“BABEŞ-BOLYAI” UNIVERSITY
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

CONTRIBUTIONS TO THE COORDINATION CHEMISTRY OF ORGANOPHOSPHORUS LIGANDS

Abstract of the PhD Thesis

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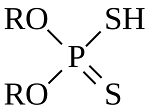
CONTENTS

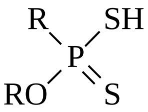
I. INTRODUCTION

Organo-phosphorus ligands play an important role in coordination chemistry due to the diversity of their composition and of their coordination modalities. This thesis limits itself to a class of organo-phosphorus ligands, namely on the study of dithio-organophosphorus acids.

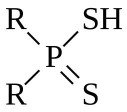
According to the number of direct phosphorus-carbon bonds, three types of dithio-organophosphorus can be distinguished:



Dithiophosphoric acid
(diester)
(phosphorodithioic acid)



Dithiophosphonic acid
(monoester)
(phosphinoditioic acid)



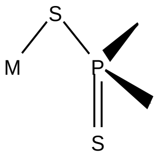
Dithiophosphinic
(phosphonodithioic acid)

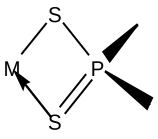
Phosphorodithioic metal derivatives have important practical applications; they are used as additives for lubricating oils, extraction agents, reagents for heavy metals separation, flotation agents for diverse minerals, addition brightening agents for electroplating, accelerators in rubber vulcanization. Some compounds present antitumor biological activity.

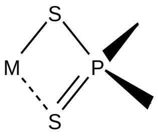
The metal derivatives of dithio-organophosphorus acids present also a particular scientific interest due to the great diversity of their composition and structure, resulting from the multiple metal-sulfur interaction modalities.

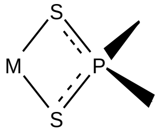
This thesis attempts to extend the concepts of *supramolecular chemistry* for describing the structure of metal dithiophosphates. Until now, numerous structures of dithio-organophosphorus metal derivatives (particularly dithiophosphates) were investigated by X-ray diffraction, but in most instances the studies were limited to the determination of molecular structure. With the development of crystallographic methods, the interest for the analysis of molecules packing in the crystals increased. In this way different modalities of molecular associations were identified, resulting in the formation of supramolecular structures [1].

Dithio-organophosphorus ligands present the following coordination modalities: monometallic mono- and biconnective, aniso- or isobidentate [2].



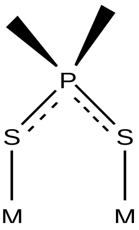


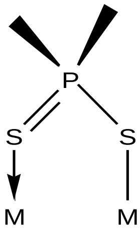


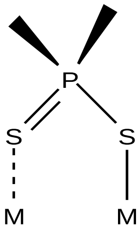


1 **2** **3** **4**

bimetallic biconnective coordination, in symmetrical or asymmetrical bridges [2]:

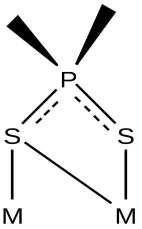






5 **6** **7**

rarely bimetallic tri- and tetraconnective [2]:



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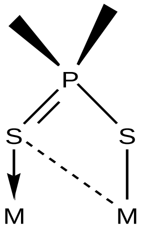

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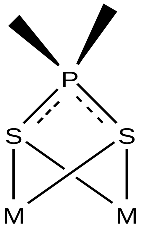

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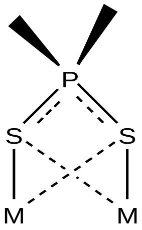

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The term of *Supramolecular Chemistry* was introduced in 1978 by J. M. Lehn who wrote: "*just as there is a field of molecular chemistry, based on the covalent bond, there is a field of supramolecular chemistry, the chemistry of molecular assemblies and of the intermolecular bond*". Presently, supramolecular chemistry is defined as "*chemistry beyond the molecule"* and studies "the *organization of high complexity entities resulting by the association of two or more chemical species bonded by intermolecular forces*" [3-5].

The supramolecular compounds of dithio-organophosphorus ligands are frequently formed by secondary interactions between the metal and the sulfur atom.

II. ORIGINAL CONTRIBUTIONS

II.1. Supramolecular self-assembly in the orto-phenantroline adduct of lead(II) bis(di-iso-butyldithiophosphate) [Pb{$S_2P(OBu^i)_2$}$_2$·1,10-Phen]

In the sulfur compounds of lead(II) there is a general tendency to self-assembly, leading to the formation of supramolecular structures [6]. It is mostly accomplished through Pb···S secondary [7, 8] or “closed-shell” interactions [9], characterized by interatomic distances intermediate between the sum of covalent radii (Pb-S 2,44 Å) and the sum of van der Waals radii (Pb···S 4,15 Å) [10].

Lead(II) dithiophosphates, [Pb{$S_2P(OR)_2$}$_2$], combine a diversity of coordination patterns found for lead(II) and present coordination numbers from two to eight, with a remarkable diversity of the coordination geometries presented by dithiophosphorus ligands [11].

In this chapter, the structure of the 1,10-phenanthroline adduct of lead(II) dithiophosphate is presented. X-ray diffraction analysis of the compound [Pb{$S_2P(OBu^i)_2$}$_2$·Phen] reveals a dimeric centrosymmetric supermolecule, formed by Pb···S secondary bonds.

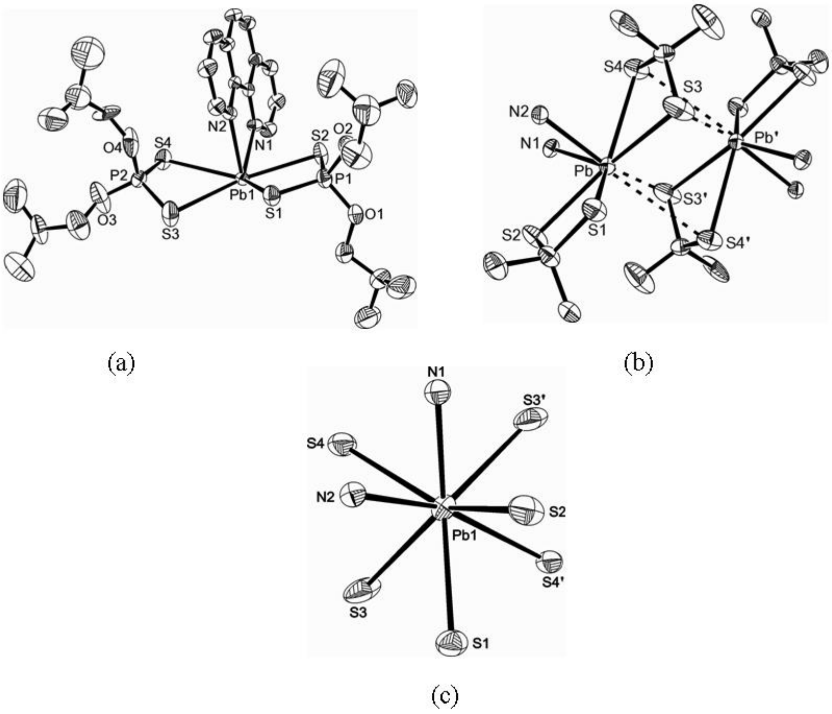
Because of the dimerization, the two dithiophosphoric ligands coordinated to lead are no more equivalent; for instance the P_1 ligand is terminal, being bidentate chelate (monometallic monoconnective) [2], while P_2 is a bridging ligand (bimetallic tetraconnective). Table 1 presents the main bond lengths and angles for the Pb(II) compound.

Table 1: Bond lengths and angles for the compound $[Pb\{S_2P(OBu^i)_2\}_2{\cdot}Phen]$

Bond lengths (Å)	
Pb(1)-S(1)	3.0026(11)
Pb(1)-S(2)	2.8946(11)
Pb(1)-S(3)	3.1676(12)
Pb(1)-S(4)	3.1364(12)
Pb(1)-N(1)	2.612(3)
Pb(1)-N(2)	2.483(3)
S(1)-P(1)	1.9783(16)
S(2)-P(1)	1.9770(16)
S(3)-P(2)	1.9472(16)
S(4)-P(2)	1.9606(15)
Bond angles (^{o})	
S(1)-Pb(1)-S(3)	72.92(3)
S(1)-Pb(1)-S(4)	130.93(3)
S(1)-Pb(1)-N(1)	132.45(7)
S(1)-Pb(1)-N(2)	83.20(8)
S(2)-Pb(1)-S(3)	141.28(3)
S(2)-Pb(1)-S(4)	147.40(3)
S(2)-Pb(1)-N(1)	72.17(8)
S(1)-Pb(1)-S(2)	68.50(3)
S(2)-Pb(1)-N(2)	81.78(8)
S(3)-Pb(1)-S(4)	63.46(3)
S(3)-Pb(1)-N(1)	137.90(7)
S(3)-Pb(1)-N(2)	90.74(8)
S(4)-Pb(1)-N(1)	76.88(8)
S(4)-Pb(1)-N(2)	76.25(8)
N(1)-Pb(1)-N(2)	65.50(10)
S(3')Pb(1)-S(4')	53.95(3)

Subsequently the dimer associates through weak C-H···O and C-H···S hydrogen bonds, forming a bidimensional supramolecular structure.

In the monomeric structure unit the lead(II) atom is six-coordinated by four sulfur atoms, from the two chelate dithiophosphorus ligands and by two nitrogen atoms belonging to 1,10-phenantroline (Figure 1a).



(a) (b)

(c)

Fig.1. Molecular structure of the $[Pb\{S_2P(OBu^i)_2\}_2{\cdot}Phen]$ compound: (a) monomeric unit, (b) association of monomeric units into dimeric supermolecule, (c) coordination sphere around the lead atom

Dimerization occurs by Pb···S secondary bonds, between S(3) and S(4) and the Pb(1)' center (figure 1b).

The coordination number of lead(II) in the dimer is eight, if considering the two secondary interactions. It is most difficult to characterize the coordination geometry for the eight-coordinated atom, since the bond angles present irregular values. It seems that in the case of our compound, the coordination geometry for lead(II) in the dimer is a distorted square antiprism (Figure 1c).

The dimeric supermolecules of the compound $[Pb\{S_2P(OBu^i)_2\}_2 \cdot Phen]$ are subsequently self-assembled into a bidimensional supramolecular structure (Figure 2).

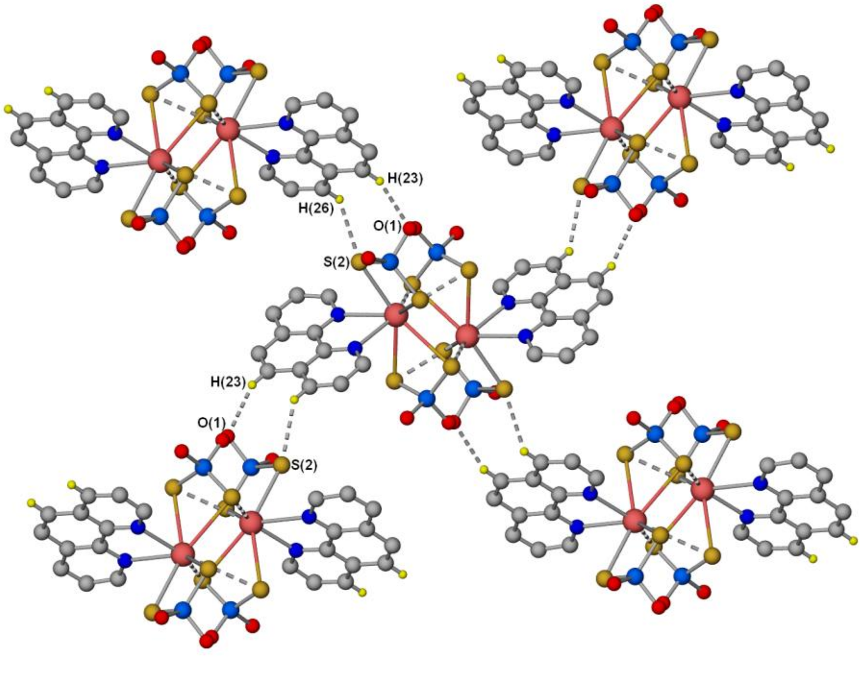


Fig.2. Supramolecular structure of the compound $[Pb\{S_2P(OBu^i)_2\}_2 \cdot Phen]$

The self-assembly occurs through weak hydrogen bonds, between the hydrogen atoms of 1,10-phenantroline and the sulfur and oxygen atoms of the dithiophosphorus ligands from different dimeric units.

II.2. Hydrogen bond self-assembly in nickel(II) dithiophosphates [Ni{$S_2P(OR)_2$}$_2$], R = sec-Bu, iso-Bu and in their adducts with pyrazole

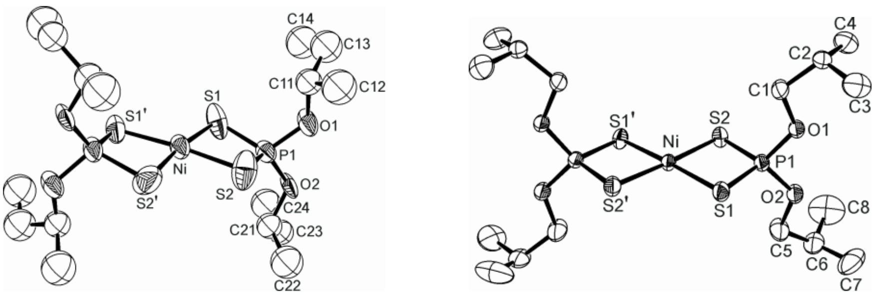
The family of nickel dithiophosphates was intensely investigated in relation to their structure [2, 11], but their crystal packing and the potential to form supramolecular structures were generally ignored.

The chapter presents the crystal structures of the homoleptic compounds of [Ni{$S_2P(OR)_2$}$_2$] type, where R = sec-butyl (**1**) and iso-butyl (**2**) as well as the structures of some heteroleptic compounds (adducts with bis-pyrazole) (**3**) and (**4**).

The X-ray diffraction of the compounds (**1**) and (**2**) reveals monomeric structures with a square planar geometry around the central metal atom (Figure 3). The nickel atom is four-coordinated, by four sulfur atoms from two different dithiophosphoric ligands. Table 2 presents some bond lengths and angles for compounds (**1**) and (**2**).

Table 2: Bond lengths and angles for compounds (1) and (2)

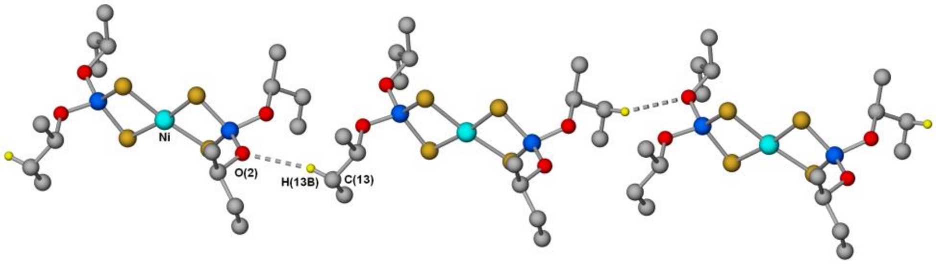
	(1)	(2)
Bond lengths (Å)		
Ni-S(1)	2.178(5)	2.2244(5)
Ni-S(2)	2.252(5)	2.2278(5)
S(1)-P(1)	1.978(7)	1.9984(7)
S(2)-P(1)	1.962(7)	1.9950(7)
P(1)-O(1)	1.597(6)	1.5661(12)
P(1)-O(2)	1.554(8)	1.5667(13)
Bond angles (^{o})		
S(1')-Ni-S(1)	101.7(3)	177.03(3)
S(1')-Ni-S(2)	171.3(3)	91.695(16)
S(1)-Ni-S(2)	87.01(16)	88.389(16)
S(2)-Ni-S(2')	84.3(3)	176.78(3)
O(2)-P(1)-O(1)	93.3(4)	97.30(7)
O(2)-P(1)-S(2)	115.7(6)	114.68(6)
O(1)-P(1)-S(2)	110.1(4)	114.41(6)
O(2)-P(1)-S(1)	122.8(6)	115.24(6)
O(1)-P(1)-S(1)	113.5(4)	113.92(6)
S(2)-P(1)-S(1)	101.46(15)	102.01(3)



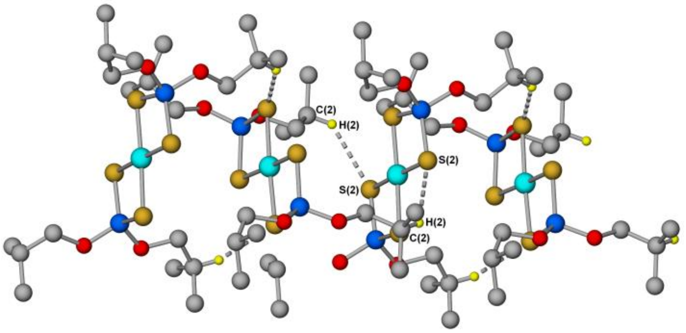
(1) **(2)**

Fig.3. Molecular structure of nickel(II) bis(di-sec-butyl) dithiophosphate (1) and nickel(II) bis(di-iso-butyl) dithiophosphate (2)

Both compounds (**1**) and (**2**) are self-assembled into supramolecular structures, through weak hydrogen bonds (Figure 4).



(1)

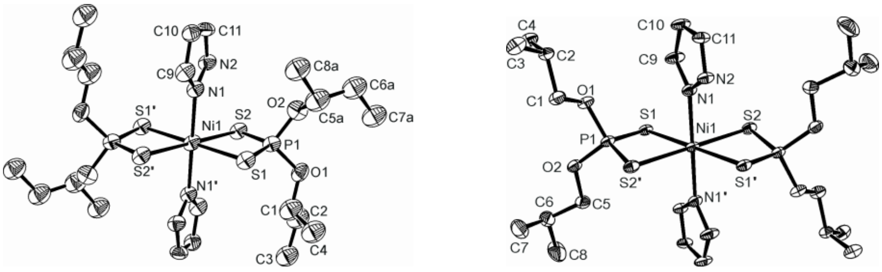


(2)

Fig.4. Supramolecular self-assembly in crystals for compounds (1) and (2)

It is surprising that in compound (**2**) the self-assembly occurs through C-H···S type interactions, while in compound (**1**) self-assembly through C-H···O type interactions are preferred.

X-ray diffraction analysis for compounds (**3**) and (**4**) reveals a distorted octahedral geometry around the central metal atom of nickel(II) (Figure 5).



(3) **(4)**

Fig. 5. Molecular structures of adducts with pyrazole

The Ni-S bond lengths in adducts with pyrazole [Ni(1)-S(1) 2.495(2) Å, Ni(1)-S(2) 2.476(2) Å in compound (**3**) and Ni(1)-S(1) 2.5157(6) Å, Ni(1)-S(2) 2.4988(6) Å in compound (**4**)], are longer than the Ni-S bond lengths in four-coordinated compounds with square planar geometry. In Table 3 are presented the main bond lengths and angles for compounds (**3**) and (**4**).

Table 3: Bond lengths angles for compounds (3) and (4)

	(**3**)	(**4**)
Bond lengths (Å)		
Ni(1)-S(1)	2.495(2)	2.5157(6)
Ni(1)-S(2)	2.476(2)	2.4988(6)
P(1)-S(1)	1.976(3)	1.9820(9)
P(1)-S(2)	1.983(3)	1.9793(8)
Ni(1)-N(1)	2.083(7)	2.0815(18)
P(1)-O(1)	1.589(6)	1.5761(15)
P(1)-O(2)	1.574(7)	1.5826(18)

Bond angles (^{o})		
N(1')-Ni(1)-N(1)	180.0	180.0
S(2)-Ni(1)-S(1)	82.47(7)	98.46(2)
S(1)-Ni(1)-S(1')	180.0	180.0
S(2)-Ni(1)-S(2')	180.0	180.0
S(2')-Ni(1)-S(1)	97.53(7)	81.54(2)
S(2')-Ni(1)-S(1')	82.47(7)	98.46(2)
N(1')-Ni(1)-S(2)	89.51(19)	91.19(6)
N(1)-Ni(1)-S(2)	90.49(19)	88.81(6)
N(1)-Ni(1)-S(2')	89.51(19)	91.19(6)
N(1')-Ni(1)-S(1)	90.5(2)	90.28(5)
N(1)-Ni(1)-S(1)	89.5(2)	89.72(5)
N(1)-Ni(1)-S(1')	90.5(2)	90.28(5)
O(2)-P(1)-O(1)	99.3(4)	100.33(9)
O(2)-P(1)-S(1)	114.7(3)	112.71(7)
O(1)-P(1)-S(1)	111.4(3)	107.02(7)
O(2)-P(1)-S(2)	106.3(3)	110.95(7)
O(1)-P(1)-S(2)	112.8(3)	113.83(7)
S(1)-P(1)-S(2)	111.71(15)	111.51(4)
P(1)-S(1)-Ni(1)	82.62(10)	82.56(3)
P(1)-S(2)-Ni(1)	83.00(9)	83.06(3)

In compound (**3**) two hydrogen bonding types are present: C(3)-H···S(1) 2.965 Å and N(2)-H···O(2) 2.502 Å. The compound is self-assembled into a bidimensional supramolecular structure (Figure 6).

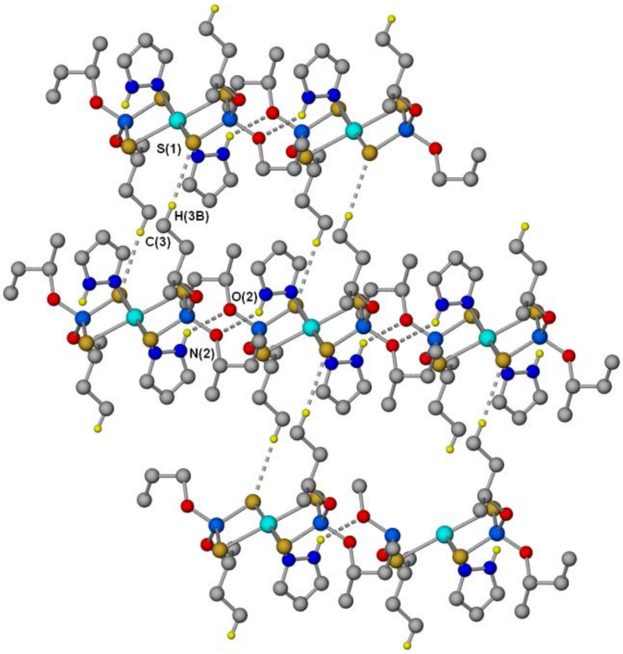


Fig. 6. Bidimensional supramolecular self-assembly structure for compound (3)

Compound (**4**) is self-assembled only through weak hydrogen bonds of the N(2)-H···S(2) type (2.728 Å) and forms a linear supramolecular chain (Figure 7).

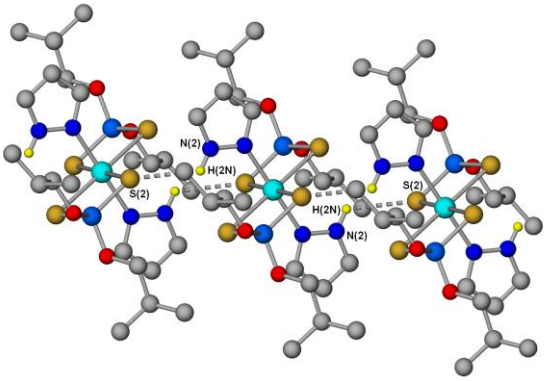


Fig. 7. Supramolecular self-assembly in the structure for compound (4)

II.3. A dinuclear adduct of cadmium(II) bis(di-sec-butyldithiophosphate built around hexamethylenetetramine cage as coordination center

In this chapter is presented the structure for a dinuclear adduct of cadmium(II), namely cadmium(II) bis(di-sec-butyldithiophosphate) (**1**), built around hexamethylenetetramine (urotropine) as coordination center.

X-ray diffraction analysis on compound (**1**), reveals a dinuclear complex, with the cadmium(II) atoms connected to two nitrogen atoms belonging to hexamethylenetetramine. The structure is presented in Figure 8.

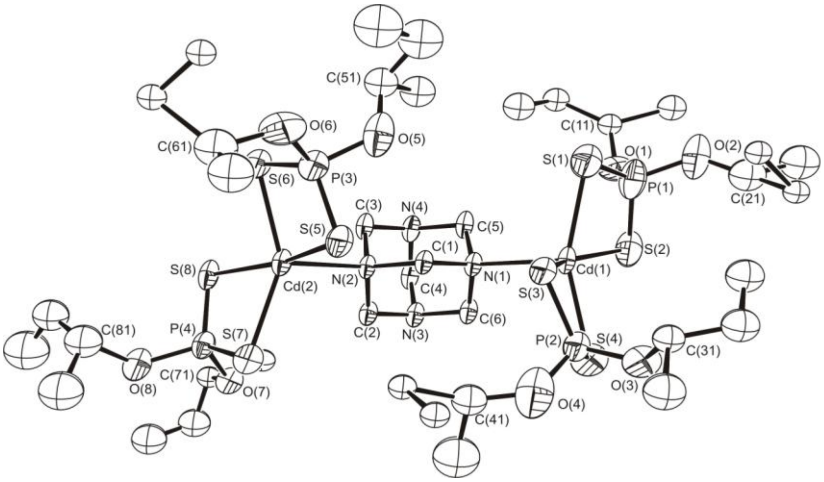


Fig. 8. Crystal structure of the compound $[2Cd\{S_2P(OCHMeEt)_2\}_2{\cdot}(CH_2)_6N_4]$

Table 4 presents some bond lengths and angles for the Cd(II) compound.

Table 4. Bond lengths and angles for the compound

$[2Cd\{S_2P(OCHMeEt)_2\}_2 \cdot (CH_2)_6N_4]$

Bond lengths (Å)	
Cd(1)-N(1)	2.344(6)
Cd(1)-S(2)	2.601(3)
Cd(1)-S(3)	2.605(2)
Cd(1)-S(1)	2.618(3)
Cd(1)-S(4)	2.637(4)
Cd(2)-N(2)	2.355(5)
Cd(2)-S(7)	2.570(3)
Cd(2)-S(6)	2.576(3)
Cd(2)-S(5)	2.660(3)
Cd(2)-S(8)	2.716(2)
S(1)-P(1)	1.955(6)
S(2)-P(1)	1.957(7)
S(3)-P(2)	1.976(3)
S(4)-P(2)	1.948(4)
S(5)-P(3)	1.947(5)
S(6)-P(3)	2.000(4)
S(7)-P(4)	1.986(4)
S(8)-P(4)	1.980(3)
Bond angles (^{o})	
N(1)-Cd(1)-S(2)	100.92(17)
N(1)-Cd(1)-S(3)	102.68(15)
S(2)-Cd(1)-S(3)	156.40(11)
N(1)-Cd(1)-S(1)	101.45(19)
S(2)-Cd(1)-S(1)	77.38(15)
S(3)-Cd(1)-S(1)	97.67(11)
N(1)-Cd(1)-S(4)	100.85(19)
S(2)-Cd(1)-S(4)	98.14(17)
S(3)-Cd(1)-S(4)	77.59(9)
S(1)-Cd(1)-S(4)	157.70(14)
N(2)-Cd(2)-S(7)	104.08(17)
N(2)-Cd(2)-S(6)	106.78(17)
S(7)-Cd(2)-S(6)	148.73(10)
N(2)-Cd(2)-S(5)	97.77(15)
S(7)-Cd(2)-S(5)	102.73(10)
S(6)-Cd(2)-S(5)	78.07(10)
N(2)-Cd(2)-S(8)	94.44(15)
S(7)-Cd(2)-S(8)	77.30(8)
S(6)-Cd(2)-S(8)	95.30(8)
S(5)-Cd(2)-S(8)	167.36(9)
S(1)-P(1)-S(2)	113.0(2)
S(4)-P(2)-S(3)	113.61(18)
S(5)-P(3)-S(6)	113.39(19)
S(8)-P(4)-S(7)	112.78(16)

The crystal structure is centered around a cage molecule, viz. urotropine, with the cadmium(II) atoms coordinated at two nitrogen atoms belonging to this molecule. On their part, the cadmium(II) atoms are coordinated by two dithiophosphoric ligands, presenting a distorted square pyramidal geometry, corresponding to a five-coordinated center.

The compound $[2Cd\{S_2P(OCHMeEt)_2\}_2{\cdot}(CH_2)_6N_4]$ can be described as an example of “inverse coordination”, where the coordination center is a molecule, while the metals reside in the second coordination sphere.

II.4. Theoretical calculations

The dithiophosphates described in this thesis were the object of a theoretical study using the Gaussian 09 program. Calculations were made applying the Hartree-Fock method with a LANL2DZ basis set. The investigation aimed to achieve the geometry optimization, the calculation of total energy for each molecule, the calculation of vibrations and of the bond lengths and angles.

In Table 5 are comparatively presented the calculated vibrations with the experimentally determined ones.

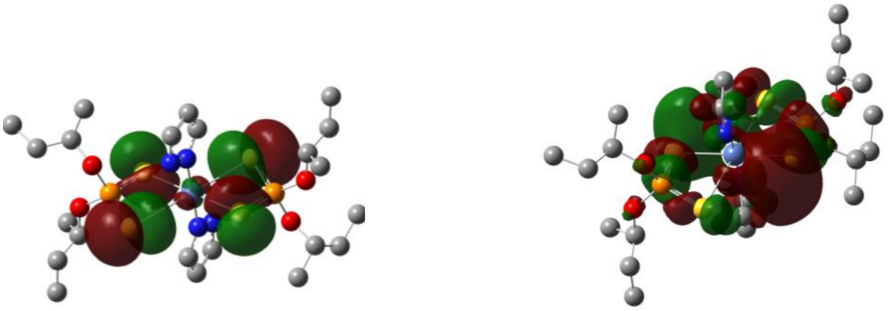
Table 5. Calculated and experimentally determined vibrations

Compound		$\upsilon_{as}(PS_2)$	$\upsilon_s(PS_2)$	υ(P-OC)	υ(PO-C)
$Ni[S_2P(OR)_2]_2$ R = sec-butyl	Experimental	636	586	1014	1172
	Calculated	600	579	1036	1134
$Ni[S_2P(OR)_2]_2$ R = iso-butyl	Experimental	682	568	997	1130
	Calculated	612	601	1064	1130
$Ni[S_2P(OR)_2]_2 \cdot 2Pz$ R = sec-butyl	Experimental	651	516	1018	1155
	Calculated	603	540	1039	1134
$Ni[S_2P(OR)_2]_2 \cdot 2Pz$ R = iso-butyl	Experimental	659	559	1043	1122
	Calculated	605	553	1062	1126
$2Cd[S_2P(OCHMeEt)_2]_2 \cdot$ $(CH_2)_6N_4$	Experimental	659	586	997	1172
	Calculated	613	590	1007	1168
$Pb[S_2P(OBu^i)_2]_2 \cdot$ 1,10-Phen	Experimental	673	592	950	1002
	Calculated	621	536	948	1014

The calculated values for the vibrations of some significant bonds for the investigated dithiophosphates are in agreement with the experimental values [12, 13].

Calculated bond lengths are larger than the experimental ones. However, they are in agreement with bond lengths mentioned in the literature for some experimentally determined dithiophosphates. For instance, Tiekink et al. [14] found that in nickel(II) di-iso-butyldithiophosphate with bipyridyl as additional ligand, the Ni-S bond length is 2.47 Å, while for our investigated compound the calculations gave a value of 2.52 Å.

The HOMO and LUMO orbitals were also calculated. It was found that HOMO orbitals are built by a larger contribution of sulfur atoms, while LUMO orbitals are built by a contribution of the metal atom too (Figure 9):



$[Ni\{S_2P(OR)_2\}_2{\cdot}2Pyz]$ R = sec-butyl
HOMO

$[Ni\{S_2P(OR)_2\}_2{\cdot}2Pyz]$ R = sec-butyl
LUMO

Fig. 9. HOMO and LUMO orbitals for $[Ni\{S_2P(OR)_2\}_2{\cdot}2Pyz]$ R = sec-butyl

III. CONCLUSIONS

1. The 1,10-phenantroline adduct of lead(II) bis(di-iso-butyldithiophosphate is a dimeric centrosymmetric supermolecule, formed by Pb$\cdots$S secondary interactions.

2. In the monomeric unit, the metal center is six-coordinated (with two nitrogen atoms from 1,10-phenantroline and four sulfur atoms from two different dithiophosphoric ligands).

3. In the dimer there are two additional secondary bonds between the lead(II) atom from a monomeric unit and the sulfur atoms from another monomeric unit, thus resulting in the increase of the coordination number around the metal center from six to eight.

4. In the crystal, the dimers are interconnected into a bidimensional supramolecular structure through weak hydrogen bonds of the C-H$\cdots$S, and C-H$\cdots$O type, between sulfur and oxygen

atoms from the dithiophosphoric ligands of a dimeric unit and the hydrogen atoms of 1,10-phenantroline from another dimeric unit.

5. The reaction between nickel(II) nitrate and potassium dithiophosphates (di-sec-butyl, di-iso-butyl) in methanol leads to the formation of complexes of the 1:2 type, which were characterized by IR and NMR spectroscopy. Their pyrazole adducts were also obtained.

6. The X-ray diffraction investigation of the compounds indicates a square planar geometry around the nickel(II) atom, which is four-coordinated in the homoleptic compounds and six-coordinated in the pyrazole adducts; in the last case the metal presents a distorted octahedral coordination geometry. In all the investigated compounds the dithiophosphoric ligands act as isobidentate chelating ligands.

7. In the compound $[Ni\{S_2P(OBu^s)_2\}_2]$ the molecules are associated through C-H$\cdots$O hydrogen bonds (2.652 Å), while in the compound $[Ni\{S_2P(OBu^i)_2\}_2]$ the molecules are associated through weak C-H$\cdots$S hydrogen bonds (2.948 Å).

8. In the compound $[Ni\{S_2P(OBu^s)_2\}_2 \cdot 2Pyz]$ bidimensional supramolecular assemblies are formed by N-H$\cdots$O (2.502 Å) and N-H$\cdots$S bonds (2.965 Å), while in the compound $[Ni\{S_2P(OBu^i)_2\}_2 \cdot 2Pyz]$ linear supramolecular chains are formed only by N-H$\cdots$S bonds (2.728 Å).

9. Cadmium(II) bis(di-sec-butyldithiophosphate) forms with hexamethylenetetramine (urotropine) a 2:1 adduct, which was characterized by IR and NMR spectroscopy and X-ray diffraction.

10. The compound is a dinuclear complex, where the two cadmium atoms are coordinated at two nitrogen atoms from hexamethylenetetramine, which is the coordination center.

11. The cadmium(II) atoms are five-coordinated, having a distorted square pyramidal geometry. Each cadmium atom is connected to two dithiophosphoric groups, one of them presenting slight anisobidentate coordination (with P-S bonds slightly different), while the other dithiophosphoric group presents an isobidentate chelatic coordination pattern.

12. The compound can be considered as an example of “inverse coordination”, where the coordination center is an organic molecule, having around molecules of a coordination compound linked with metal center.

13. Theoretical calculations on the investigated compounds were carried out using the Hartree-Fock method with the LANL2DZ basis set.

14. For isomers, the total molecule energy is the same, both for the simple compounds and the pyrazole adducts.

15. Calculated values of the bond vibrations for the investigated dithiophosphates are close to the experimental values and in agreement with literature data.

16. Calculated bond lengths are slightly longer than the experimental ones. This is due to the fact that in calculations an isolated molecule was considered, the compound being assumed to be in gaseous state.

17. In the investigated compounds, the HOMO orbitals are formed with the participation of the sulfur atoms, while LUMO orbitals are formed with the participation of the metal atom too.

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