds (2.830 Å) [137], whereas the diphenyldithioarsinate is a dimer, $[Ph_2Sb{-}S(S)AsPh_2]_2$, also formed through Sb···S secondary bonds (3.369 Å) [78].



Scheme 2.



Scheme 3.



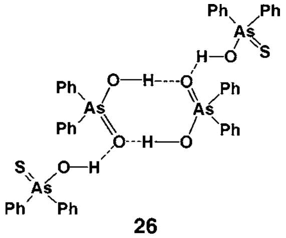
Scheme 4.

Bismuth(III) dimethyldithioarsinate, $Bi(S_2AsMe_2)_3$ was found to be a dimer formed through Bi–S secondary bonding, with pentagonal bipyramidal geometry at the bismuth centers [138], the structure being similar to that of the analogous bismuth(III) dimethyldithiophosphinate.

A sulfotropic molecular rearrangement (Scheme 2) of diphenylphosphinyl diorganodithioarsinates, $R_2As(S){-}S{-}PPh_2$, with the formation of diorganoarsenic(III) diphenyldithiophosphinates, $R_2As{-}S(S)PPh_2$, was discovered when Ph_2PCl was reacted with sodium dithioarsinates, NaS_2AsR_2 (R = Me, Ph) [139].

Another sulfotropic molecular rearrangement of tetraorganodiarsine disulfides (Scheme 3) was found when diphenylarsenic dichloride reacted with sodium dithioarsinates [140].

The oxidation of $(Ph_2As)_2Q$ (Q = O or S) with *tert*-butylhydroperoxide and sulfur in 1:1 and 1:2 molar ratio produces the compounds $Ph_2As(Q){-}Q{-}AsPh_2$ and $Ph_2As(Q){-}Q{-}AsPh_2Q$ (Q = O or S), respectively. The dioxidation products are less stable and on recrystalisation an unusual mixed supramolecular adduct, $[Ph_2As(O)OH\cdot Ph_2As(S)OH]_2$ self-assembled through hydrogen bonds (**26**), was isolated [141].



26

The first oxygen-bridged diorganoarsenic(V) compound, $Me_2As(S){-}O{-}As(S)Me_2$, along with $Me_2As(S){-}S{-}As(O)Me_2$, was obtained by oxidation of tetramethyldiarsine disulfide $(Me_2AsS)_2$ with *tert*-butylperoxide under anhydrous conditions; the molecular structure of the former was established by single crystal X-ray diffraction. The formation of the oxo-bridged isomer is unexpected and can be rationalized in terms of an oxotropic rearrangement of the sulfur-bridged compound (Scheme 4).

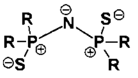
Ab initio calculations predict that the oxo-bridged species are more stable than the thio-bridged isomer [142].

9. Other thioligands

Some other sulfur-containing ligands were occasionally used in our laboratory. Examples include the synthesis and characterization of some nickel(II) [143] and cobalt(II) [144] diphenylthiophosphinylthioureas, organotin dithiocarboxylates [145,146], salts and complexes of the $P_2S_8^{-2}$ anion [147], tetrathiomolybdates and tetrathioarsenates [148]. These topics were not developed further. I had also some interest and plans in sulfur–nitrogen chemistry [149–151] but the first experimental investigations were disappointing and I gave up the subject.

10. Dichalcogenoimidodiphosphinates and related inorganic chelate rings

The dichalcogenoimidodiphosphinato anions, introduced by Alfred Schmidpeter [152], are versatile, readily prepared ligands, extremely useful for the formation of six-membered, inorganic (carbon-free) chelate rings [153]. We became interested in this class in the early 1970s [154], and the subject was developed later with my coworker Cristian Silvestru, in collaboration with various foreign colleagues, in particular Raymundo Cea-Olivares in Mexico and John E. Drake in Canada. The structure of the neutral dithio proligand $Ph_2(S)P-NH-P(S)Ph_2$ was determined independently in three different laboratories [155] and was followed by the synthesis and X-ray structure analysis of unsymmetrical $Me_2(S)P-NH-P(S)Ph_2$ [156], $Ph_2(O)P-NH-P(S)Ph_2$ and its dimeric sodium salt $\{Na[OPh_2PNPPh_2S]{\cdot}THF\}_2$ [157], isomeric $Me_2(S)P-NH-P(O)Ph_2$ and $Me_2(O)P-NH-P(S)Ph_2$ [158], the diphenyl-alkoxy derivative $Ph_2(S)P-NH-P(O)(OEt)_2$, its potassium salt $K[SPh_2PNP(OEt)_2O]{\cdot}H_2O$ and $Ph_2(O)P-NH-P(O)(OEt)_2{\cdot}1/2HCl{\cdot}1/4H_2O$ [159]. In all these neutral proligands and their anions the P–N–P fragment is bent (**27**), but unexpectedly, a linear P–N–P fragment (**28**) was found in the anion $[SPh_2PNPPh_2S]^-$ present in the crystal structure of bis(triphenylphosphine)iminium dithiotetraphenylimidodiphosphinate, $[Ph_3PNPPh_3]^+[SPh_2PNPPh_2S]^-$ [160].



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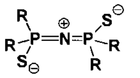

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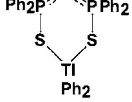
The neutral molecules are associated through N–H···S or N–H···O hydrogen bonds, to form dimers or chain-like polymers, and the potassium salt cited forms a supramolecular architecture based upon electrostatic interactions.

When we became interested in dichalcogenoimidodiphosphinato ligands, most of the compounds reported in the literature were transition metal homoleptic chelate complexes $M(QR_2PNPR_2Q)_n$, where Q = O, S and n = oxidation state of the metal. For this reason we concentrated our attention mostly on the identified niche: (a) Main Group metal derivatives; (b) monocyclic compounds; and (c) compounds containing organometallic coordination centers. In the following, the results will be briefly presented in the order of Periodic Table.

A spiro-bicyclic chelate complex, bis(tetraphenylimidodiphosphinato)beryllium, $Be(OPh_2PNPPh_2O)_2$, an inorganic analog of beryllium bis(β-diketonates), was known in the literature [161], but its molecular structure was established by X-ray diffraction in collaboration with Brazilian crystallographers [162]. The only other Group 2 known complex is a solvated barium derivative, $Ba(SPh_2PNPPh_2S)_2{\cdot}2dme$ (dme = dimethoxyethane) [163].

A monocyclic diphenylthallium(III) tetraphenyldithioimidodiphosphinate, $[Ph_2Tl(SPPh_2)_2N]$ (**29**), containing a new inorganic (carbon-free) TlS_2P_2N metallocycle, was prepared and structurally characterized in a collaboration with Spanish coleagues [164].



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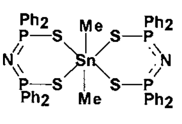
A series of organotin deriatives, $R_{4-n}Sn(SPh_2PNPPh_2S)_n$ (n = 2, R = Me, Bu; n = 1, R = Me, Bz, Ph) was prepared and characterised by spectroscopic methods [165]. Some derivatives were investigated by X-ray diffraction. Thus, $Me_2Sn(SPh_2PNPPh_2)_2$ was found to contain octahedrally coordinated tin, in a symmetrical spiro-bicyclic structure (**30**) [166], whereas (tetraphenyldithioimidodiphosphinato)trimethyltin(IV) displays an unique supramolecular, chain-like structure (**31**) containing a bridging SPR_2NPR_2S ligand, which forms a primary Sn–S bond (2.517 Å) and a secondary Sn···S bond (3.627 Å) leading to intermolecular association [167]. With oxothioimidodiphosphinates the first crystal structures (**32**) of mixed chalcogen derivatives, $R_2Sn(OPh_2PNPPh_2S)_2$ (R = Me or Ph) were reported [168]. The dioxoligand derivative $Bu_2Sn(OPh_2PNPh_2O)_2$, is also a *trans*-octahedral spiro-bicyclic compound [169].



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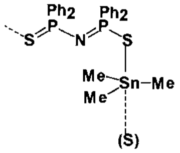

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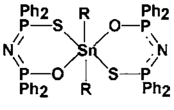


R = Me, Ph

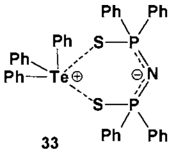
32

The lead(II) derivative, $Pb(SPh_2PNPPh_2S)_2$, is a spiro-bicyclic compound containing a new inorganic (carbon-free) PbS_2P_2N chelate ring and $Pb{\cdots}(\eta^6\text{-}C_6H_5)$ interactions [170]. Organolead derivatives were also prepared [171].

Dichlorodiphenylantimony(V) derivatives of oxo- and thioimidodiphosphinic acids, containing novel inorganic SbO_2P_2N and $SbOSP_2N$ rings and distorted octahedral antimony, $Ph_2SbCl_2(OPh_2PNPPh_2X)$ (X =

O, S), were prepared and characterized by X-ray diffraction [172].

Triphenyltelluronium(IV) dichalcogenoimidodiphosphinates, containing novel six-membered $TeXYP_2N$ chelate quasi-cyclic structures were prepared and the X-ray structures of $Ph_3Te^+[(SPPh_2)_2N]^-$ (**33**) [92], $Ph_3Te^+[SPh_2PNPPh_2O]^-$ and $Ph_3Te^+[(OPPh_2)_2N]^-$ [173] were determined. Thus, $Ph_3Te^+[(SPPh_2)_2N]^-$ is a quasi-cyclic species in which the Ph_3Te^+ cations and $[(SPPh_2)_2N]^-$ anions are chelated through long Te···S bonds (3.264 and 3.451 Å) and five-coordinate tellurium is in a distorted square planar geometry.



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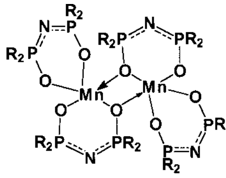
Some work with transition metal dichalcogenoimidodiphosphinates was also performed by our group, at home or during visits abroad.

The manganese(II) complexes of dichalcogenoimidodiphosphinato ligands show a peculiarity. Thus, the monothio ligand forms a monomeric complex, $Mn(SPPh_2NPPh_2O)_2$ with a distorted tetrahedral MnO_2S_2 core, whereas the dioxo ligand gives a dimeric $[Mn(OPPh_2NPPh_2O)_2]_2$ complex (**34**), with a four-membered Mn_2O_2 ring associated with six-membered MnO_2P_2N rings, and containing five-coordinate trigonal bipyramidal manganese [174]. With the dithio ligand only the monocyclic $(CO)_4Mn(SPh_2P)_2N$ is formed [175].



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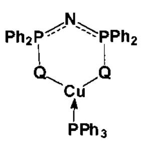
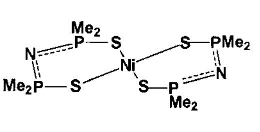
The X-ray crystal structure analysis of (tetraphenyldithioimidodiphosphinato) (triphenylphosphine)-copper(I), $(Ph_3P)Cu(SPPh_2)_2N$, confirmed the first monocyclic compound, obtained from $Cu(PPh_3)_2NO_3$ with the potassium salt of the ligand [176a]. The related gold(I) compound $(Ph_3P)Au(SPPh_2)_2N$, has also been prepared and characterized structurally; it contains an unsymmetrical AuSPNPS quasi-cylic system [176b]. Displacement of triphenylphosphine from $Cu(PPh_3)_2$-NO_3 and $Co(PPh_3)_2Cl_2$ occurred with a diselenoimidodiphosphinato ligand, with the formation of $(PPh_3)Cu(SePh_2P)_2N$ and $Co(SePh_2PNPPh_2Se)_2$, containing the novel $CuSe_2P_2N$ and $CoSe_2P_2N$ inorganic metallocycles (**35**), as established by X-ray diffraction [177].



35a Q = S
35b Q = Se

The tetramethyldithioimidodiphosphinato ligand was found to form a cobalt(II) complex, $Co(SMe_2$-$PNPMe_2S)_2$, containing a rare tetrahedral CoS_4 core [178], also found in $Co(SMe_2PNPPh_2S)_2$ [156].

An unexpected result was obtained in nickel complexes. Both tetrahedral and square planar NiS_4 cores were found in nickel(II) bis(dithioimidodiphosphinato) chelates $Ni(SPh_2PNPR_2S)_2$ (R = Me, Ph). With R = Me the metal coordination is square planar (**36**), whereas for R = Ph a tetrahedral coordination geometry (**37**) is observed [179]. This situation was called ‘heterogeometrism’ [33,80]. The monothio ligand formed the first nickel(II) complex containing a tetrahedral NiO_2S_2 coordination center [180].



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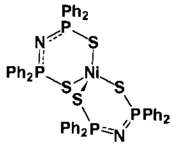

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The reaction with trinuclear ruthenium carbonyls produced a rupture of a P=S bond in the dithioimidodiphosphinate and the X-ray crystal structures of $[(\mu_2\text{-}H)Ru_3(\mu_3\text{-}S)(\mu_2\text{-}SPPh_2NPPh_2)(CO)_8]$ and $[(\mu_2\text{-}H)Ru_3(\mu_2\text{-}SPPh_2NPPh_2)(CO)_9]$ formed in this reaction were determined [181].

11. Theoretical studies

Theoretical studies were carried out in my group by Ioan Silaghi-Dumitrescu. In the beginning he used punched cards, going back and forth to the University Computer Center. Then, we managed to get a PC without monitor and he used his home TV for this purpose. After 1990, when the computing facilities improved greatly so did our theoretical interests expand, to include inorganic (carbon-free) fullerene analogues (cited above) and other species not related to this review.

The first theoretical calculations dealt with normal coordinate analyses, Urey–Bradley force field calculations and interpretation of vibrational spectra of dimethyldithiophosphinato anion [182] (a subject revisited recently [183]) and of its nickel(II) chelate $Ni(S_2PMe_2)_2$ [184], as well as of bis(*O*-isopropylethyldithiophosphonato)nickel(II) [185], which gave a clearer picture of the relation between the vibrational spectra and coordination behavior of organodithiophosphorus ligands [186].

The theoretical studies at the time also included: CNDO/2 calculations of electronic structures of $R_2P(S)SH$ (R = OMe, OPr, Me) and their anions [187]; a molecular orbital study of bis(dimethyldithiophosphinato)nickel(II) [188]; the chelating versus bridging coordination of dithiophosphates in copper complexes discussed on the basis of an EHMO study [189].

The normal coordinate analysis of the vibrational spectrum was also applied to the dimethyldithioarsinato anion, $Me_2AsS_2^-$ [190].

Other theoretical works reported include the study of the electronic structure and force constants of the dithionitronium cation NS_2^+ [191] and the electronic structure and bonding in the thiophosphoryl cation PS^+ [192].

In the chemistry of chalcogeno–organoarsenic compounds the heats of formation were determined from molecular orbital calculations for di- and tetrahalogeno derivatives of tetramethyldiarsine oxide [193] and tetramethyldiarsane–chalcogen derivatives [194].

12. Biological activity

Some of the organometallic (tin and antimony) derivatives prepared in our laboratory were found to display antitumor activity [195–197]. Thus, the first organoantimony(III) compounds possessing antitumor properties were the diphenylantimony(III) derivatives of dithiophosphorus ligands, $Ph_2SbS(S)PPh_2$ and $Ph_2SbS(S)P(OPr^i)_2$. In collaboration with Dr Carmen Socaciu, my former PhD student turned biochemist, and Dr Adela Bara from the Oncologic Institute of Cluj-Napoca, the antitumor activity and inhibitory effects of some diphenyltin(IV) and diphenylantimony(III) derivatives, $Ph_2M(S_2PR_2)_n$ (M = Sn, $n = 2$; M = Sb, $n = 1$; R = Ph, OPr^i) in vitro and in vivo on Ehrlich ascites tumor [198,199], as well as the in vivo activity against P388 leukemia [200]. The mutagenic potential of some diphenylantimony(III) dithiophosphorus derivatives [201] and the genotoxicity of these metal-based antineoplastics was evaluated by SOS Chromotest and cytogenetic analysis [202]. The activity of organoatimony compounds is similar or sometimes higher than that of the analogous organotin compounds. In view of the intensive investigation of organotin compounds as potential antitumor agents [203] this suggests that organoantimony compounds would deserve more attention.

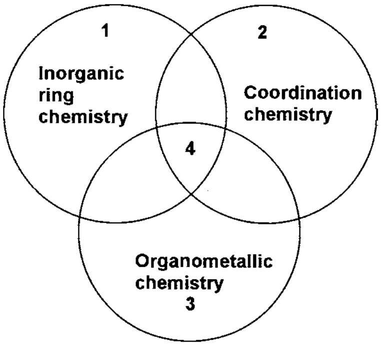

Fig. 1. Interdisciplinary areas of inorganic chemistry from the overlap of traditional areas. 1–2: inorganic (carbon-free) chelate rings; 1–3: inorganic rings containing organometallic moieties; 2–3: complex compounds with organometallic coordination centers; 4: inorganic (carbon-free) chelate rings with organometallic coordination centers.

13. Conclusions and outlook

The results presented here demonstrate the versatility of sulfur containing ligands (dithiophosphates, -phosphinates and -phosphonates, dithioarsinates and dichalcogenoimidodiphosphinates) and their oxo analogues. The compounds investigated display a broad diversity of compositions and structures and include metal and organometallic derivatives, at the interface between the traditional branches of inorganic chemistry: coordination, organometallic and inorganic ring chemistry (Fig. 1). Quite often some Main Group metal derivatives undergo intermolecular self-assembly and self-organisation in the solid state, thus opening the entry into supramolecular organometallic chemistry [204]. The research described was carried out in a broad international cooperation.

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References

[1] M. Goehring, Ergebnisse und Probleme der Chemie der Schwefelstickstoff Verbindungen, Akademie Verlag, Berlin, 1957.
[2] K. Niedenzu, Boron–Nitrogen Compounds, Academic Press, London, 1965.
[3] S. Pantel, M. Becke-Goehring, Sechs- und achtgliedrige Ringsysteme in der Phosphorus-Stickstoff Chemie, Springer Verlag, Berlin, 1969.
[4] H.R. Allcock, Phosphorus–Nitrogen Compounds. Cyclic, Linear and High-Polymeric Systems, Academic Press, New York, 1972.
[5] H.G. Heal, The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus, Academic Press, London, 1970.
[6] (a) I. Haiduc, Introducere in chimia ciclurilor anorganice [Introduction to the chemistry of inorganic rings], Editura

Academiei, Bucuresti, 1960 (in Roumanian). (b) I. Haiduc, Wstep do chemii nieorganicznych zwiazkow pierscienyowych, PWN Warszawa, 1964 (Polish translation).

[7] I. Haiduc, The Chemistry of Inorganic Ring Systems, vols. 1–2, Wiley–Interscience, London, 1970.

[8] (a) H. Garcia-Fernandez, Les hétérocycles en chimie minérale, Hermann, Paris, 1964 (in French). (b) H. Garcia-Fernandez, Quimica heterociclica inorganica, Editorial Alhambra, Madrid, 1973 (in Spanish).

[9] H.R. Allcock, Heteroatom Ring Systems and Polymers, Academic Press, New York, 1967.

[10] D.A. Armitage, Inorganic Rings and Cages, Edward Arnold, London, 1972.

[11] I. Haiduc, D.B. Sowerby (Eds.), The Chemistry of Inorganic Homo- and Heterocycles, vols. 1–2, Academic Press, London, 1987.

[12] H.W. Roesky, Rings, Clusters and Polymers of Main Group and Transition Elements, Elsevier, Amsterdam, 1989.

[13] R. Steudel (Ed.), The Chemistry of Inorganic Ring Systems, Elsevier, Amsterdam, 1992 (Plenary lectures at the IRIS VI Symposium in Berlin, 18–22 August, 1991).

[14] My works published during this period are listed in Rev. Roum. Chim. 42 (1997) 494 in a presentation on the occasion of my 60th anniversary.

[15] L. Silaghi-Dumitrescu, I. Haiduc, Synth. React. Inorg. Metal-Org. Chem. 13 (1983) 475.

[16] I. Haiduc, C. Silvestru, Inorg. Synth. 23 (1985) 194.

[17] I. Haiduc, I. Silaghi-Dumitrescu, Coord. Chem. Rev. 74 (1986) 127.

[18] I. Haiduc, Rev. Inorg. Chem. 2 (1980) (1980) 219.

[19] I. Haiduc, in: R. Steudel (Ed.), The Chemistry of Inorganic Ring Systems, Elsevier, Amsterdam, 1992, p. 451.

[20] I. Haiduc, Chem. Britain 17 (1981) 330.

[21] I. Haiduc, Rev. Inorg. Chem. 4 (1982) 179.

[22] I. Haiduc, J. Chem. Inf. Comput. Sci. 23 (1983) 74.

[23] I. Haiduc, Phosphorus Sulfur Silicon 64 (1992) 169.

[24] P. Clare, D.B. Sowerby, I. Haiduc, J. Organomet. Chem. 236 (1982) 293.

[25] P. Clare, D.B. Sowerby, I. Haiduc, J. Organomet. Chem. 310 (1986) 161.

[26] (a) I. Silaghi-Dumitrescu, I. Haiduc, Inorg. Chim. Acta 112 (1986) 159. (b) F. Lara-Ochoa, I. Silaghi-Dumitrescu, I. Haiduc, Main Group Chem. 1 (1996) 387. (c) I. Silaghi-Dumitrescu, F. Lara-Ochoa, I. Haiduc, J. Mol. Struct. (TEOCHEM) 397 (1997) 213.

[27] (a) I. Haiduc, I. Silaghi-Dumitrescu, Rev. Roum. Chim. 36 (1991), 527. (b) I. Haiduc, I. Silaghi-Dumitrescu, Phosphorus Sulfur Silicon 65 (1992) 53. (c) I. Silaghi-Dumitrescu, I. Haiduc, Stud. Univ. Babes-Bolyai Chem. 38 (1993) 183. (d) I. Silaghi-Dumitrescu, I. Haiduc, Phosphorus Sulfur Silicon 91 (1994) 21. (e) I. Silaghi-Dumitrescu, A. Horea, S. Pascu, L. Silaghi-Dumitrescu, I. Haiduc, Phosphorus Sulfur Silicon 124–125 (1997) 441. (f) I. Silaghi-Dumitrescu, F. Lara-Ochoa, I. Haiduc, Main Group Chem. 2 (1998) 309.

[28] (a) I. Silaghi-Dumitrescu, I. Haiduc, D.B. Sowerby, Inorg. Chem. 32 (1993) 3755. (b) I. Silaghi-Dumitrescu, F. Lara-Ochoa, P. Bishof, I. Haiduc, J. Mol. Struct. (THEOCHEM) 367 (1996) 47. (c) I. Silaghi-Dumitrescu, F. Lara-Ochoa, I. Haiduc, J. Mol. Struct. (THEOCHEM) 370 (1996) 17. (d) I. Silaghi-Dumitrescu, A. Kuhn, I. Haiduc, Fullerene Sci. Technol. 7 (1999) 841.

[29] I. Haiduc, Rev. Inorg. Chem. 3 (1981) 353.

[30] I. Haiduc, D.B. Sowerby, S.-F. Lu, Polyhedron 14 (1995) 3389.

[31] C. Silvestru, I. Haiduc, Coord. Chem. Rev. 147 (1996) 117.

[32] I. Haiduc, D.B. Sowerby, Polyhedron 15 (1996) 2469.

[33] I. Haiduc, Coord. Chem. Revs 158 (1997) 325.

[34] J.R. Wasson, G.M. Woltermann, H.J. Stoklosa, Fortschr. Chem. Forsch. Top. Curr. Chem. 35 (1973) 65.

[35] R. Micu-Semeniuc, L. Dumitrescu-Silaghi, I. Haiduc, Inorg. Chim. Acta 17 (1976) 5.

[36] R. Constantinescu, F. Martinas, I. Haiduc, Inorg. Chim. Acta 19 (1976) 105.

[37] R. Micu-Semeniuc, L. Dumitrescu-Silaghi, I. Haiduc, Inorg. Chim. Acta 33 (1979) 281.

[38] R. Micu-Semeniuc, F. Vesa, I. Haiduc, Stud. Univ. Babes-Bolyai Chem. 25 (1980) 44.

[39] R. Micu-Semeniuc, L. Silaghi-Dumitrescu, N. Chirila, I. Haiduc, Rev. Roum. Chim. 25 (1980) 1025.

[40] R. Micu-Semeniuc, C. Opris, I. Haiduc, Rev. Roum. Chim. 25 (1980) 1489.

[41] I. Haiduc, R. Micu-Semeniuc, L. Silaghi-Dumitrescu, Syn. React. Inorg. Metal-Org. Chem. 23 (1993) 1629.

[42] D.B. Sowerby, I. Haiduc, Inorg. Chim. Acta 17 (1976) L15.

[43] D.B. Sowerby, I. Haiduc, Inorg. Nucl. Chem. Lett. 12 (1976) 791.

[44] J.S. Casas, E.E. Castellano, J. Ellena, I. Haiduc, A. Sánchez, J. Sordo, J. Chem. Crystallogr. 29 (1999) 831.

[45] F.T. Edelmann, M. Riekhoff, I. Haiduc, I. Silaghi-Dumitrescu, J. Organomet. Chem. 447 (1993) 203.

[46] M. Rieckhoff, M. Noltemeyer, F.T. Edelmann, I. Haiduc, I. Silaghi-Dumitrescu, J. Organomet. Chem. 469 (1994) C19.

[47] (a) P.F. Hu, W. Cheng, Sci. Sinica 6 (1957) 661. (b) P.F. Hu, W. Cheng, Chem. Abstr. 52 (1958) 7186h.

[48] F. Bonati, G. Mighetti, Inorg. Chim. Acta 3 (1969) 161.

[49] (a) F.A. Hartman, A. Wojcicki, Inorg. Nucl. Chem. Lett. 2 (1966) 303. (b) R. Lambert, T.A. Manuel, Inorg. Chem. 5 (1966) 1287.

[50] I. Haiduc, E. Veres, Syn. React. Inorg. Metal-Org. Chem. 5 (1975) 115.

[51] I. Haiduc, F. Martinas, D. Ruse, M. Curtui, Syn. React. Inorg. Metal-Org. Chem. 5 (1975) 103.

[52] E.M. Vazquez-Lopez, A. Castineiras, A. Sanchez, J.S. Casas, J. Sordo, J. Crystallogr. Spectrosc. Res. 22 (1992) 403.

[53] M.G. Begley, C. Gafney, P.G. Harrison, A. Steel, J. Organomet. Chem. 289 (1985) 281.

[54] K.C. Molloy, M.B. Hossain, D. Van der Helm, J.J. Zuckerman, I. Haiduc, Inorg. Chem. 18 (1979) 3507.

[55] J.L. Lefferts, K.C. Molloy, J.J. Zuckerman, I. Haiduc, C. Guta, D. Ruse, Inorg. Chem. 19 (1980) 1662.

[56] K.C. Molloy, M.B. Hossain, D. Van der Helm, J.J. Zuckerman, I. Haiduc, Inorg. Chem. 19 (1980) 2041.

[57] J.L. Lefferts, K.C. Molloy, J.J. Zuckerman, I. Haiduc, M. Curtui, C. Guta, D. Ruse, Inorg. Chem. 19 (1980) 2861.

[58] B.W. Liebich, M. Tomassini, Acta Crystallogr. Sect. B 34 (1978) 944.

[59] C. Silvestru, M. Curtui, I. Haiduc, M.J. Begley, D.B. Sowerby, J. Organomet. Chem. 426 (1992) 49.

[60] G.E. Coates, R.N. Mukherjee, J. Chem. Soc. (1964) 1295.

[61] F. Bonati, S. Cenini, R. Ugo, J. Organomet. Chem. 9 (1967) 395.

[62] W. Kuchen, A. Judat, J. Metten, Chem. Ber. 98 (1965) 3981.

[63] C. Silvestru, R.A. Toscano, J. Cardenas, R. Cea-Olivares, A. Silvestru, I. Haiduc, Polyhedron 14 (1995) 2231.

[64] C. Silvestru, I. Haiduc, S. Klima, U. Thewalt, M. Gielen, J.J. Zuckerman, J. Organomet. Chem. 327 (1987) 181.

[65] C. Silvestru, F. Ilies, I. Haiduc, M. Gielen, J.J. Zuckerman, J. Organomet. Chem. 330 (1987) 315.

[66] C. Silvestru, I. Haiduc, J. Organomet. Chem. 365 (1989) 83.

[67] R. Gavino-Ramirez, R.A. Toscano, C. Silvestru, I. Haiduc, Polyhedron 15 (1996) 3857.

[68] M.G. Newton, I. Haiduc, R.B. King, C. Silvestru, J. Chem. Soc. Chem. Commun. (1993) 1229.

[69] C. Silvestru, I. Haiduc, R. Cea-Olivares, S. Hernandez-Ortega, Inorg. Chim. Acta 233 (1995) 151.

[70] K.H. Ebert, H.J. Breunig, C. Silvestru, I. Stefan, I. Haiduc, Inorg. Chem. 33 (1994) 1695.
[71] C. Silvestru, A. Silvestru, I. Haiduc, R.G. Ramirez, R. Cea-Olivares, Heteroatom Chem. 15 (1994) 327.
[72] S.N. Olafson, T.N. Petersen, P. Andersen, Acta Chem. Scand. 50 (1996) 745.
[73] F.T. Edelmann, I. Haiduc, H.-G. Schmidt, M. Noltemeyer, C. Silvestru, Polyhedron 17 (1998) 2043.
[74] M.J. Begley, D.B Sowerby, I. Haiduc, J. Chem. Soc. Chem. Commun. (1980) 64.
[75] M.J. Begley, D.B. Sowerby, I. Haiduc, J. Chem. Soc. Dalton Trans. (1987) 145.
[76] D.B. Sowerby, I. Haiduc, A. Barbul-Rusu, M. Salajan, Inorg. Chim. Acta 68 (1983) 8796.
[77] J. Zukerman-Schpector, I. Haiduc, C. Silvestru, R. Cea-Olivares, Polyhedron 14 (1995) 3087.
[78] C. Silvestru, L. Silaghi-Dumitrescu, I. Haiduc, M.J. Begley, M. Nunn, D.B. Sowerby, J. Chem. Soc. Dalton Trans. (1986) 1031.
[79] M.N. Gibbons, C. Silvestru, I. Haiduc, D.B. Sowerby, Polyhedron 15 (1996) 4573.
[80] I. Haiduc, Phosphorus Sulfur Silicon 93/94 (1994) 345.
[81] K.H. Ebert, H.J. Breunig, C. Silvestru, I. Haiduc, Polyhedron 13 (1994) 2531.
[82] C. Silvestru, I. Haiduc, R. Kaller, K.H. Ebert, H.J. Breunig, Polyhedron 12 (1993) 2611.
[83] C. Silvestru, D.B. Sowerby, I. Haiduc, K.H. Ebert, H.J. Breunig, Main Group Metal Chem. 17 (1994) 505.
[84] R. Cea-Olivares, J.-G. Alvarado, G. Espinosa-Perez, C. Silvestru, I. Haiduc, J. Chem. Soc. Dalton Trans. (1994) 2191.
[85] F.T. Edelmann, M. Noltemeyer, I. Haiduc, C. Silvestru, R. Cea-Olivares, Polyhedron 13 (1994) 547.
[86] D.B. Sowerby, I. Haiduc, J. Chem. Soc. Dalton Trans. (1987) 1257.
[87] K.H. Ebert, R.E. Schulz, H.J. Breunig, C. Silvestru, I. Haiduc, J. Organomet. Chem. 470 (1994) 93.
[88] A. Silvestru, I. Haiduc, K.H. Ebert, H.J. Breunig, Inorg. Chem. 33 (1994) 1253.
[89] A. Silvestru, I. Haiduc, K.H. Ebert, H.J. Breunig, D.B. Sowerby, J. Organomet. Chem. 284 (1994) 253.
[90] M.G. Newton, R.B. King, I. Haiduc, A. Silvestru, Inorg. Chem. 32 (1993) 3795.
[91] A. Silvestru, I. Haiduc, H.J. Breunig, K.H. Ebert, Polyhedron 14 (1995) 1175.
[92] A. Silvestru, I. Haiduc, R.A. Toscano, H.J. Breunig, Polyhedron 14 (1995) 2047.
[93] I. Haiduc, R.B. King, M.G. Newton, Chem. Rev. 94 (1994) 301.
[94] F. Dogar, L. Silaghi-Dumitrescu, R. Grecu, I. Haiduc, Rev. Roum. Chim. 31 (1986) 79.
[95] (a) R. Landtiser, J.T. Mague, M.J. Fink, C. Silvestru, I. Haiduc, Inorg. Chem. 34 (1995) 6141. (b) L.Y. Goh, W.K. Leong, P.H. Leung, Z. Weng, I. Haiduc, J. Organomet. Chem. 607 (2000) 64.
[96] S.P. Bone, D.B. Sowerby, R. Constantinescu, I. Haiduc, J. Chem. Res. (S)69 (1979) (M)0933.
[97] J.P. Fackler, Jr, L.D. Thompson, Inorg. Chim. Acta 48 (1981) 45.
[98] I. Haiduc, L. David, O. Cozar, R. Micu-Semeniuc, G. Mezei, M. Armenean, J. Mol. Struct. 482/483 (1999) 153.
[99] R. Grecu, R. Constantinescu, I. Silaghi-Dumitrescu, I. Haiduc, J. Mol. Struct. 218 (1990) 111.
[100] O. Cozar, R. Semeniuc, V. Znamirovschi, I. Haiduc, Rev. Roum. Phys. 33 (1988) 1131.
[101] J.S. Casas, A. Castiñeiras, I. Haiduc, A. Sánchez, J. Sordo, E. Vázquez-López, Polyhedron 16 (1997) 781.
[102] J.S. Casas, A. Castiñeiras, I. Haiduc, A. Sánchez, J. Sordo, E.M. Vázquez-López, Polyhedron 13 (1994) 1865.
[103] C.C. Landry, A. Hynes, A.R. Barron, I. Haiduc, C. Silvestru, Polyhedron 15 (1996) 391.
[104] A. Silvestru, J.E. Drake, C. Silvestru, J. Yang, I. Haiduc, F. Caruso, Polyhedron 16 (1997) 949.
[105] I. Haiduc, C. Silvestru, F. Caruso, M. Rossi, M. Gielen, Rev. Roum. Chim. 39 (1994) 53.
[106] C. Silvestru, I. Haiduc, F. Caruso, M. Rossi, B. Mahieu, M. Gielen, J. Organomet. Chem. 448 (1993) 75.
[107] M.J. Begley, D.B. Sowerby, D.M. Wesolek, C. Silvestru, I. Haiduc, J. Organomet. Chem. 316 (1986) 281.
[108] C. Silvestru, I. Haiduc, K.H. Ebert, H.J. Breunig, D.B. Sowerby, J. Organomet. Chem. 468 (1994) 113.
[109] G. Marcu, M. Curtui, I. Haiduc, J. Inorg. Nucl. Chem. 39 (1977) 1415.
[110] M. Curtui, G. Marcu, M. Diaconeasa, I. Haiduc, Stud. Univ. Babes-Bolyai Chem. 21 (1976) 63.
[111] M. Curtui, G. Marcu, I. Haiduc, Stud. Univ. Babes-Bolyai Chem. 21 (1976) 74.
[112] I. Haiduc, G. Marcu, M. Curtui, Rev. Roum. Chim. 22 (1977) 626.
[113] G. Marcu, I. Haiduc, M. Curtui, Stud. Univ. Babes-Bolyai Chem. 22 (1977) 49.
[114] M. Curtui, I. Haiduc, G. Marcu, J. Radioanal. Chem. 44 (1978) 109.
[115] M. Curtui, I. Haiduc, J. Inorg. Nucl. Chem. 43 (1981) 1076.
[116] M. Curtui, I. Haiduc, J. Radioanal. Nucl. Chem. Lett. 86 (1984) 281.
[117] I. Haiduc, M. Curtui, I. Haiduc, J. Radioanal. Nucl. Chem. Art. 99 (1986) 257.
[118] M. Curtui, I. Haiduc, @J. Radioanal. Nucl. Chem. Letters 1993, 233.
[119] M. Curtui, I. Haiduc, C. Pop, Stud. Univ. Babes-Bolyai, Chem. 40 (1995) 183.
[120] M. Curtui, I. Haiduc, Radiochem. Radioanal. Letters 50 (1981) 55.
[121] M. Curtui, Iov. Haiduc, Rev. Chim. (Bucuresti) 39 (1988) 1099.
[122] M. Curtui, I. Haiduc, Iov. Haiduc, J. Radioanal. Nucl. Chem. Lett. 165 (1992) 95.
[123] M. Curtui, I. Haiduc, J. Radioanal. Nucl. Chem. 186 (1994) 273.
[124] M. Curtui, I. Haiduc, Stud. Univ. Babes-Bolyai Chem. 34 (1989) 89.
[125] M. Curtui, I. Haiduc, J. Radioanal. Nucl. Chem. Lett. 164 (1992) 91.
[126] T. Braun, P. Bull, J. Fardy, I. Haiduc, F. Makasek, W.J. McDowell, N.Z. Misak, J.D. Návratil, T. Sato, J. Radioanal. Nucl. Chem. 84 (1984) 461.
[127] I. Haiduc, M. Curtui, Iov. Haiduc, I. Silaghi-Dumitrescu, Solvent extraction of uranium, thorium and rare earths with dialkyldithiophosphoric acids, in: Chemical Aspects of Nuclear Methods of Analysis, IAEA-TECDOC-350, a technical document issued by the International Atomic Energy Agency, Vienna, 1985, p. 101.
[128] I. Haiduc, M. Curtui, Syn. React. Inorg. Metal-Org. Chem. 6 (1976) 125.
[129] A.E. Storey, F. Zonnevijlle, A.A. Pinkerton, D. Schwarzenbach, Inorg. Chim. Acta 75 (1983) 103.
[130] I. Haiduc, L. Silaghi-Dumitrescu, in: J.F. Bunnett, M. Mikolajczyk (Eds.), Chemical Problems Associated with Old Arsenical and Mustard Munitions, NATO ASI Series 1. Disarmament Technologies, vol. 19, Kluwer Academic Publishers, Dordrecht, 1998, p. 149.
[131] S. Pascu, L. Silaghi-Dumitrescu, A.J. Blake, I. Haiduc, D.B. Sowerby, Polyhedron 17 (1998) 4115.
[132] L. Silaghi-Dumitrescu, L.A. Avila-Diaz, I. Haiduc, Rev. Roum. Chim. 31 (1986) 335.

[133] L. Silaghi-Dumitrescu, I. Silaghi-Dumitrescu, I. Haiduc, R.-A. Toscano, V. Garcia-Montalvo, R. Cea-Olivares, Z. Anorg. Allg. Chem. 625 (1999) 347.
[134] L. Silaghi-Dumitrescu, I. Haiduc, J. Organomet. Chem. 259 (1983) 65.
[135] I. Haiduc, L. Silaghi-Dumitrescu, J. Organomet. Chem. 225 (1982) 225.
[136] L. Silaghi-Dumitrescu, I. Haiduc, J. Weiss, J. Organomet. Chem. 263 (1984) 159.
[137] D.B. Sowerby, M.J. Begley, L. Silaghi-Dumitrescu, I. Silaghi-Dumitrescu, I. Haiduc, J. Organomet. Chem. 469 (1994) 45.
[138] R. Cea-Olivares, K.H. Ebert, L. Silaghi-Dumitrescu, I. Haiduc, Heteroatom Chem. 8 (1997) 317.
[139] L. Silaghi-Dumitrescu, I. Haiduc, J. Organomet. Chem. 252 (1983) 295.
[140] L. Silaghi-Dumitrescu, I. Silaghi-Dumitrescu, I. Haiduc, Rev. Roum. Chim. 34 (1989) 305.
[141] L. Silaghi-Dumitrescu, M.N. Gibbons, I. Silaghi-Dumitrescu, J. Zukerman-Schpector, I. Haiduc, D.B. Sowerby, J. Organomet. Chem. 517 (1996) 101.
[142] L. Silaghi-Dumitrescu, S. Pascu, A.J. Blake, I. Haiduc, D.B. Sowerby, J. Organomet. Chem. 549 (1997) 187.
[143] A. Ziegler, V.P. Botha, I. Haiduc, Inorg. Chim. Acta 12 (1975) 123.
[144] V.P. Botha, A. Ziegler, I. Haiduc, Inorg. Chim. Acta 17 (1976) 13.
[145] V. Coldea, I. Haiduc, Syn. React. Inorg. Metal-Org. Chem. 10 (1980) 417.
[146] V. Coldea, M. Coldea, I. Haiduc, Rev. Roum. Chim. 26 (1981) 71.
[147] R. Micu-Semeniuc, S. Popse, I. Haiduc, Rev. Roum. Chim. 28 (1983) 605.
[148] I. Gergen, R. Micu-Semeniuc, I. Haiduc, Syn. React. Inorg. Metal-Org. Chem. 7 (1977) 183.
[149] I. Haiduc, in: G. von Herausgegeben, H. Zimmer, K. Niedenzu (Eds.), Methodicum Chimicum, Band 7. Hauptgruppenelemente und deren Verbindungen, Thieme Verlag, Stuttgart, 1976, p. 811.
[150] I. Haiduc, in: H. Zimmer, K. Niedenzu (Eds.), Methodicum Chimicum. Main Group Elements and their Compounds, vol. 7B, Academic Press, New York, 1979, p. 789.
[151] I. Haiduc, in: H. Zimmer (Ed.), Annual Reports in Inorganic and General Synthesis — 1976, Academic Press, New York, 1977, p. 350.
[152] (a) A. Schmidpeter, R. Böhm, H. Groeger, Angew. Chem. 76 (1964) 860; Angew. Chem. Int. Ed. Engl. 3 (1964) 704. (b) A. Schmidpeter, K. Stoll, Angew. Chem. 79 (1967) 242; Angew. Chem. Int. Ed. Engl. 6 (1967) 252. (c) A. Schmidpeter, K. Stoll, Angew. Chem. 80 (1968) 558; Angew. Chem. Int. Ed. Engl. 7 (1968) 549.
[153] (a) I. Haiduc, in: J.D. Woollins (Ed.), Inorganic Experiments, VCH Weinheim, New York, 1994, p. 145. (b) J.D. Woollins, J. Chem. Soc. Dalton Trans. (1996) 2893. (c) T.Q. Ly, J.D. Woollins, Coord. Chem. Rev. 176 (1998) 451.
[154] I. Haiduc, V.P. Botha, 1er Symposium International de Chimie Hétérocyclique Minérale, Besançon, 16–19 Juin, 1975, p. 437.
[155] (a) P.B. Hitchcock, J.F. Nixon, I. Silaghi-Dumitrescu, I. Haiduc, Inorg. Chim. Acta 96 (1985) 77. (b) H. Nöth, Z. Naturforsch. Teil b 37 (1982) 149. (c) S. Husebye, K. Maartmann-Moe, Acta Chem. Scand. A 37 (1983) 439.
[156] C. Silvestru, R. Rösler, J.E. Drake, J. Yang, G. Espinosa-Perez, I. Haiduc, J. Chem. Soc. Dalton Trans. (1998) 73.
[157] J. Yang, J.E. Drake, S. Hernandez-Ortega, R. Rösler, C. Silvestru, Polyhedron 16 (1997) 4061.
[158] R. Rösler, M. Stanciu, J. Yang, J.E. Drake, C. Silvestru, I. Haiduc, Phosphorus Sulfur Silicon 132 (1998) 231.
[159] G. Balázs, J.E. Drake, C. Silvestru, I. Haiduc, Inorg. Chim. Acta 287 (1999) 61.
[160] I. Haiduc, R. Cea-Olivares, S. Hernandez-Ortega, C. Silvestru, Polyhedron 14 (1995) 2041.
[161] K.L. Paciorek, R.H. Kratzer, Inorg. Chem. 5 (1966) 538.
[162] I. Haiduc, J. Zukerman-Schpector, E. Castellano, R. Cea-Olivares, Heteroatom. Chem. 11 (2000) 244.
[163] G. Krauter, S.K. Sunny, W.S. Rees, Jr, Polyhedron 17 (1998) 391.
[164] J.S. Casas, A. Castineiras, I. Haiduc, A. Sanchez, J. Sordo, E.M. Vázquez-López, Polyhedron 14 (1995) 805.
[165] R. Rösler, C. Silvestru, I. Haiduc, F. Kayser, M. Gielen, B. Mahieu, Main Group Metal Chem. 16 (1993) 435.
[166] I. Haiduc, C. Silvestru, H.W. Roesky, H.G. Schmidt, M. Noltemeyer, Polyhedron 12 (1993) 69.
[167] K.C. Molloy, M. Mahon, I. Haiduc, C. Silvestru, Polyhedron 14 (1995) 1169.
[168] R. Rösler, J.E. Drake, C. Silvestru, J. Yang, I. Haiduc, J. Chem. Soc. Dalton Trans. (1999) 391.
[169] C. Silvestru, I. Haiduc, R. Cea-Olivares, A. Zimbron, Polyhedron 13 (1994) 3159.
[170] J.S. Casas, A. Castiñeiras, I. Haiduc, A. Sánchez, J. Sordo, E.M. Vázquez-López, Polyhedron 13 (1994) 2873.
[171] R.A. Varga, C. Silvestru, I. Haiduc, Syn. React. Inorg. Met.-Org. Chem. 30 (2000) 485.
[172] C. Silvestru, R. Rösler, I. Haiduc, R.A. Toscano, D.B. Sowerby, J. Organomet. Chem. 515 (1996) 131.
[173] J.E. Drake, A. Silvestru, J. Yang, I. Haiduc, Inorg. Chim. Acta 271 (1998) 75.
[174] I. Székely, C. Silvestru, J.E. Drake, G. Balázs, S.I. Farcas, I. Haiduc, Inorg. Chim. Acta 299 (2000) 247.
[175] N. Zuniga-Villareal, C. Silvestru, M. Reyes-Lezama, S. Hernadez-Ortega, C. Alvarez-Toledano, J. Organomet. Chem. 496 (1955) 169.
[176] (a) I. Haiduc, R. Cea-Olivares, R.A. Toscano, C. Silvestru, Polyhedron 14 (1995) 1067. (b) I. Haiduc, A. Fischer, F.T. Edelmann, Rev. Roum. Chim. 44 (1999) 805.
[177] J. Novosad, M. Necas, J. Marek, P. Veltsistas, C. Papadimitriou, I. Haiduc, M. Watanabe, J.D. Woollins, Inorg. Chim. Acta 290 (1999) 256.
[178] C. Silvestru, R. Rösler, I. Haiduc, R. Cea-Olivares, G. Espinosa-Perez, Inorg. Chem. 34 (1995) 3352.
[179] R. Rösler, C. Silvestru, G. Espinosa-Perez, I. Haiduc, R. Cea-Olivares, Inorg. Chim. Acta 241 (1996) 47.
[180] A. Silvestru, D. Bilc, R. Rosler, J.E. Drake, I. Haiduc, Inorg. Chim. Acta 305 (2000) 106.
[181] E.V. Garcia-Baez, M.J. Rozales-Hoz, H. Nöth, I. Haiduc, C. Silvestru, Inorg. Chem. Commun. 3 (2000) 173.
[182] I. Silaghi-Dumitrescu, I. Haiduc, Rev. Roum. Chim. 25 (1980) 815.
[183] C.A. Tellez, S. De La Riva, E. Hollauer, I. Haiduc, C. Silvestru, Spectrosc. Lett. 31 (1998) 1469.
[184] I. Silaghi-Dumitrescu, I. Haiduc, Rev. Roum. Chim. 25 (1980) 823.
[185] I. Haiduc, I. Silaghi-Dumitrescu, R. Grecu, R. Constantinescu, L. Silaghi-Dumitrescu, J. Mol. Struct. 114 (1984) 467.
[186] I. Silaghi-Dumitrescu, R. Grecu, L. Silaghi-Dumitrescu, I. Haiduc, Stud. Univ. Babes-Bolyai Chem. 1 (1989) 97.
[187] I. Silaghi-Dumitrescu, I. Haiduc, Phosphorus Sulfur 12 (1982) 205.
[188] I. Silaghi-Dumitrescu, I. Haiduc, Rev. Roum. Chim. 31 (1986) 955.
[189] I. Silaghi-Dumitrescu, L. Serban, L. Silaghi-Dumitrescu, I. Haiduc, Rev. Roum. Chim. 39 (1994) 1397.
[190] I. Silaghi-Dumitrescu, L. Silaghi-Dumitrescu, I. Haiduc, Rev. Roum. Chim. 27 (1982) 911.
[191] I. Silaghi-Dumitrescu, I. Haiduc, J. Mol. Struct. 106 (1984) 217.

[192] I. Silaghi-Dumitrescu, I. Haiduc, Phosphorus Sulfur 22 (1985) 85.
[193] L. Silaghi-Dumitrescu, R. Silaghi-Dumitrescu, I. Silaghi-Dumitrescu, I. Haiduc, Stud. Univ. Babes-Bolyai Chem. 42 (1997) 69.
[194] L. Silaghi-Dumitrescu, S. Pascu, I. Silaghi-Dumitrescu, I. Haiduc, Rev. Roum. Chim. 42 (1997) 747.
[195] I. Haiduc, C. Silvestru, M. Gielen, Bull. Soc. Chim. Belge 92 (1983) 187.
[196] C. Silvestru, C. Socaciu, A. Bara, I. Haiduc, Anticancer Res. 10 (1990) 803.
[197] C. Silvestru, I. Haiduc, in: V.G. Kumar Das (Ed.), Main Group Elements and their Compounds, Narosa Publishing House, New Delhi, India, 1996, p. 453.
[198] A. Bara, C. Socaciu, C. Silvestru, I. Haiduc, Anticancer Res. 11 (1991) 1651.
[199] C. Socaciu, A. Bara, C. Silvestru, I. Haiduc, In Vivo 5 (1991) 425.
[200] B.K. Keppler, C. Silvestru, I. Haiduc, Metal-Based Drugs 1 (1994) 75.
[201] C. Socaciu, I. Pasca, C. Silvestru, A. Bara, I. Haiduc, Metal-Based Drugs 1 (1994) 291.
[202] C. Socaciu, I. Pasca, C. Silvestru, I. Haiduc, Metal-Based Drugs 3 (1996) 91.
[203] I. Haiduc, C. Silvestru, Organometallics in Cancer Chemotherapy. Main Group Metal Compounds, vol. 1, CRC Press, Boca Raton, FL, 1989.
[204] I. Haiduc, F.T. Edelmann, Supramolecular Organometallic Chemistry, Wiley–VCH, Weinheim, 1900.