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Thio-ligands in Monomeric Pt(Ii) Complexes – Structural Aspects

Milan Melník[1], Peter Mikuš[1] and Clive E. Holloway[2]

[1]Department of Pharmaceutical Analysis and Nuclear Pharmacy, Faculty of Pharmacy, Comenius University in Bratislava, Odbojárov 10, SK-832 32 Bratislava, Slovak Republic, [2]York University, 4700 Keele st., North York M 3J 1P3, Ontario, Canada.

ABSTRACT

This review includes over three hundred derivatives in which each Pt(II) atom is in a distorted square planar environment with inner coordination spheres of PtS4, PtS3X, PtS2X2, PtSX3, PtS2XY, PtSX2Y and PtSXYZ. There is a wide variety of mono-, bi- , ter- , and tetra-dentate ligands, all incorporating both homo- and hetero-dentate varieties. The most common ligands are dimethylsulphoxide and triphenylphosphine. The chelating ligands create a wide variety of metallocyclic rings, where the effects of both steric and electronic factors are observed. Examples of cis- and trans- isomerism exists in these derivatives as well as distortion isomerism, which is much more common. Ligands exerting the trans- effect in these Pt(II) complexes are stronger in the order: OL, NL < Cl < Br < I < SL < H ~ AsL ~ PL ~ CN. Several relationships between the structural parameters were found and are discussed. The complexes crystallized in five crystal classes: hexagonal (0.4%) < tetragonal (1.5%) < orthorhombic (13.8%) < triclinic (23.7%) < monoclinic (60.7%).

KEYWORDS: thio-ligands, Pt(II) complexes, structure, trans-effect, isomers

***Correspondence to Author:**
Milan Melník. Department of Pharmaceutical Analysis and Nuclear Pharmacy, Faculty of Pharmacy, Comenius University in Bratislava, Odbojárov 10, SK-832 32 Bratislava, Slovak Republic. Email: qmelnik@ stuba.sk

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1. INTRODUCTION

Organosulphides are very attractive and useful ligands providing wide variability of stereochemistry about central transition metals, including platinum. Platinum can exist in a wide range of oxidation state from zero to six, of which +2 and +4 are the most common, particularly in coordination chemistry. This has stimulated considerable research activity into the chemistry resulting in the determination of a considerable number of structures by diffraction techniques. Since structure is often related to chemical and biological activity it seemed appropriate to prepare a comprehensive overview of such structures. In this review we classify and analyze structural parameters of square-planar geometry Pt(II) coordination complexes in the presence of organosulphides as ligands.

2. MONOMERIC SQUARE PLANAR Pt(II) COMPLEXES

There are over three hundred monomeric square planar Pt(II) complexes which contain at least one thio-ligand. These complexes are subdivided into several groups with wide variability of the inner coordination sphere about the Pt(II) atoms.

2.1 PtS$_4$ Derivatives

There are over sixty derivatives with PtS$_4$ inner coordination sphere. These crystallize in four crystal classes: tetragonal (x2) < orthorhombic (x5) < triclinic (x17) < monoclinic (x39). Square planar geometry, with different degree of distortion, is realized by mono-, bi- and tetradentate S-donor ligands. In thirteen derivatives only four equal monodentate ligands are involved: [Pt(SCN)$_4$](-2anion)[1-3], [Pt(Me$_2$S)$_4$](+2cation)[4], [Pt(tx)$_4$](+2cation)[4], [Pt(Stu)$_4$](+2cation)[5,6], [Pt(Ettu)$_4$](+2cation)[7], [Pt(Me$_2$tu)$_4$](+2cation)[8], [Pt(Et$_2$tu)$_4$](+2cation)[9], [Pt(PhS)$_4$](-2anion)[10] and [Pt(C$_4$H$_6$N$_2$S)$_4$](+2cation)[11,]12. The Pt-S bond distances range from 2.30 Å to 2.34 Å (average 2.32 Å). The maximum deviations of *cis*- and *trans*- S-Pt-S bond angles, from the ideal values of 90º and 180º, are 9º and 10º, respectively.

Two derivatives [Pt(η^2-EtOCS$_2$)(EtOCS$_2$)$_2$](-1anion)[13] and [Pt{η^2-MeSCH(Me)CH(Me)}(C$_6$F$_5$S)$_2$][14] use one bidentate and pair of monodentate ligands to form a distorted square planar geometry about each Pt(II) atom. The geometry about the Pt(II) atom is more distorted in the former than in the latter. This is because the chelate rings, which is four- in the former and six-membered in the latter, with S-Pt-S "bite" angles of 76.5(10)º and 88.59(5)º, respectively.

The most common derivatives are those with a pair of bidentate (S,S) ligands. The size of the chelate rings include four-membered, [Pt(η^2-EtOCS$_2$)$_2$][15], [Pt(η^2-i-mnt)$_2$](-2anion)[16], [Pt(η^2-Et$_2$NCS$_2$)$_2$][17], [Pt{η^2-(C$_2$H$_4$OH)$_2$NCS$_2$}$_2$][17], [Pt{η^2-(hm)$_2$NCS$_2$}$_2$][18], [Pt{η^2-(Pr^{i}O)$_2$PS$_2$}$_2$][19], and [Pt{η^2-Pt(OEt)PS$_2$}$_2$][20] with a mean Pt-S bond distance of 2.32 Å and mean S-Pt-S "bite" angles of 75.0º for RCS$_2$ ligands, and 2.34 Å and 83.6º for RPS$_2$ ligands. Another derivative [Pt{η^2-C$_5$H$_9$S$_2$)(η^2-C$_5$H$_9$S$_3$)][21] has a distorted square planar geometry of four- and five-membered metallocyclic rings. The S-Pt-S "bite" angles within the two rings are 73.0(1)º and 93.6(1)º, respectively. The pairs of Pt-S bond distances are corresponding different at 2.323 Å and 2.242 Å.

In several other derivatives, [Pt(η^2-S$_4$)$_2$](-2anion)[22], [Pt(η^2-dtox)$_2$](-2anion)[23-27], [Pt(η^2-eebt)$_2$][28], [Pt(η^2-mnt)$_2$](-2anion)[29-35], [Pt(η^2-dmit)$_2$](-2anion)[36,37], [Pt(η^2-dtsq)$_2$](-2anion)[38], [Pt(η^2-btst)$_2$][39], [Pt(η^2-tdt)$_2$](-2anion)[40], [Pt(η^2-C$_3$S$_5$)$_2$](-2anion)[41], [Pt(η^2-ttc)$_2$](+2cation)[42], [Pt(η^2-HBu$^n_2$dto)$_2$][43], [Pt(η^2-dpedt)$_2$][44], [Pt(η^2-dchtpf)$_2$][45], [Pt(η^2-ddbt$_2$][46], [Pt(η^2-[10]aneS$_3$)$_2$](+2cation)[47-49] and [Pt(η^2-odtc)$_2$](+2cation)[50], two identical bidentate (S,S) ligands in each case form two five- membered rings about the Pt(II) atoms, representing the most common situation for PtS$_4$ chromophores. The Pt-S bond distances range from 2.24 to 2.32 Å with a mean value of 2.29 Å. The S-Pt-S "bite" angles range from 86.5º to 92.0º/(average 89.3º).

In another three derivatives, [Pt(η^2-ptt)$_2$](+2cation)[51], [Pt(η^2-dtbu)$_2$][52] and [Pt{η^2-N(Pr$^i_2$PS)$_2$}$_2$][53,] (Fig.1) a pair of bidentate (S,S) ligands form two six-membered chelate rings. All three differ in the ring atoms involved, with the ring angle closing in the order 97.56(4)º (SC$_3$S)[51] > 92.7(7)º (SCNCS)[52] > 90.0(1)º (SPNPS)[53]. The mean Pt-S bond distance elongates in the same order, 2.335Å > 2.295Å > 2.280Å.

In the remaining nine derivatives, [Pt(η^4-bmptp)][54], [Pt(η^4-[12]aneS$_4$)](+2cation)[55,56], [Pt(η^4-[16]aneS$_4$)](+2cation)[57], [Pt(η^4-[14]andS$_4$)](+2cation)[58], [Pt(η^4-tt[6.6]OC)](+2cation)[59], [Pt(η^4-dottc)](+2cation)[50], [Pt(η^4-[18]aneS$_6$)](+2cation)[60] and [Pt(η^4-[20]aneS$_6$)](+2cation)[49], a tetradentate (S,S,S,S) ligand is bonded to the Pt(II) atom. In the first a tetradentate ligand forms two five- and two six- membered metallocycles with the mean S-Pt-S "bite" angles of 89.3(2)º and 90.6(2) º, respectively[54]. In the next the tetradentate ligands create four five-membered metallocycles with the mean S-Pt-S "bite" angle of 88.9º, and mean Pt-S bond distance of 2.287(4)Å[55,56]. In the next example[57] a tetradentate ligand forms four six-membered metallocycles with the mean S-Pt-S "bite" angle of 98.9º. The next[58,59] has tetradentate ligands forming two pairs of non-equivalent chelate rings in *trans* positions five- and seven-membered metallocyclic rings with the mean S-Pt-S "bite" angle of 87.0º and 93.0º. The mean Pt-S bond distances reflect the size of the respective metallocycle, with the values of 2.352(five-) and 2.246Å (seven-membered). Then tetradentate ligands create two pairs of six- and eight-membered metallocyclic rings in *trans* related positions[49,50,60]. The mean S-Pt-S "bite" angles are 84.0º and 90.3º, respectively, and the mean Pt-S bond distance is 2.305Å.

There are three derivatives[2,28,42] which contain two crystallographically independent molecules within the same crystal, differing mostly by degree of distortion. These are examples of distortion isomerism[61,62].

In this series of monomeric Pt(II) complexes with PtS$_4$ chromophore, the mean Pt-S bond distance elongates in the order: 2.30Å (bi-, tetra-) < 2.32Å (monodentate). In the series of bidentate (S,S) ligands the mean Pt-S bond distance reflects the size of the chelate rings and elongates in the sequence: 2.29 Å (five-) < 2.30 Å (six-) < 2.32 Å (four-membered).

The effects of both electronic and steric factors of the coordinated ligands can be seen in the opening of the S-Pt-S bond angles of the respective metallocycles. The mean S-Pt-S "bite" angle opens in the sequence: 75.0º (SCS) < 83.6º (SPS) < 86.5º (SCPS) < 89.3º (SC$_2$S) < 93.4º (SS$_2$S) < 93.6º (SCPS) < 93.7º (SC$_3$S) < 95.3º (SC$_4$S).

2.2 PtS$_3$X (X = O, N, Cl, P, As or I) Derivatives

There are eleven such derivatives for which crystallographic and structural parameters are available. These complexes crystallize in two crystal classes, triclinic (x4) and monoclinic (x7). In orange [Pt(C$_5$H$_5$NOS)$_2$(η^2-C$_5$H$_4$NOS)](+1cation) the inner coordination sphere PtS$_3$O is created by pair of monodentate (S) ligands and heterobidentate (O,S) ligand [63]. There are two crystallographically independent molecules within the same crystal, differing mostly by degree of distortion. The sum of all four (Pt-S(x3) plus Pt-O(x1)) bond distances are 8.91Å (molecule 1) and 8.94Å (molecule 2), indicating that molecule 1 is somewhat more crowded than the molecule 2. The five-membered chelate rings have values of O-Pt-S "bite" angles of 86.4(5)º (molecule 1) and 85.1(5)º (molecule 2).

In [Pt(η^3-bmtmp)(SCN)](+1cation)[64], is terdentate (S,N,S) ligand with the S atoms in the *trans* positions to each other[64]. The fourth coordination site, trans to the N atom, is occupied by the S atom of a SCN group. The Pt-L bond distance elongates in the order: 2.014(3)Å (N) < 2.285(1) Å (η^2-S) < 2.289(1)Å (SCN). The terdentate-S,N,S ligand forms pair of five- membered metallocyclic rings with N-atom in the center. The five-membered chelate rings have the mean N-Pt-S "bite" angle of 85.6º.

There are three derivatives [Pt(ptc)$_3$Cl](+1cation)[65], [Pt(η^2-Et$_2$NCS$_2$)(η-MeS$_2$CNEt$_2$)Cl][66] and [Pt(η^3-dmt)Cl](+1cation)[67] with PtS$_3$Cl chromophore. In the first[65], three monodentate S donor ligands plus the Cl atom form (PtS$_3$Cl), with the mean Pt-S bond distance of 2.298 Å and Pt-Cl of 2.318(4)Å. In the second[66], a bidentate (S,S) ligand forms a four-membered ring with S-Pt-S "bite" angle of 74.1(1)º. The Pt-L bond distances are 2.300(2)Å (mono-S), 2.329(2)Å (η^2-S) and 2.323(2)Å (Cl). In the third[67] the Pt-S value of the central (S) atom of the terdentate ligand is 2.256(4)Å and much shorter than the mean value of the satellite S atoms (2-304Å). The Pt-Cl bond distance is 2.327(4)Å. The six-membered chelate rings have a mean S-.Pt-S "bite" angle of 93.6(2)º. The sum of all four (Pt-S(x3) plus Pt-Cl) bond distances increases in the order: 9.19Å[67] < 9.21Å[65] < 9.28Å[66].

There are four derivatives: [Pt(η^3-dmtt)(PPh$_3$)](+1cation)[67], (Fig. 2) [Pt(η^2-Et$_2$NCS$_2$)(η-Et$_2$NCS$_2$)

$(PPh_3)]$[68], $[Pt\{\eta^2\text{-}(EtO)_2PS_2\}\{\eta\text{-}(EtO_2PS_2\}(PPh_3)]$[68] and $[Pt\{\eta^2\text{-}Bu^tNCS_2\}(\eta\text{-}Bu^tNCS)(Pcy_3)]$[69]. In the first[67] a terdentate (S,S,S) ligand plus a PPh_3 ligand form a distorted square planar geometry about the Pt(II) atom, (PtS_3P). The mean Pt-S bond distance of 2.338 Å is only slightly longer than the Pt-Cl bond distance (2.332Å). The chelating ligand forms two six-membered metallocycles with the mean S-Pt-S "bite" angle of 91.7º. In the remaining three derivatives[68,69] the respective chromophore is build up of a bidentate–S,S ligand, plus a monodentate-S ligand and a PR_3 group. The mean Pt-L bond distance elongates in the order 2.253Å (P) < 2.328Å (mono- SL) < 2.348Å (bi- SL). Each chelate ligand creates a four-membered metallocyclic ring with a S-Pt-S "bite" angle of 74.2º (SCS)[69] < 74.6º (SCS)[68] < 82.7º (SPS)[68].

In yellow $[Pt\{\eta^2\text{-}(EtO)_2PS_2\}\{\eta\text{-}(EtO)_2PS_2\}(ape)]$[70] a chelating-(S,S) ligand plus a monodentate-S ligand and ape(As) group forms a distorted square planar geometry about the Pt(II) atom, (PtS_3As). The chelate ligand creates a four-membered metallocycle with the S-Pt-S "bite" angle of 83.2(1)º (SPS). The Pt-L bond distance elongates in the order 2.342(2)Å (mono-S) < 2.350(2)Å (η^2S, average) < 2.361(1)Å (As).

In orange $[Pt(\eta^3\text{-}dptt)I](+1cation)$[67] a terdentate-S,S,S ligand plus an iodine atom forms the PtS_3I chromophore. The terdentate ligand creates two six-membered metallocyclic rings with mean S-Pt-S "bite" angle of 95.2º. The mean Pt-S bond distance is 2.287 Å and Pt-I am 2.602(7)Å.

In the series of PtS_3X derivatives the mean Pt-S bond distance elongates in the order 2.304Å (η^3-SL) < 2.305Å (η-SL) < 2.340Å (η^2-SL). The mean value of the monodentate Pt-L bond distance elongates in the order 2.26Å (PL) < 2.305Å (SL) < 2.33Å (Cl) < 2.36Å (AsL) < 2.60Å (I).

In PtS_3X derivatives the total mean Pt-X (trans to S) bond distances elongated in the sequence: 2.05Å (O) < 2.277Å (P) < 2.323Å (Cl) < 2.360Å (As) < 2.602Å (I). The mean Pt-S (trans to X) bond distance elongated in the sequence: 2.282Å (Cl) < 2.285Å (O) < 2.289Å (N) < 2.291Å (I) < 2.364Å (P) < 2.373Å (As). The mean Pt-S (trans to S) bond distance is 2.133Å. The sum of all four (Pt-S(x3) + Pt-X(x1)) bond distances growing in the order: 8.87Å (PtS_3N) < 8.92Å (PtS_3O) < 9.22Å (PtS_3Cl) < 9.30Å (PtS_3P) < 9.40Å (PtS_3As) < 9.47Å (PtS_3I) which follows quite well covalent radius of X, except N.

2.3 PtS_2X_2 (X = O, N, C, Cl, P, Br, I or As) Derivatives

There are seven yellow derivatives in which a distorted square planar geometry about the Pt(II) atom has the PtS_2O_2 chromophore. These derivatives crystallize in three crystal classes, hexagonal (x1) < triclinic and monoclinic (each x3). In *cis*-$[Pt(dmso)_4](+2cation)$[71] two dmso molecules coordinate via S atoms and the remaining two via O atoms. In another *cis*-$[Pt(dmso)_2(ONO_2)_2]$[72] a pair of dmso S-donor and pair of NO_3 groups O-donor create the PtS_2O_2 chromophore. In two derivatives $[Pt(\eta^2\text{-}ox)(SCN)_2](-4anion)$[73] and $[Pt(\eta^2\text{-}cbdc)(dmso)_2]$[74] bidentate-O,O ligands with monodentate-S ligands create the same chromophore. The oxalate ligand[73] form five-membered metallocycles, and the cbdc ligand[74] forms a six-membered metallocycle. In the former O-Pt-O "bite" angle is 82.2º and in the latter the value is 88.3º.

The remaining three derivatives $[Pt(\eta^2\text{-}mtabm)_2]$[75], $[Pt(\eta^2\text{-}bbtu)_2]$[76] and $[Pt(\eta^2\text{-}bntu)_2]$[77] (Fig. 3) have a pair of heterobidentate (O,S) donor ligands. Unfortunately, for the first derivative[75] only unit cell dimensions are available. In the derivatives[76,77] the heterobidentate (O,S) ligands create six-membered metallocycles with a mean O-Pt-S "bite" angle of 94.0º. The mean Pt-L bond distance in this series elongates in the order 2.03Å (η^2-OL) < 2.04Å (OL) < 2.24Å (SL). For heterobidentate ligands the mean values are 2.01Å (O) and 2.24Å (S).

There are over thirty derivatives in which a distorted square planar geometry about the Pt(II) atom has the PtS_2N_2 chromophore. These derivatives crystallize in three crystal classes: orthorhombic (x4) < triclinic (x9) < monoclinic (x21). The types of ligand environment found in these derivatives can be separated into the following groups:

a) monodentate N- as well as S-donor ligands: *trans*-$[Pt(NH_3)_2(tu)_2](+2cation)$[6], *trans*-$[Pt(MeNH_2)_2(tu)_2](+2cation)$[6], *trans*-$[Pt(py)_2(SCN)_2]$[78] and *trans*-$[Pt(hyp)_2(tu)_2]$[79];

b) monodentate N-donor ligands with bidentate S,S-donor (five- membered ring)

$[Pt(NH_3)_2(\eta^2\text{-dtcym})]$[80];

c) bidentate N,N-donors (four- membered ring) with two monodentate S-donor, $[Pt(\eta^2\text{-dbbpy})(4\text{-Spy})_2]$[81] and $[Pt(\eta^2\text{-en})(dmso)_2]$ (+2cation)[82];

d) bidentate N,N´-donors (five-membered ring) with bidentate S,S-donors (four- membered ring), $[Pt(\eta^2\text{-dach})(\eta^2\text{-dtcym})]$[83] and $[Pt(\eta^2\text{-dach})(\eta^2\text{-bmtmy})]$[84];

e) bidentate N,N- as well as S,S-donors (both five-membered rings), $[Pt(\eta^2\text{-by})(\eta^2\text{-pddt})]$[85], $[Pt(\eta^2\text{-bpy})(\eta^2\text{-bdt})]$[86], $[Pt(\eta^2\text{-bpy})(\eta^2\text{-bdtO}_4)]$[86], $[Pt(\eta^2\text{-bdm})(\eta^2\text{-mnt})]$[87], $[Pt(\eta^2\text{-Me}_2\text{bpy})(\eta^2\text{-met})]$[88], and $[Pt(\eta^2\text{-phen})(\eta^2\text{-[9]aneS}_4)]$[89];

f) a pair of heterobidentate N,S-donors (five-membered rings), $[Pt\{\eta^2\text{-N(Pr}^i\text{)NC(S)SMe}\}_2]$[90], $[Pt\{\eta^2\text{-N(Bu}^t\text{)NC(S)SMe}\}_2]$[90], $[Pt\{\eta^2\text{-N(CH}_2\text{Ph)NC(S)SMe}\}_2]$[91], $[Pt(\eta^2\text{-C}_6\text{H}_8\text{N}_2\text{S}_2)_2]$[92], $[Pt(\eta^2\text{-o-atp})_2]$[93], $[Pt(\eta^2\text{-tscb})_2]$(+2cation)[94], $[Pt(\eta^2\text{-C}_7\text{H}_{10}\text{NS}_2)_2]$[95], and $[Pt(\eta^2\text{-ptmqu})_2]$[96];

g) terdentate S,N,S-donors (six-membered rings) plus monodentate N-donor, $[Pt(\eta^3\text{-bmtmp})(py)]$(+2cation)[64] and $[Pt(\eta^3\text{-bmtmp})(p\text{-NCpy})]$[97];

h) h) tetradentate S,N,N,S-donors (five-membered rings), $[Pt(\eta^4\text{-ddbt})]$[98] (Fig. 4); tetradentate -N,N,S,S-donors (five- and eight-membered rings) $[Pt(\eta^4\text{-ttphen})]$(+2cation)[99] and tetradentate -N,N,S,S-donors (six- and eight-membered rings) $[Pt(\eta^4\text{-C}_{13}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_3)]$[100].

There are *trans*-[6,64,78,79,90-97] and *cis*-[80-89,98-100] derivatives. The molecule of $[Pt(\eta^3\text{-bmtmp})(p\text{-NCpy})](ClO_4)_2$[97] contains two crystallographically independent molecules within the same crystal, differing mostly by degree of distortion. The mean values of Pt-L (monodentate) bonds are 2.045Å (N) and 2.302Å (S). For homo-bidentate and heterobi-, ter- and tetradentate ligands the mean values of the Pt-L bond and L-Pt-L “bite” angles of the chelate rings are given in Table 1.

From the data (Table 1) it can be seen that the mean Pt-N bond distances are shorter than the Pt-S bond distances, as expected. The mean Pt-L bond distances in homo-ligands are somewhat longer than those in hetero-ligands. The chelate ring opens as the number of ring atoms increases, as expected.

In pale yellow $[Pt(CNMe)_2(\eta^2\text{-mnt})]$[101] the respective ligands create a distorted square planar arrangement about the Pt(II) atom (PtS_2C_2), with the mean Pt-L bond distances of 1.95Å (C) and 2.284Å (S). The chelating ligand forms four- membered matallocycle with the value of S-Pt-S bite angle of 75º.

There are forty mostly yellow derivatives in which each Pt(II) atom has an inner coordination sphere of PtS_2Cl_2. These derivatives crystallize in four crystal classes, tetragonal, triclinic (each x2) < orthorhombic (x9) < monoclinic (x27). In most of them, $[Pt(Me_2S)_2Cl_2]$[102,103], $[Pt(Et_2S)_2Cl_2]$[104], $[Pt(dmso)_2Cl_2]$[105,106], $[Pt(emso)_2Cl_2]$[107], $[Pt(dpso)_2Cl_2]$[107,108], $[Pt(bmso)_2Cl_2]$[109,110], $[Pt(pmso)_2Cl_2]$[110,111], $[Pt(dbso)_2Cl_2]$[112], $[Pt(1,4\text{-tx})_2Cl_2]$[113], $[Pt(dmtc)_2Cl_2]$[114,115], $[Pt(mtso)_2Cl_2]$[116,117], $[Pt(thto)_2Cl_2]$[118], $[Pt(bptu)_2Cl_2]$[119], $[Pt(dds)_2Cl_2]$[120], $[Pt(tht)_2Cl_2]$[121], $[Pt(C_8H_8S)_2Cl_2]$[122], and $[Pt(C_6H_{10}S)_2Cl_2]$[123], only monodentate ligands are involved. The mean Pt-L bond distances *cis* vs *trans* are: 2.255Å (S) and 2.308Å (Cl) vs 2.302Å (S) and 2.302Å (Cl).

In the remaining *cis*-derivatives, beside chlorine atoms, bidentate S,S-ligands are involved. In $[Pt(\eta^2\text{-gapy})Cl_2]$[124] the bidentate ligand forms a four-membered ring. In $[Pt(\eta^2\text{-bmtfe})Cl_2]$[125], $[Pt(\eta^2\text{-bpse})Cl_2]$[126] (Fig. 5), $[Pt(\eta^2\text{-rac-bphse})Cl_2]$[127,128], $[Pt(\eta^2\text{-meso-bphse})Cl_2]$[128], $[Pt(\eta^2\text{-bphsal})Cl_2]$[129], $[Pt(\eta^2\text{-tfp})Cl_2]$[130], $[Pt(\eta^2\text{-btfp})Cl_2]$[131,132], $[Pt(\eta^2\text{-bpte})Cl_2]$[133], $[Pt(\eta^2\text{-ctttv})Cl_2]$[134] and $[Pt(\eta^2\text{-ttc})Cl_2]$[135] the bidentate ligands form five-membered rings, in $[Pt(\eta^2\text{-[10]aneS}_3)Cl_2]$[48] a bidentate ligand forms a six-membered ring, and in $[Pt(\eta^2\text{-dt18C}_6)Cl_2]$[136] the bidentate ligand forms an eleven-membered ring. The mean Pt-Cl bond distance of 2.318 Å is about 0.010 Å longer than that found in derivatives where only monodentate S-ligands are involved. The mean Pt-S (bidentate) bond distance of 2.240Å is about 0.026Å shorter than that found in derivatives in which only monodentate S ligands are involved (2.266Å). The chelate ring (S-Pt-S) “bite” angle opens in the order, 78.3º (four-) < 87.0º (eleven-) < 90.0º (five-) < 103.5º (six-membered) rings.

There are three derivatives which exist in two isomeric forms *cis*- and *trans*-: $[Pt(Me_2S)_2Cl_2]$[102,103], $[Pt(tx)_2Cl_2]$[113] and $[Pt(dmtc)_2Cl_2]$[114,115]. Another four derivatives[48,110,116,122] contain two crystallographically independent molecules within the same crystal, differing mostly by degree of distortion, and are examples of distortion isomerism[61,62]. Overall, the sum of all four (Pt-S (x2) plus Pt-Cl (x2)) bond distances is somewhat smaller for *cis*-derivatives than for *trans*-derivatives, 9.12 and 9.21Å, respectively. The *cis*- Cl-Pt-Cl bond angles in the series of derivatives in which monodentate S-donor ligands are involved range from 87.5º to 90.5º (average 88.5º), which is smaller than those found in the derivatives with bidentate S,S-donor ligands of mean value of 91.5º (range 90.0 – 93.5º).

There are almost sixty, mostly yellow Pt(II) derivatives, with a PtS_2P_2 chromophore. These crystallize in three crystal classes: orthorhombic (x7) < triclinic (x20) < monoclinic (x30). Six derivatives, three *cis*-$[Pt(SH)_2(PPh_3)_2]$[137,138] and $[Pt(tipt)_2(PPh_3)_2]$[139], and three *trans*-$[Pt(SO_3Me)_2(PPh_3)_2]$[140], $[Pt(SC{\equiv}CSMe_2)_2(PPh_3)_2]$[141] and $[Pt(Bu^t{}_2NCS_2)_2(PMe_2Ph)_2]$[142], have pairs of monodentate ligands creating a slightly distorted square planar geometry about each Pt(II) atom. In thirty two *cis*-derivatives, a bidentate S,S-ligands with a pair of monodentate P-donor ligands create these chromophore (PtS_2P_2). In $[Pt(\eta^2\text{-}S_2CO)(PPh_3)_2]$[142,143], $[Pt(\eta^2\text{-}S_2CO)\{P(OMe)Ph_2\}_2]$[144], $[Pt(\eta^2\text{-}S_2CH_2)\{P(py)Ph_2\}_2]$[145], $[Pt(\eta^2\text{-}S_2CH_2)(PMe_2Ph)_2]$[146], $[Pt(\eta^2\text{-}S_2CF_2)(PPh_3)_2]$[147], $[Pt(\eta^2\text{-}S_3O)(PPh_3)_2]$[148], $[Pt(\eta^2\text{-}Et_2NCS_2)\{P(S)Ph_2\}_2]$(-1anion)[149], $[Pt(\eta^2\text{-}PhCH_2NCS_2)(PEt_3)_2]$[150], $[Pt(\eta^2\text{-}dtba)(PEt_3)_2]$[151], $[Pt(\eta^2\text{-}dtba)(PBu_3)_2]$[151], $[Pt(\eta^2\text{-}MeNNCS_2)(PPh_3)_2]$[152], $[Pt\{\eta^2\text{-}PhClO)(CHCCS_2\}(PPh_3)_2]$[153] and $[Pt\{\eta^2\text{-}4\text{-}MeOC_6H_4P(S)S_2\}(PPh_3)_2]$[154] the chelating ligands create four-membered metallocyclic rings. In $[Pt(\eta^2\text{-}S_3N)(PEt_3)_2]$(+1cation)[155], $[Pt(\eta^2\text{-}S_3N)(PMePh_2)_2]$(+1cation)[155], $[Pt(\eta^2\text{-}SCH{=}CHS)(PBu_3)_2]$[156], $[Pt\{\eta^2\text{-}S(PH_2)_2S\}(PPh_3)_2]$[157,158], $[Pt(\eta^2\text{-}mnt)(PMe_2Ph)_2]$[159], $[Pt(\eta^2\text{-}met)\{P(OMe)_3\}_2]$[88], $[Pt(\eta^2\text{-}dmm)(PPh_3)_2]$[160], $[Pt(\eta^2\text{-}dmid)(PPh_3)_2]$[161] and $[Pt(\eta^2\text{-}S_4)(PPh_3)_2]$[162] the chelating S,S-ligands created five-membered metallocycles. In $[Pt\{\eta^2\text{-}SNC(Ph)NS\}(PPh_3)_2]$[163], $[Pt\{\eta^2\text{-}SP(Ph)_2NP(Ph)_2S\}(PEt_3)_2]$[164], $[Pt\{\eta^2\text{-}SP(OPh)_2NP(OPh_2S\}(PMe_3)_2]$[164] and $[Pt(\eta^2\text{-}dpdtar)(PPh_3)_2]$[165] (Fig. 6), the chelating ligands create six-membered metallocycles. In $[Pt(\eta^2\text{-}dpdtar)(PPh_3)_2]$[166] and $[Pt(\eta^2\text{-}sbs)(PPh_3)_2]$[167] seven-membered metallocycles occur. In three derivatives a pair of monodentate S-donor ligands with bidentate P,P-ligands form a distorted square planar geometry, with four- $[Pt(PhS)_2(\eta^2\text{-}dppm)]$[168] and with five-membered metallocycles $[Pt(PhS)_2(\eta^2\text{-}dppe)]$[169] and $[Pt(mmp)_2(\eta^2\text{-}dppe)]$[170]. Bidentate S,S- as well as P,P-donor ligands are found in another seven derivatives with distorted *cis*-square planar geometry. The chelates form four- S-Pt-S with five- P-Pt-P membered rings in $[Pt(\eta^2\text{-}S_2CO)(\eta^2\text{-}dppe)]$[142] and $[Pt(\eta^2\text{-}dtba)(\eta^2\text{-}dppe)]$[151]; in $[Pt(\eta^2\text{-}dmit)(\eta^2\text{-}dppe)]$[171], $[Pt(\eta^2\text{-}mnt)(\eta^2\text{-}dppe)]$[172], $[Pt(\eta^2\text{-}mnt)(\eta^2\text{-}dppb)]$[172] and $[Pt(\eta^2\text{-}S_4)(\eta^2\text{-}dppe)]$[173] both S,S and P,P ligands create five-membered metallocycles. In $[Pt\{\eta^2\text{-}S(CH_2)_3S\}(\eta^2\text{-}dppm)]$[174] chelating S,S-ligand form six- and chelating P,P-ligand four-membered metallocyclic rings.

A pair of heterobidentate S,P-ligands are found in another four derivatives, $[Pt(\eta^2\text{-}ptf)_2]$[175], $[Pt(\eta^2\text{-}dcptf)_2]$[176], $[Pt(\eta^2\text{-}ptpc)_2]$[177] and $[Pt(\eta^2\text{-}diop)_2]$[178], which create a distorted square planar geometry about the Pt(II) atom which has pair of four-[175,176] and five-[177,178] membered metallocycles.

In another four derivatives tetradentate S_2P_2-donor ligands create the PtS_2P_2 chromophore, $[Pt(\eta^4\text{-}C_{30}H_{32}P_2S_2]$(+2cation)[179] (Fig. 7), $[Pt(\eta^4\text{-}dpdtc)]$(+2cation)[180], $[Pt(\eta^4\text{-}dpdh)]$(+2cation)[181] and $[Pt(\eta^4\text{-}dpth)]$(+2cation)[177]. The macrocyclic ligands form five-membered S-Pt-S and P-Pt-P rings[179]; five- S-Pt-P, six- S-Pt-S and P-Pt-P rings[180]; five- S-Pt-P and six- S-Pt-P rings[181]; and six-membered S-Pt-P rings[177].

The mean Pt-L (monodentate) bond distances *cis*- vs *trans* are 2.355Å vs 2.300Å (S), and 2.285 vs 2.330Å (P). In the series of bidentate chelating ligands, the effect of both electronic and steric factors can be observed in the opening of the L-Pt-L bond angles for the metallocyclic rings. For example, in the four-membered rings the S-Pt-S "bite" angle opens in the sequence (mean values): 73.5º (SCP) < 75.0º (SCS) < 81.0º (SSS) < 81.7º (SPS). In the five-membered rings the sequence is: 88.0º (SC_2S) < 90.0º (SSNS) < 92.0º (SS_2S). For the six-membered rings the sequence is: 87.0º (SC_3S) < 92.5º (SC_3P) < 96.0º (SPNPS). The mean P-Pt-P "bite" angle opens in the order: 73.2º (PCP) < 87.5º (PC_2P < 94.2º (PCSCP).

There are four yellow monoclinic derivatives, *cis*-$[Pt(dmso)_2Br_2]$[182,183], *trans*-$[Pt(tx)_2Br_2]$[184] and *cis*-$[Pt(\eta^2\text{-}bphse)Br_2]$[129] in which each Pt(II) atom has a PtS_2Br_2 chromophore. In some cases[182-184] only monodentate ligands are involved. In another[129] a chelating ligand creates a five-membered metallocycle with S-Pt-S "bite" angle of 91.1(2)º. The mean Pt-L bond distance elongates in the order: 2.225Å (bi- S) < 2.260Å (S) < 2.435Å (Br).

In another six derivatives, each Pt(II) atom has PtS_2I_2 inner coordination sphere. These derivatives crystallize in two crystal classes, monoclinic and triclinic (each x3). In *trans*-$[Pt(dmso)_2I_2]$[182], $[Pt(Me_2S)_2I_2]$[184], $[Pt(tht)_2I_2]$[186], $[Pt(bbtu)_2I_2]$[187] and $[Pt(etc)_2I_2]$[188] only monodentate ligands are involved. In *cis*-$[Pt(\eta^2\text{-bphse})I_2]$[129] the chelating ligand forms a five-membered metallocycle with S-Pt-S "bite" angle of 91.00(8) º. The mean Pt-L bond distances in the *cis*-derivatives are 2.265Å (S) and 2.600Å (I). These values are somewhat shorter than those found in *trans*-derivative[129], with the values of 2.30Å (S) and 2.610Å (I).

In two yellow examples, *trans*-$[Pt(\eta^2\text{-}C_8H_{10}SAs)_2]$[189] and $[Pt(\eta^2\text{-}C_{11}H_{18}O_2SAs)_2]$[190], a pair of heterobidentate S,As-ligands create a distorted square planar geometry about each Pt(II) atom. Each chelating ligand forms a five-membered metallocycle with the mean S-Pt-As "bite" angle of 88.7(1)º. The mean Pt-L bond distances are 2.30 Å (S) and 2.366 Å (As).

The total mean values of Pt-L bond distances in PtS_2X_2 derivatives can be devided into the three groups. In *cis*- derivatives the mean Pt-S (trans to X) elongated in the sequence: 2.242Å (X=O) < 2.250Å (Cl,Br) < 2.265Å (I) < 2.275Å (N) < 2.280Å (CN) < 2.335Å (P). The mean Pt-X (trans to S) elongated in the sequence: 1,95Å (CN) < 2.025Å (N) < 2.042Å (O) < 2.293Å (P) < 2.310Å (Cl) < 2.440Å (Br) < 2.600Å (I).

In *trans*- PtS_2X_2 derivatives tha mean Pt-L (trans to X) and Pt-S (trans to S) are: 1.98Å (O) and 2.250Å (S); 2.055Å (N) and 2.317Å (S); 2.301Å (Cl) and 2.303Å (S); 2.314Å (P) and 2.320Å (S); 2.420Å (Br) and 2.280Å (S); 2.260Å (I) and 2.318Å (S); 2.566Å (As) and 2.303Å (S).

Tha sum of all four (Pt-S(x2) + Pt-X(x2)) bond distances, *cis*- vs *trans*- configuration are 8.55Å vs 8.46Å (PtS_2O_2); 8.56Å vs 8.74Å (PtS_2N_2); 8.46Å vs 0 (PtS_2C_2); 9.19Åvs 9.27Å (PtS_2P_2; 9.38Å vs 9.40Å (PtS_2Br_2); 9.73Å vs 9.85Å (PtS_2I_2); 0 vs 9.34Å (PtS_2As_2). As can be seen the inner coordination spheres in *cis*- derivatives, except PtO_2S_2 are somewhat less crowded and more distorted than in their *trans*- partners.

2.4 $PtSX_3$ (X = N, Cl, P or Br) Derivatives

There are two red derivatives triclinic $[Pt(\eta^3\text{-trpy})\{S(CH_2)_2OH\}]NO_3$[192] and orthorhombic $[Pt(\eta^3\text{-trpy})\{S(CH_2)_2OH\}]$(+1cation)[193] in which terdentate trpy (N,N,N) ligand with monodentate S donor ligand created a distorted square planar geometry about each Pt(II) atom- ($PtSN_3$). Unfortunately only for triclinic derivative X-ray data are available and for orthorhombic only unit cell dimensions. The terdentate ligand forms pair of five- membered metallocycle with the mean N-Pt-N "bite" angle of 80.7º. The Pt-N bond to the central N atom at 1.968(5)Å is about 0.06Å shorter than to the "satellites" N atoms (2.027Å). The Pt-S bond distance is 2.303(2)Å.

There are thirteen mostly yellow derivatives in which besides three Cl atoms a monodentate S ligand: Me_2S[193], dmso[194-201], Et_2SO[202], demso[203] and Ph_2SO[111,204], created a distorted square planar geometry about each Pt(II) atom ($PtCl_3S$). These derivatives crystallized in three crystal classes: triclinic (x1) < orthorhombic (x3) < monoclinic (x9). The mean Pt-L bond distances elongated in the order: 2.300Å (Cl, trans to Cl) < 2.305Å (S) < 2.324Å (Cl, trans to S). The maximum deviations of *cis*-Cl-Pt-Cl and Cl-Pt-S bond angles from the ideal 90º are 1.9º and 3.2º; for the ideal *trans* (180º) the deviations are 4.9 and 4.3º, respectively.

In three yellow triclinic derivatives: $[Pt(PMe_2Ph)_3(SO_3)]$[205], $[Pt(\eta^2\text{-dppm})\{\eta^2\text{-}Ph_2PN(Et)C{=}(NEt)S\}]$[206] and $[Pt\{\eta^3\text{-}PhP(CH_2CH_2PPh_2)_2\}(\eta\text{-}Et_2NCS_2)]$[207] each Pt(II) atom has PtP_3S inner coordination sphere. In[205] only monodentate ligand are available, in[206] homobidentate -P,P with heterobidentate -P,S ligands, and in[207] a terdentate -P,P,P with monodentate S ligand created PtP_3S chromophore. In[206] homobidentate P,P ligand forms four- membered metallocycle with the P-Pt-P "bite" angle of 71.40(6)º, and heterobidentate -S,P ligand forms five-membered metallocycle (S-Pt-P, 85.72(6)º). In[207] homoterdentate -P,P,P ligand forms pair of five- membered metallocycles with the mean P-Pt-P "bite" angle of 85.0º. The mean Pt-P bond distance elongated in the order: 2.270Å (η^3-P) < 2.306Å (η^2-P) < 2.337Å (η-P). The mean Pt-S bond distance is 2.306Å and for heterobidentate -S,P ligand the Pt-L bond values are 2.269(2)Å (P) and 2.291(2)Å (S).

In two orange triclinic derivatives: $[PtBr_3(Et_2SO)]$(-1anion)[208] and $[PtBr_3(Ph_2SO)]$(-1anion)[111] the respective ligands created a distorted square-planar geometry ($PtBr_3S$). The mean Pt-L bond distances are 2.222 Å (S) and 2.425 Å (Br). The mean *cis*- as well as *trans*- Br-Pt-Br bond angles are somewhat smaller (88.9º and 175.3º) than those of Br-Pt-S bond angles with the mean values of 91.3º and 176.4º, respectively.

The total means values in $PtSX_3$ derivatives of Pt-S bond distances elongated in the sequences:

Pt-S (trans X): 2.201Å (Cl) < 2.220Å (P) < 2.303Å (N) < 2.344Å (P)

Pt-X (trans X): 1.996Å (N) < 2.290Å (P) < 2.300Å (Cl) < 2.420Å (Br)

Pt-X (trans S): 2.03Å (N) < 2.314Å (Cl) < 2.315Å (P) < 2.434Å (Br)

The sum of all four (Pt-X(x3) + Pt-S) bond distance growing in the sequence: 8.32Å ($PtSN_3$) < 9.11Å ($PtSCl_3$) < 9.24Å ($PtSP_3$) < 9.49Å $PtSBr_3$), which corresponds well with are increasing covalent radius of X-atom.

1.5 PtA_2XY Derivatives

There are several derivatives in which inner coordination sphere about Pt(II) atom is build up by three different donor atoms.

2.5.1 PtS_2NX (X = Cl, P or Br), PtS_2ClX (X = P, Br or I) and PtS_2BrI Derivatives

Yellow orthorhombic *trans*-[Pt{η^3-bmtmp)Cl](ClO_4)[209] is only example with PtS_2NCl chromophore. A distorted square planar arrangement is created by terdentate- (S,N,S) ligand plus Cl atom. The terdentate ligand created two five- membered metallocycles with the mean S-Pt-N "bite" angle of 87.2º. The Pt-L bond distance elongated in the order: 2.004(9)º (N) < 2.271Å (S, average) < 2.291(4)Å (Cl).

wo yellow monoclinic *trans*-[Pt{η^2-$(Bu^tHN)_2POS$}{η-$(Bu^tHN)_2POS$}(PPh_3)][210] and *trans*-[Pt{η^2-(SNSNH)}(η-SSO_3)(PPh_3)][211] contain PtS_2NP chromophore. The chelating (N,S) ligands forms a four- in the former and five- membered metallocycles in the latter example with the N-Pt-S "bite" angles of 78.3(3)º and 84.9(4) º, respectively. The Pt-L bond distances for heterobidentate ligands are: 2.132(10)Å (N) and 2.338(2)Å (S) in the former which are somewhat longer than those in the latter with the values of 2.020(10)Å and 2.257(5)Å, respectively. On the other hand, the Pt-L values for monodentate ligands in the former are somewhat shorter than in the latter with the values of 2.225(2) Å (P) and 2.341(3) Å (S), vs 2.242(5)Å (P) and 2.349(5) Å (S). The reason of such differences can be chelate rings (four- vs five-).

Structure of yellow triclinic *trans*-[Pt{η^3-dmtmp)Br](Br)[209] is similar to its Cl analogous[209]. The mean value of N-Pt-S "bite" angle is 85.7º. The mean Pt-L bond distance elongated in the order: 2.004(7)Å (N) < 2.281Å (S, mean) < 2.423(1) Å (Br). While the mean values of N-Pt-S "bite" angles in the Br analogous is about 1.5º smaller than in its Cl analogous, the sum of all four Pt-L bond distances are 8.37Å (Cl, derivative) and 8.99Å (Br, derivative), as reason of covalent radii (Cl/0.90Å vs Br/1.13Å).

There are three *cis*- yellow derivatives: orthorhombic [Pt{η^2-Et_2NCS_2)Cl(PPh_3)][212], two monoclinic [Pt{η^2-$C(PPh_2S)_3$}Cl(PEt_3)][213] and [Pt{η^2-$N(SPPh_2)_2$}Cl(PPh_3)][214] (Fig. 8) in which chelating -S,S ligand with Cl atom and PR_3 ligand created a distorted square planar arrangement about each Pt(II) atom (PtS_2ClP). In[212] chelating ligand forms four- membered metallocycle with S-Pt-S "bite" angle of 74.9(3)º and in the remaining two six- membered with the mean S-Pt-S "bite" angle of 96.8º. Noticeable, the Pt-L bond distances in the three derivatives are almost constant with the Pt-L bond distances elongated in the order: 2.253Å (P) < 2.325Å (S) < 2.332Å (Cl).

Structures of yellow *cis*-[Pt(η^2-bphse)(Cl)(Br)][129], [Pt(η^2-bphase)(Cl)(I)][129] and [Pt(η^2-bphase)(Br)(I)][129] are very similar. In each homobidentate -S,S ligand forms five- membered metallocycles with the mean S-Pt-S "bite" angle of 91.0º and the respective halogen atoms completed a distorted square planar geometry about each Pt(II) atom (PtS_2ClBr, PtS_2ClI and PtS_2BrI). The mean Pt-L bond distance elongated in the order: 2.280Å (S)

< 2.355Å (Cl) < 2.454Å (Br) < 2.575Å (I) which follow the covalent radius of the respective atoms.

The sum of all four Pt-L bond distances in these derivatives growing in the sequence: 8.84Å (*trans*-PtS$_2$NCl) < 8.95Å (*trans*-PtS$_2$NP) < 8.99Å (*trans*-PtS$_2$NBr) < 9.24Å (*cis*-PtS$_2$ClP) < 9.25Å (*cis*-PtS$_2$ClBr) < 9.48Å (*cis*-PtS$_2$ClI) < 1006Å (*cis*-PtS$_2$BrI), corresponds well the covalent radius of the respective atoms.

2.5.2 PtO$_2$ClS, PtN$_2$SX (X = O, Cl or P), PtC$_2$NS, PtCl$_2$SX (X = O, N, P or Te)

Derivatives

Monoclinic *cis*-[Pt(η^2-hcda)Cl(dmso)][215] is only example with PtO$_2$ClS chromophore. The chelating bidentate -O,O ligand forms six- membered metallocycle with the O-Pt-O "bite" angle of 81.9(2)º. The Pt-L bond distance elongated in the order 1.976Å (O, average) < 2.217(2)Å (S) < 2.301(2)Å (Cl).

In three triclinic *cis*-[Pt(η^2-dach)(cbde)(dmso)][216], [Pt(η^2-2,2´-bpm)(OSO$_3$)(dmso)][217] and [Pt(η^2-bchpen)(OSO$_3$)(SOMe$_2$)][218] chelating -N,N ligand with monodentate -O and S- donor ligands form PtN$_2$OS chromophore. The chelating ligand created five- membered metallocycles with the mean N-Pt-N "bite" angle of 83.5º. In trigonal *cis*-[Pt(η^2-en)(η^2-soa)](+1cation)[219] homobidentate -N,N with heterobidentate -O,S ligands created a distorted square planar geometry about Pt(II) atom (PtN$_2$OS). Both chelating ligands form five- membered metallocycles with the N-Pt-N and O-Pt-S "bite" angles of 82.6(3)º and 85.4(2)º, respectively. In triclinic *cis*-[Pt(η^2-dach)(η^2-dtym)][83] the homobidentate -N,N ligand forms five- and heterobidentate -O,S ligand forms six- membered metallocycles with the N-Pt-N and O-Pt-S "bite" angles of 83.7(2)º and 95.3(1)º. The Pt-L bond distance elongated in the order: 1.999(4)Å (O) < 2.042Å (N, average) < 2.242(2)Å (S). In[216] the same crystal contains four crystallographically independent molecules differing mostly by degree of distortion and are examples of distortion isomerism[61,62]. The sum of all four (Pt-N(x2) + Pt-S + Pt-O) bond distances and N-Pt-N bite angles are: 8.30Å and 86.2º (molecule 1); 8.39Å and 82.6º (molecule 2), 8.37Å and 84.3º (molecule 3), 8.81Å and 84.9º (molecule 4).

There are thirteen derivatives in which Pt(II) atoms have PtN$_2$ClS chromophore. These derivatives crystallized in three crystal classes: orthorhombic (x3) < triclinic (x4) < monoclinic (x6). In two *trans*-[Pt(NH$_3$)$_2$Cl(dmso)]Cl[220] and [Pt(NH$_3$)$_2$Cl(dmso)](ClO$_4$)$_{0.8}$(Cl$_{0.2}$)[221] only monodentate ligands form such chromophore. The mean Pt-L bond distance elongated in the order: 2.066 Å (N) < 2.200 Å (S) < 2.309 Å (Cl). The *cis*- and *trans*- L-Pt-L bond angles deviated from the ideal 90º and 180º, by 3.5º and 5º.

In five *cis*- derivatives, [Pt(η^2-NL)Cl(dmso)], η^2-NL are dach[222], vala[223]; DL-alaa[223], amp[224], tmen[225], the chelating -N,N ligands form five- membered metallocycles with the mean N-Pt-N "bite" angle of 82.6º. In *cis*-[Pt(η^2-dmbg)Cl(dmso)][226] chelating ligand forms six- membered metallocycle with the N-Pt-N "bite" angle of 88.9(3)º. In the remaining two *cis*- derivatives [Pt(η^2-NL)Cl(dmso)], η^2-NL are dab[227] forms seven- and mbdaa[228] forms eight- membered metallocycles with the N-Pt-N "bite" angle of 86.0(3)º and 88.5(3)º, respectively. The mean Pt-L bond distance elongated in the order: 2.03Å (η^2-N) < 2.24Å (S) < 2.316Å (Cl).

In the remaining three *cis*- derivatives [Pt(η^3-N$_2$SL)(Cl)] terdentate ligand -N,N,S, namely, ampts[229], glymt[230] and L-methionine[231] with Cl atom form a distorted square planar geometry (PtN$_2$SCl). The chelating ligand in[229] created two five- membered rings, N-Pt-N and N-Pt-S, with the "bite" angles of 80.6(4)º and 85.4(3)º, in[230,231] five- (N-Pt-N) and six- (N-Pt-S) membered metallocycles with the mean angles of 84.8º and 99.3º, respectively. The mean Pt-L bond distance elongated in the order: 2.038Å (N) < 2.254Å (S) < 2.304Å (Cl).

Yellow monoclinic *cis*-[Pt(η^3-C$_{28}$H$_{24}$N$_2$S$_2$)(PPh$_3$)][232] is only example with PtN$_2$SP chromophore. Heteroterdentate ligand forms two five- membered metallocycles with N-Pt-N and N-Pt-S "bite" angles of 78.5(3)º and 81.6(2)º, respectively. The Pt-L bond distance elongated in the order: 2.01Å (N, average) < 2.266(3)Å (S) < 2.279(3)Å (P).

Yellow orange orthorhombic *cis*-[Pt(CN)$_2$(η^2-S$_2$N$_2$H)][233] is only example in which Pt(II) atom has PtC$_2$NS chromophore. The mean Pt-L bond distance elongated in the order: 1.98Å (C, average) < 2.02Å (N) < 2.26Å (S). Yellow orthorhombic *cis*- [PtCl$_2$(H$_2$O)(dmso)][215] is only example with $PtCl_2OS$ chromophore and only monodentate ligands are involved. The Pt-L bond distance elongated in the order: 2.076(6)Å (O) < 2.191(4)Å (S) < 2.315Å (Cl, average). The *cis*- and *trans*- L-Pt-L bond angles are deviated from the ideal (90º and 180º) by 1.5º and 1.9º.

There are over thirty derivatives in which each Pt(II) atom has $PtCl_2NS$ chromophore. These derivatives crystallized in three crystal classes: triclinic (x5) < orthorhombic (x12) < monoclinic (x14). In ten *cis*- derivatives: $PtCl_2$(dmso)(NL) with NL, MeCN[234,235], EtCN[236], PhCN[237], cycloC_3H_3CN[238], Bu^tNH_2[239], py[240], Mepy[241], thiazole[245] and cpa[243], only monodentate ligands are involved. The mean Pt-L bond distance elongated in the order: 1.993Å (N) < 2.215Å (S) < 2.304Å (Cl). The *cis*- and *trans*- L-Pt-L bond angles are deviated from the ideal values of 90º and 180º by 2.2º (mean) and 4.0º (mean), respectively.

In eleven *cis*-$PtCl_2(\eta^2$-NSL) derivatives, with heterobidentate N,S ligands: Mecys[244], Etcys[245], qutm[246], aems[247], mamsb[247], mps[248], DL-methionine[231,249], metso[250] and Memethionine[251], created a distorted square planar geometry about each Pt(II) atom ($PtCl_2NS$). In[244-247] the chelating ligands form five- membered metallocycles with the mean N-Pt-S "bite" angles of 86.4º. In[231,248,251] the chelating ligands form six- membered metallocycles with the mean N-Pt-S "bite" angle of 95.4º. The mean Pt-L bond distance elongated in the order: 2.06Å (N) < 2.213Å (S) < 2.307Å (Cl).

Only monodentate ligands created *trans*-derivatives of the composition $PtCl_2$(dmso)(NL), where NL are: py[252], 2-Mepy[241], thiazole[242], NH_3[254], ipa[255], pip[256], cytidine[257], thiamine[258], tnt[259] and [$PtCl_2$(1-MeCN)(Pr^i_2SO)][260] in which each Pt(II) atom has a distorted square planar geometry ($PtCl_2NS$). The mean Pt-L bond distance elongated in the order: 2.055 Å (N) < 2.220 Å (S) < 2.295 Å (Cl). The *cis*- and *trans*- L-Pt-L bond angles are deviated from the ideal values of 90º and 180º by 3.2º (mean), and 4.4º (mean). These deviations are somewhat larger than those found in *cis*- $PtCl_2NS$ with monodentate ligands (2.2º and 4.0º).

There are three complees which exist in two isomeric forms monoclinic *cis*- and triclinic *trans*-[$PtCl_2$(py)(dmso)][240,252] monoclinic *cis*- and monoclinic *trans*-[$PtCl_2$(2-Mepy)(dmso)][241,253] and orthorhombic *cis*- and orthorhombic *trans*-$PtCl_2$(thiazole)(dmso)[242]. The sum of all four Pt-L bond distances in cis- isomers of 8.81Å is smaller than the sum in *trans*- isomers, 8.85Å. This indicates that the inner coordination sphere in the *cis*- isomers is somewhat more crowded and more distorted than in *trans*- isomers.

The *cis*-$PtCl_2(\eta^2$-Etcys)[245], *cis*-$PtCl_2(\eta^2$-mes)[248] and *trans*-$PtCl_2$(py)(dmso)[252] contain within the same crystal two crystallographically independent molecules differing mostly by degree of distortion are examples of distortion isomerism.

In another six *cis*- derivatives inner coordination sphere about each Pt(II) atom is $PtCl_2SP$. These derivatives crystallized in two crystal classes, tetragonal (x1) and monoclinic (x5). In [$PtCl_2(Et_2S)$(cep)][261], [$PtCl_2(Et_2S)(PMeBz_2)$][262], and [$PtCl_2(Bu^n_2$ S)(PBu^n_3)][263] only monodentate ligands are involved. The mean Pt-L bond distance elongated in the order: 2.237Å (P) < 2.280Å (S) < 2.314Å (Cl, trans to S) < 2.363Å (Cl, trans to P), indicates that the trans influence of P is over S. The *cis*- and *trans*- L-Pt-L bond angles deviated from the ideal values (90º and 180º) by 3.9º (mean) and 3.4º (mean).

In the remaining three *cis*- derivatives [$PtCl_2\{\eta^2$-$Ph_2PN(Ph)P(Ph_2)S\}$][264], [$PtCl_2\{\eta^2$-$Ph_2P(CH_2)_2SMe\}$][265] and [$PtCl_2(\eta^2$-ptpc)][266] besides two Cl atoms bidentate S,P ligands completed a distorted square planar environment about Pt(II) atom ($PtCl_2SP$). The chelating ligands form six membered metallocycles with the mean S-Pt-P "bite" angle of 88.6º. The mean Pt-L bond distance elongated in the order: 2.205Å (P) < 2.273Å (S) < 2.318Å (Cl, trans to S) < 2.364Å (Cl, trans to P). In[263] two crystallographically independent molecules are present within the same crystal differing by degree of distortion.

In yellow triclinic *cis*-[$PtCl_2\{\eta^2$-$MeS(CH_2)_2Te(C_6H_4OEt$-4)\}][267] two Cl atoms with chelating -S,Te ligand created a distorted square planar geometry ($PtCl_2STe$). The chelating ligand forms five- membered metallocycle with S-Pt-Te "bite" angle of 91.45(8)º. The mean Pt-L bond distance elongated in the order: 2.258Å (S) < 2.330Å (Cl, mean) < 2.514Å (Te).

In these derivatives the sum of all four Pt-L bond distances growing in the sequences: 8.28Å (*cis*-

PtC_2NS) < 8.33Å (*cis*-PtN_2OS) < 8.47Å (*cis*-PtO_2ClS) < 8.56Å (*cis*-PtN_2SP) < 8.60Å (*cis*-PtN_2ClS) < 8.82Å (*cis*-$PtCl_2NS$) < 8.90Å (*cis*-$PtCl_2OS$) < 9.12Å (*cis*-$PtCl_2SP$) < 9.43Å (*cis*-$PtCl_2STe$); for *trans*- derivatives the values are 8.64Å PtN_2ClS) and 8.86Å ($PtCl_2NS$). As can be seen the sum of *trans*- derivatives is somewhat larger than those in their cis- partners, which indicates that the inner coordination spheres in cis- derivatives are somewhat more crowded.

2.5.3 PtP_2SX (X = H, O, N or Cl), $PtBr_2NS$, PtI_2SX (X = N or P) and $PtAs_2SCl$ Derivatives

In two triclinic *trans*-$[Pt(Pcy_3)_2(H)(\eta^1\text{-}SCHS)]$[268] and $[Pt(Pcy_3)_2(H)\{\eta^1\text{-}(EtCH_2)_2NCS_2\}]$[269] only monodentate ligand are involved and created a distorted square planar geometry about the Pt(II) atom (PtP_2HS). The mean Pt-L bond distances are 2.287Å (P) and 2.386Å (S). For the Pt-H bond distances values are not available.

There are five yellow *cis*- derivatives: triclinic $[Pt(PPh_3)_2\{\eta^2\text{-}OC(C_6H_4Me\text{-}4)NS\}]$[270], monoclinic $[Pt(PPh_3)_2\{\eta^2\text{-}ON(Ph)C(NPh)S\}]$[271], monoclinic and orthorhombic $[Pt(PPh_3)_2\{\eta^2\text{-}OC(CF_3)_2CH_2SMe\}](BF_4)$[272], and monoclinic $[Pt(PPh_3)_2\{\eta^2\text{-}1,2\text{-}SC_6H_4COO)]$[273] (Fig. 9) which have similar structures. A distorted square planar arrangement about each Pt(II) atom is build by pair of PPh_3 ligands and heterobidentate -O,S ligand (PtP_2OS). Each chelate ligand forms five- membered metallocycle with the mean O-Pt-S "bite" angle of 83.6º. The mean Pt-L bond distance elongated in the order: 2.06Å (O) < 2.275Å (P) < 2.310Å (S).

There are twenty two mostly yellow and green, twenty one *cis* and one *trans*, with PtP_2NS inner coordination sphere. These derivatives crystallized in three crystal classes: orthorhombic (x3) < triclinic (x6) < monoclinic (x13). In $[Pt\{P(C{\equiv}CBu^t)Ph_2\}_2(NCS)(SCN)]$[274], $[Pt(PPh_3)_2(phe)(SSCHMe_2)]$[275] and *trans*-$[Pt(PPh_3)_2(phe)(SSCHMe_2)]$[276] only monodentate ligands created a distorted square planar geometry, PtP_2NS. The mean Pt-L bond distance elongated in the order: 2.055Å (N) < 2.297Å (P) < 2.329Å (S). The deviations of *cis*- and *trans*-L-Pt-L bond angles from the ideal values of 90º and 180º are 6.0 and 5.2º, respectively.

In all remainders pair of monodentate -P (mostly PPh_3) ligands and chelating -N,S ligands are involved. In $[Pt(PPh_3)_2(\eta^2\text{-dietu})]$[277], $[Pt(PPh_3)_2(\eta^2\text{-tdatma})]$[278], $[Pt(PPh_3)_2(\eta^2\text{-pyt})]PF_6$[279] and $[Pt(PPh_3)_2(\eta^2\text{-}C_{19}H_{15}N_2S_2P)]$[280] the chelating ligands created four- membered metallocycles with the mean N-Pt-S "bite" angle of 69.8º. In $[Pt(PMe_3)_2(\eta^2\text{-NSNS})]$[281], monoclinic $[Pt(PPh_3)_2(\eta^2\text{-NSNS})]$[282], triclinic $[Pt(PPh_3)_2(\eta^2\text{-NSNS})$[283], $[Pt(PMe_2Ph)_2(\eta^2\text{-NSNS})]$[284], $[Pt(PMe_2Ph)_2\{\eta^2\text{-N(H)SNS}\}]Cl$[284], $[Pt(PMe_2Ph)_2\{\eta^2\text{-N(H)SNS}\}](PF_6)$[284], $[Pt(PMe_2Ph)_2\{\eta^2\text{-NSNS})](BF_4)$[285], $[Pt(PMe_3)_2\{\eta^2\text{-N(H)SNS}\}](PF_6)$[285], $[Pt(PEt_3)_2\{\eta^2\text{-N(H)SNS}\}](PF_6)$[286], $[Pt(PEt_3)_2\{\eta^2\text{-N(H)SNS}\}][Me_2SnCl_3]$[287], $[Pt(PBu^n_3)_2\{\eta^2\text{-N(H)SNS}\}](PF_6)$[287], $[Pt(PEt_3)_2(\eta^2\text{-tgly})]Cl$[288] and $[Pt(PPh_3)_2\{\eta^2\text{-}S_2CN(Me)C(O)NPh\}]$[289] each chelating -N,S ligand forms five-membered metallocycle with the mean N-Pt-S "bite" angle of 84.8º. In $[Pt(PPh_3)_2(\eta_2\text{-xaxas})]$[290] and $[Pt(PPh_3)_2\{\eta^2\text{-NC(CN)NC(CN)S}\}]$[291], the chelating ligands created six- membered metallocycles with the mean N-Pt-S "bite" angle of 90.9º. The mean Pt-L bond distance in $PtP_2(\eta^2N,S)$ derivatives elongated in the order: 2.046Å (N) < 2.280Å (P) < 2.300Å (S).

There are four derivatives, in which a distorted square planar geometry about each Pt(II) atom has PtP_2ClS inner coordination sphere. In two monoclinic *cis*- $[Pt(PPh_3)_2(Cl)(2,4,6\text{-}Pr^i_3C_6H_2S)]$[139] and *trans*-$[Pt(PMe_2Ph)_2\{S(O_2)CH_2CH{=}CH_2\}Cl]$[292] only monodentate ligands are involved. The Pt-L bond distances in[139] elongated in the order 2.268 Å (P, average) < 2.328 Å (S) < 2.335 Å (Cl) and in[292] the order is: 2.235 Å (S) < 2.336 Å (P, average) < 2.345 Å (Cl). In monoclinic *trans*-$[Pt(PEt_3)\{\eta^2\text{-}Ph_2PCH_2P(S)Bu^t_2\}Cl]ClO_4$[293] besides Cl atom, and monodentate PEt_3 ligand, the chelating -P,S ligand build up a distorted square-planar geometry, PtP_2ClS. The chelating ligand forms five- membered metallocycle (PtPCPS) with the P-Pt-S "bite" angle of 91.0(1)º. The Pt-L bond distance elongated in the order: 2.282Å (S) < 2.296Å (P) < 2.319Å (PEt_3) < 2.326Å (Cl). In triclinic *trans*-$[Pt\{\eta^3\text{-}(Ph_2PCH_2CH_2)_2SO\}Cl](ClO_4)$[294], the terdentate -P,S,P ligand with Cl atom forms, PtP_2ClS chromophore. The terdentate ligand forms pair of five-membered metallocycles with the S-atom in the center. The mean Pt-Pt-S bite angle is 85.1º. The L-Pt-L bond angles are not available. The Pt-L bond distance elongated in the order: 2.182Å (S) < 2.318Å (Cl)

< 2.319Å (P, average).

In yellow triclinic *cis*-[$PtBr_2$)(MeCN)(dmso)][235] only monodentate ligands are involved and it is only example with $PtBr_2NS$ chromophore. This derivative contains two crystallographically independent molecules within the same crystal. The Pt-L bond distances (molecule 1 vs molecule 2) elongated in the order: 1.983Å (N) < 2.228Å (S) < 2.413Å (Br, average) vs 1.986Å (N) < 2.233Å (S) < 2.411Å (Br, average). The deviations of the *cis*- and *trans*- L-Pt-L bond angles from the ideal values of 90º and 180º (molecule 1 vs molecule 2) are 3.5º and 1.8º vs 4.2º and 2.8º, respectively.

Another single example is *trans*-[Pt(η^3-asa)Cl](ClO_4)[295] (Fig.10) in which terdentate -As,S,As ligand with Cl atom created $PtAs_2SCl$ inner coordination sphere. The chelating ligand forms two six- membered metallocycles with the mean S-Pt-As "bite" angle of 93.0º. The Pt-L bond distance elongated in the order: 2.249Å (S) < 2.314Å (Cl) < 2.403Å (As, average).

Another single example is orange orthorhombic *trans*-[PtI_2(3,5-Me_2py)(dmso)][296], in which the monodentate ligands created a distorted square planar geometry, PtI_2NS. The Pt-L bond distance elongated in the order: 2.08Å (N) < 2.233Å (S) < 2.605Å (I, average).

In yellow monoclinic *cis*-[PtI_2(η^2-ptpe)][176] the chelating -S,P ligand forms six- membered metallocycle with S-Pt-P "bite" angle of 86.9(3)º. The Pt-L bond distance elongated in the order: 2.242Å (P) < 2.280Å (S) < 2.619Å (I, average).

The total sum of all four Pt-L bond distances in these derivatives growing in the sequences: *cis*- derivatives: 8.92Å (PtO_2ClS; PtP_2NS) < 9.04Å ($PtBr_2NS$) < 9.19Å (PtP_2ClS) < 9.75Å (PtI_2SP); *trans*- derivatives: 8.65Å (PtP_2HS) < 9.03ÅPtP_2NS < 9.20Å (PtP_2ClS) < 9.37Å ($PtAs_2NS$) < 9.52Å (PtI_2NS). The *cis*-PtP_2NS and *cis*-PtP_2ClS derivatives have an inner coordination sphere somewhat more crowded than their *trans* partners.

2.6 PtONClS, PtNClSP, PtNSPX (X = Br or I) Derivatives

There is nine derivatives in which all four donor atoms which form a distorted square planar geometry about Pt(II) atom are heterogeneous. The derivatives crystallized in three crystal classes: triclinic (x1) < monoclinic and orthorhombic (each x4). In five derivatives: [Pt(Cl)(dmso)(η^2-O,NL)] with η^2-O,NL: η^2-sar[297], η^2-opro[298], oproH[299], η^2-pyca[300] and η^2-sala[301], the chelating -O,N ligands with Cl atom and monodentate dmso(S) ligand forms PtONClS chromophore. In[297-300] the chelating ligands created five- membered metallocycles with the mean O-Pt-N "bite" angle of 81.5º and in[301] six- membered with the angle of 90.8(2)º. The mean Pt-L bond distance elongated in the order: 2.017Å (N) < 2.018Å (O) < 2.184Å (S) < 2.303Å (Cl).

An orange [Pr(η^3-tsc)Cl][302] is only example, in which terdentate -S,N,P ligand with Cl atom forms a distorted square planar geometry, PtNClSP. The terdentate ligand forms five- (SCNN) and six- (NC_3P)- membered metallocycles with the N-Pt-S and N-Pt-P "bite" angles of 84.9(4)º and 95.8(4)º. The Pt-L bond distance elongated in the order: 2.03Å (N) < 2.239Å (P) < 2.298Å (S) < 2.304Å (Cl).

Two orange [Pt{η^2-N(H)SNS}(PMe_2Ph)X] (X = Br or I)[303] (Fig. 11) are isostructural. The chelating -N,S ligand forms five- (NSNS) membered metallocycle with equal N-Pt-S "bite" angles of 85,4º, and with PMe_2Ph ligand and X atom forms a distorted square planar arrangement about each Pt(II) atom (PtNSPBr, PtNSPI). The mean Pt-L bond distance elongated with an increasing covalent radius of coordinated atoms in the order: 2.02Å (N, 0.75Å) < 2.224Å (S, 1.02Å) < 2.248Å (P, 1.06Å) < 2.475Å (Br, 1.13Å) < 2.635Å (I, 1.33Å).

In yellow [Pt(η^3-$C_{28}H_{32}N_2PS$)I]I[304] terdentate -S,N,P ligand with I atom forms a distorted square planar geometry, PtNSPI. The chelating ligand forms two six- membered metallocycles with the N-Pt-S and N-Pt-P "bite" angles of 93.2º and 89.1º. The mean Pt-L bond distance elongated in the order: 2.056Å (N) < 2.240Å (P) < 2.363Å (S) < 2.580Å (I).

The mean Pt-L bond distance in this series of complexes elongated in the sequence: 2.02Å) < 2.260Å (P) < 2.302Å (Cl) < 2.475Å (Br) < 2.580Å (I). The sum of all four Pt-L bond distances growing in the sequence: 8.52Å (PtONClS) < 8.92Å (PtNCSP) < 8.98Å (PtNSPBr) < 9.15Å (PtNSPI), corresponds with covalent radii of the respective coordinated atom.

3. CONCLUSIONS

There are over three hundred monomeric Pt(II) complexes in which thio-ligands as homo- and as well as with some other types of ligands created wide variability of square planar geometry about Pt(II) atoms with differing degree of distortion. The complexes, mostly yellow of color, crystallized in five crystal classes: hexagonal (0.4%) < tetragonal (1.5%) < orthorhombic (13.8%) < triclinic (23.7%) < monoclinic (60.7%). The most common monodentate S-donor ligand is dimethylsulphoxide. There is wide variability of ligands which created such square planar geometry about the Pt(II) atom. There is no other transition metal with as many investigated examples of square planar geometry as platinum. There are probably two main reasons for this, the great interest in the *cis* – *trans* influence and the medical importance of species such as *cis*-platin type derivatives. In this review we analyzed and classified over 300 monomeric Pt(II) complexes which contain at least one thio-ligand.

The mean Pt-L bond distance for monodentate ligands elongated in the sequence: 1.95Å (CN) > 2.04Å (OL) < 2.06Å (NL) < 2.27Å (PL) < 2.31Å (Cl) < 2.32Å (SL) < 2.36Å (AsL) < 2.44Å (Br) < 2.595Å (I). Homobidentate ligands in the sequence: 2.03Å (η^2-OL) < 2.06Å (η^2- NL) < 2.28Å (η^2-PL) < 2.29Å (η^2-SL). For homo-terdentate the values are: 2.27Å (η^3-NL) and 2.305Å (η^3-SL); and for homo-tetradentate, 2.30Å (η^4-SL). There is also wide variability of heterobidentate with the Pt-L bond values: 2.015Å (O) plus 2.02Å (N); 2.06Å (O) plus 2.31Å (S); 2.085Å (N) plus 2.365Å (As); and 2.258Å (S) plus 2.514Å (Te). For hetero-terdentate the values are: 2.18Å (S) plus 2.32Å (2P); 2.275Å (2S) plus 2.005Å (N); 2.25Å (S) plus 2.40Å (2As); and 2.035Å (N) plus 2.247Å (P) plus 2.335Å (S). For hetero-tetradentate the values are 2.280Å (2P) plus 2.323Å (2S).

The chelating ligands created wide variability of metallocycles and the effects of both electronic and steric factors of the coordinated atoms can be seen in the opening of the member rings. The mean L-Pt-L "bite" angles open in the orders: 72.5º (PCP) < 73.4º (SOP) < 74.0º (NCS) < 76.8º (SCS) < 81.0º (SSS) < 83.0º (SPS); 80.0º (NC_2N) < 81.2º (OC_2N) < 81.8º (OCNS) < 82.5º (OC_2O) < 83.0º (OC_2S) < 83.5º (ONCS) < 83.8º (NC_2S) < 84.8º (NNCS) < 85.0º (PC_2P) < 85.4º (NSNS) < 85.7º (PCNS, OC_2S) < 86.7º (SC_2P) < 87.0º (CS_2As) < 88.7º (SC_2S) < 90.0º (SCPS) < 91.0º (SPCP) < 91.4º (SC_2Te) < 93.4º (SS_2S); 88.3º (OC_3O) < 89.6º (NC_3P) < 90.8º (OC_3N) < 92.0º (SC_3S) < 93.0º (SC_3As) < 93.3º (NCNCS) < 94.0º (OC_3S) < 94.5º (SC_3P) < 95.8º (NN_2CP) < 96.3º (SPNPS) < 98.8º (SC_2NS); and 87.0º (SC_8S) < 92.2º (SC_4S) < 102.4º (SC_2SC_2S).

The stereochemistry of square planar derivatives of Pt(II) shows a wide variety of inner coordination spheres from PtS_4 (x63), PtS_3X (x11), PtS_2X_2 (x172), $PtSX_3$ (x22), PtS_2XY (x12), $PtSX_2Y$ (x14) to PtSXYZ (x10).

Two types of isomerism exist in these derivatives. There are six examples with *cis* and *trans* isomers: *cis*-[102] and *trans*-[$PtCl_2(Me_2S)_2$][103]; *cis*- and *trans*-$Pt(tx)_2Cl_2$[113], cis[114] and *trans*-$Pt(dmso)_2Cl_2$[115]; *cis*-[240] and *trans*-[$PtCl_2$(py)(dmso)][252]; *cis*- and *trans*-[$PtCl_2$(thiazine)(dmso)][242] and *cis*[241] and *trans*-$PtCl_2$(2-Mepy)(dmso)[253]. There are more examples, in which two crystallographically independent molecules are present within the same crystal differing only by degree of distortion with the inner coordination spheres: PtS_4[2,28,42], PtS_3O[63], PtN_2S_2[97], $PtCl_2S_2$[48,110,116,122], PtS_2Br_2[186], $PtCl_2NS$[234,235,245,248,252], $PtCl_2SP$[263], and PtP_2NS[287]. There is even example in which four such independent molecules are present, PtN_2OS[216]. The coexistence of two or more species differing only by the extent of distortion is typical of the general class of distortion isomerism[61,62].

In general, complexes with *cis*- configuration by far prevail over *trans*- configuration. There are complexes with an inner coordination spheres: PtO_2S_2, PtN_2S_2, PtS_2P_2, PtS_2Br_2, PtS_2I_2, PtN_2ClS, $PtCl_2NS$ and PtP_2ClS, which have *cis*- as well as *trans*- configuration. Usually, the inner coordination spheres in *cis*- derivatives are somewhat more crowded and more distorted than in their *trans*- partners. Complexes only with *cis*- configuration are with the inner coordination spheres: PtC_2S_2, PtO_2ClS, PtN_2ClS, PtN_2SP, PtC_2OS, $PtCl_2SP$, $PtCl_2STe$, PtS_2ClP, PtS_2ClBr, PrS_2ClI, PtS_2BrI, PtP_2OS, $PtBr_2NS$ and PtI_2SP. Complexes only with *trans*- configuration are with the inner coordination spheres: $PtAs_2S_2$, PtS_2NCl, PtS_2NP, PtS_2NBr, PtP_2HS, $PtAs_2ClS$ and PtI_2NS.

In the complexes with cis- configuration the

Pt-L bonds are more polar and presumably weaker than those in the examples with trans-configuration in which the Pt-L bonds are less polar and presumably stronger. One can be expected a somewhat more reactive complexes with cis- configuration than those with trans-configuration.

4. ABBREVIATIONS

[10]aneS_3: 1,4,7-trithiacyclodecne

[14]aneS_4: 1,4,8,11-tetrathiacyclotetradecane

aemso: 2-aminoethylmethylsulphoxide

amp: 2-aminomethylpyridine

ape: $Ph_2AsCH_2CH_2P(S)Ph_2$

apmts: 2-acetylpyridine 4-methylthiosemicarbazone

asa: bis(diphenylarsino)propylsulphide

bbpy: di-tert-butylpyridine

bbtu: N,N´-di(n-butyl)-N-benzylthioureate

bchpen: 1,2-bis(2-chloro-6-fluoro-5-hydroxyphenyl) ethylenediamine

bdt: 1,2-benzenedithiolate

betmp: bis(ethylthio)methylenepropanedionate

bmptp: 1,3-bis(2-mercaptophenylthio)-2-propanol(-2)

bmso: benzylmethylsulphoxide

bmtfe: 1,2-bis(methylthio)1,1-difluoro-ethane

bmtmp: 2,6-bis(methylhiomethyl)pyridine

bntu: N,N-dibutyl-N´-naphthyolthiourate

bphse: 1,2-bis(phenylsulphinyl)ethylene

bpm: bipyrimidene

bpse: 1,2-bis(propylsulphinyl)ethane

bptu: N-benzoyl-N´-propylthiourea

bpy: 2,2´-bipyridine

btfp: 1,2-bis(trifluoromethylthio)propane

btst: *cis*-(benzylthio)stilbenethiolate

$(C_2H_4OH)_2NCS_2$: do(2-hydroxyethyl)dithiocarbamate

$C_4H_6N_2S$: 1-methyl-4-imidazoline-2-thione

C_5H_5NOS: 3-hydro-2-mercaptopyridine

$C_5H_9S_2$: dithiopivalate

$C_5H_9S_3$: trithiopivalate

C_6F_5S: pentafluorohexylsulphide

$C_6H_{10}S$: 7-thiabicyclo[2.2.1]heptane

$C_6H_8N_2S_2$: methyl-N´-phenyldiazenecarbodithiolate

$C_7H_{10}NS_2$: methyl-2-amino-1-cyclopentadithiocarboxylate

$C_8H_{10}SAs$: dimethyl-o-thiolophenylarsine

C_8H_8S: 1,3-dihydrobenzo[C]thiophene

$C_{11}H_{16}O_2SAs$: (5,14-dimethyl-5,6-7,9,14,15,16,18-octahydrodibenzo[e,l]- : thiadiarsacyclotetradecin)

$C_{13}H_{22}N_2O_2S_2$: 6,6-dimethyl-5,7-dioxo-1,11-dithia-4,8-diazacyclotetradecane

$C_{28}H_{24}N_4S_2$: PhSNC(MeC_6H_4)N-NC(MeC_6H_4)NSPh

$C_{28}H_{33}N_2PS$: N-{N-[2-(diphenylphosphino)benzylidene]-D/L-methionyl} tert-butylamine

cbdc: cyclobutanedicarboxylate

cep: tri(2-cyanoethyl)phospine

cpa: cyclopenthylamine

ctttv: 2,3,7,8,12,13-hexamethoxy-10,15-dihydro-5H-5,10,15-trithia-tribenzo: [a,d,g]cyclononene

dab: 1,4-diaminobutane

dach: 1,2-diaminocyclohexane

dbso: dibutylsulphoxide

dchtpf: dicyclohexylthiophosphozyldithioformate

dcptf: dicyclohexylphosphino-N-phenyl(thioformanidinate)

ddbt: bis-2,2´-(1,2-diphenylethylenediimine)benzenethiolate

dds: 4,4´-dichlorodiphenylsulphide

dietu: 1,3-diethylthiourea

DL-alaa: alaninamidate

dmbg: 1,1-dimethylbiguanidate

dmed: 1,3-dithiole-2-oxo-4,5-dithiolate

dmit: isotrithionedithiolate

dmm: dimethyldimercaptomaleate

dmso: dimethysulphoxide

dmtc: N,N-dimethyl-O-ethylthiocarbamate

dmtt: 2,12-dimethyl-3,7,11-trithiadecane

dottc: 1,40-dioxa-4,7,13,16-tetrathiacyclooctadecane

dpdtar: 1,5-diphosphadithiatetrazocines

dpdtc: 8,12-diphenyl-1,5-dithia-8,12-diphosphacyclotetradecane

dpedt: 1,2-diphenylethylene-1,2-dithiolate

dppe: 1,3-bis(diphenylphosphino)ethane

dppm: 1,2-bis(diphenylphosphino)methane

dpso: di-n-propylsulphoxide

dpth: 5,13-diphenyl-1,9-dithia-5,13-diphosphacyclohexadecane

dptt: 1,9-diphenyl-1,5,9-trithianonane

dt18C$_6$: 4,7,13,16,tetra-oxa-1,10-dithiacyclooctadecane

dtba: 1,1-dithioyidene barbituric acid:

dteym: 1,3-dithiopane-2-ylidenemalonate

dtox: 1,2-dithiooxalate

dtsq: dithiosquarate

dtym: 1,3-dithia-2-ylidenemalonate

eebt: S-ethyl-ethene-1,2-dithiolate

emso: ethylmethylsulphoxide

en: ethylenediamine

Et$_2$NCS$_2$: N,N-diethyldithiocarbamate

Et$_2$tu: N,N´-diethylthiourea

etc: O-ethyl-N-ethylthiocrbamate

Etcys: S-ethylcysteine

EtOCS$_2$: ethoxydithiocarbamate

Ettu: N-ethylthiourea

gapy: (N,N-diethyldithiocarbamoyl)-6-deoxy-6-(di-O-isopropylidene)-1,2: 3,4-D-galactopyrannose

glymt: glycyl-(S)-methioninate

HBu$^n_2$dto: N,N´-di-n-butyldithiooxamidate

hcda: 2,2,2,2´,2´,2´-hexachlorodiacetamide

(hm)$_2$NCS$_2$: N,N-cycloheptamethylenedithiocarbamate

hyp: L-hydroxyprolinate

i-mnt: iso-maleonitriledithiolate

ipa: isopropylamine

mamsb: MeS(O)CH2CH2NH2

mbdaa: 2,2´-methylenebis(5-(dimethylamino)aniline)

1-MeC: 1-methylcytosine

Me$_2$bpy: dimethyl-2,2´-bipyridine

2-Mepy: 2-methylpyridine

3,5-Me$_2$py: 3,5-dimethylpyridine

Me$_2$S: dimethylsulphide

Me$_2$tu: N,N´-dimethylthiourea

Mecys: S-methylcysteine-S-oxide

met: 1,2-dicarbomethoxyethylene-1,2-dithiolate

metso: methionesulphoxide

mmp: 4-mercapto-1-methylpiperidine

mnt: maleonitriledithiolate

mps: 3-methylsuphinylpropylamine

mtdbm: monothiodibenzoylmethane

mtso: methyl-p-tolylsulphoxide

o-atp: o-amidothiophenolate

odtc: 1-oxa-4,7-dithiacyclononate

opro: oxo-5-prolinate

ox: oxalate

P(py)Ph$_2$: pyridinediphenylphosphine

P(S)Ph$_2$: thiodiphenylphosphine

Pcy$_3$: tricyclohexylphosphine

pddt: 6,7-dihydro-5H-1,4-dithiepin-2,3-dithiolate

phi: phthaloimidate

pip: piperidine

p-Mepy: p-methylpyridine

pmso: phenylmethylsulphoxide

p-NCpy: p-cyanopyridine

p-NH$_2$py: p-aminopyridine

PPh$_3$: triphenylphosphine

(Pr^{i}O)$_2$PS$_2$: diisoopropyloxiddithiophosphamate

2,4,6-Pr$^i_3$C$_6$H$_2$S: 2,4,6-tri-isopropylbenzylsulphide

ptc: N-propyl-O-ethylthiocarbamate

ptf: bis(dicyclohexyl)phosphinodithioformate

ptmqu: 5-phenylthio-8-mercaptoquinolinate

ptpc: 5-phenyl-1-thia-5-phosphacyclooctane

ptt: propene-3-thione-1-thiolate

py: pyridine

pyca: pyridine-2-carboxamidate

pyt: pyridine-2-thiolate

qutm: 8-quinolylthiomethyl

sala: salicylaldoximate

sar: sarcosine; (α-aminoisobutyrate)

sbs: 4-sulphido-1-butanesulphenate

soa: (methylsulfinyl)acetate

4-Spy: 4-thiopyridine

tdatma: thiadiaztrimethylenemethane

tdt: 2-thioxo-2,3-dithiole-4,5-dithiolate

tfp: 1,1,1-trifluro-2,3-bis(methylthio)propane

tgly: thioglycinate

tht: tetrahydrothiophene

thto: tetrahydrothiophene-1-oxide

tipt: 2,4,6-triisopropylbenzenethiolate

tmen: tetramethylethylenediamine

tmtu: tetramethylthiourea

tnt: tenonitrazole

trpy: 2,2´: 6´,2"-terpyridine

tsc: thiosemicarbazide-carbaldehyde

tscb: thiosemicarbazide

tt[6.6]OC: 2,5,14,17-tetrathia/6.6/-o-cyclophane

ttc: 1,4,7-trithiacyclononane

ttphen: 2,5,8-trithia[9](2,9)-1,10-phenanthrolinophane

tu: thiourea

tx: 1,4-thioxane

vala: valenamidate

xaxas: N-(3,5-xylyl)-N(3-amino-3,5-xylyl)aminosulphide

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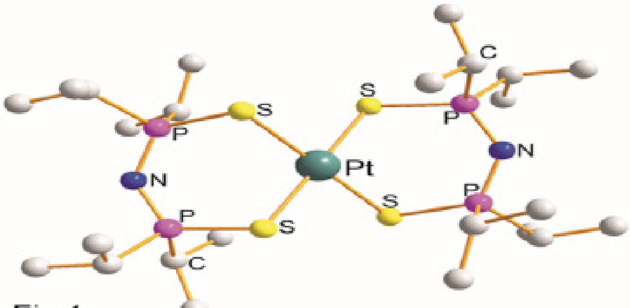
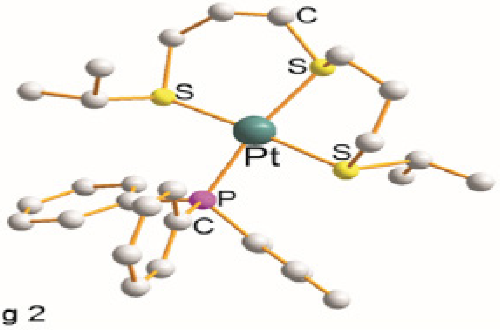


Fig 1



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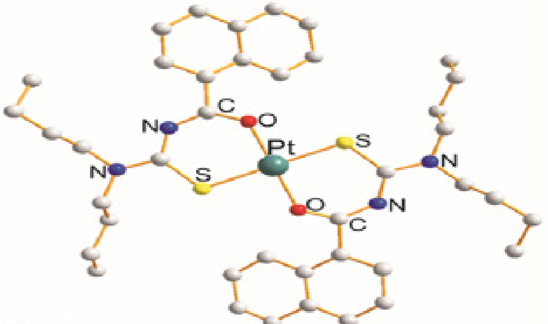

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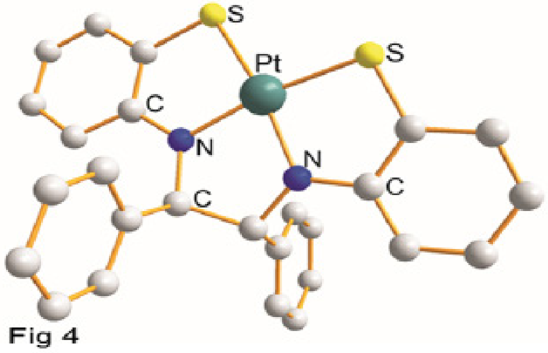

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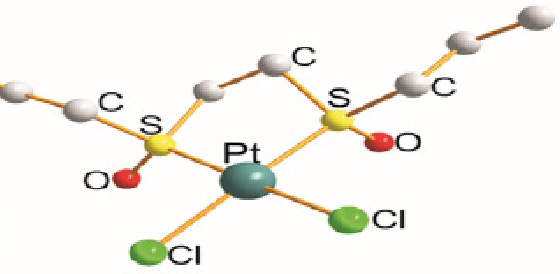

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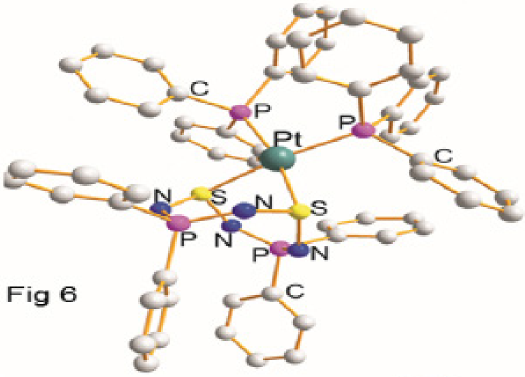

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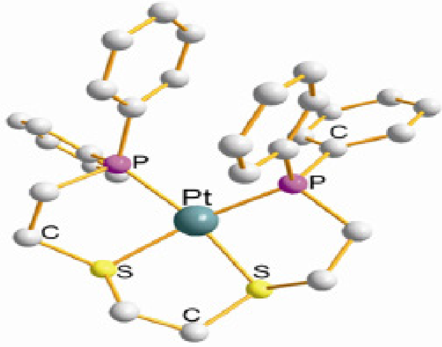

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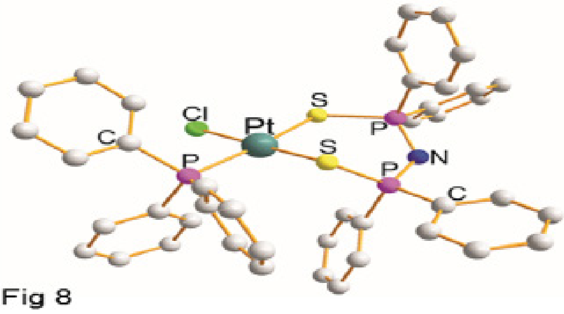

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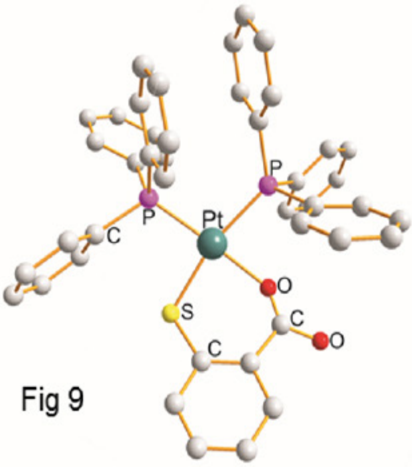

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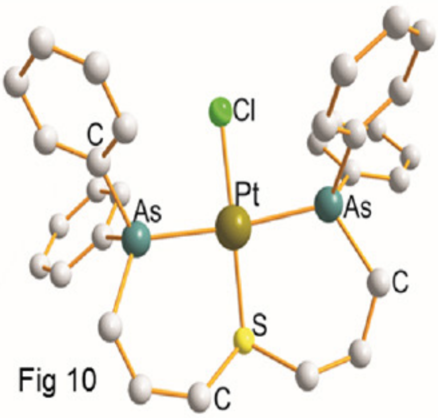

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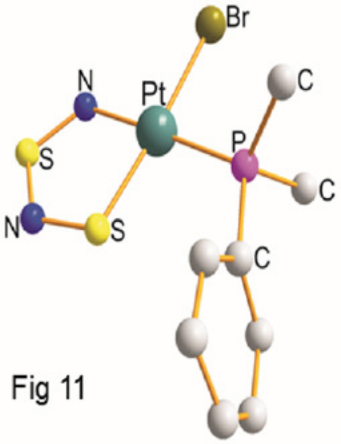

Fig 11