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Structural Aspects of Monomeric Platinum Coordination Complexes

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Abstract

This review covers structural parameters of almost two thousand monomeric Pt coordination complexes. The Pt is found in the oxidation states zero, +1, +2, +3 and +4, from which oxidation state +2 by far prevails. There is a wide variety of donor atom ligands from uni-, bi-, ter- and tetradentate with over seventeen types of donor atoms, from which by far prevails P and N donor ligands and chlorine atom. The Pt(0) atoms are two-, three- and four-coordinated; Pt(I) and Pt(III) are only four-coordinated, Pt(II) are four- and five-coordinated, and Pt(IV) are five- and six-coordinated. About 10% of these complexes exist as isomers. Included are distortion (65%), *cis-trans* (30%), mixed isomers and ligand isomerism. The structural parameters are discussed in terms of the coordination about the platinum atom, and correlations are drawn between donor atom, bond length and interbond angles with attention to any *trans*-effect.

Keywords

Structure, Platinum, Monomeric, Isomers, *Trans*-Effect

1. Introduction

It is well known that platinum has played a crucial role in the development of many branches of science. Reliable platinum crucibles were vital in classical analysis which laid the foundation of modern chemistry. Platinum exists in a wide range of oxidation states from zero to six; of which +2 and +4 are the most common, particularly in coordination chemistry. Platinum(II) has a strong preference for square planar coordination chemistry, of which the kinetic inertness has allowed extensive use of these complexes in the characterization of geometrical (*cis-trans*) isomerism and reaction mechanistic. Much work in this field has come from the Russian school such as the contributions of Chernayeav. In the 1920s he noticed that when there are alternative positions at which an

incoming ligand might be a substitution, the position chosen depends not so much on the two ligands directly involved as on the nature of the inactive ligand *trans* to that position. This became known as the "*trans* effect" and has had a considerable influence on the synthetic chemistry of platinum(II).

A resurgence of interest in complexes of platinum started in 1969 when Rosenberg and co-workers discovered the anti-tumor activity of $PtCl_2(NH_3)_2$, known as "cisplatin" [1]. This stimulated considerable research activity into the chemistry of platinum which has resulted in the determination of a considerable number of structures by diffraction technique. Since structure is often related to chemical and biological activity it seemed appropriate to prepare a comprehensive overview of such structures. Because of the huge number of structures involved this review covers only a variety of monomeric platinum coordination complexes.

The aim of this survey is to correlate the structural information available and to try to identify factors which may be responsible for the observed stereochemistry.

2. Monomeric Platinum Coordination Complexes

The huge area of structural parameters of monomeric platinum coordination complexes has been surveyed [2]-[5] with over two thousand examples noted. In this paper we brifly summarize these structures. In the series of monomeric platinum coordination compounds the platinum is found in oxidation states zero, +1, +2 (most common), +3, and +4.

2.1. Pt(0) Complexes

There are over thirty monomeric Pt(0) complexes for which structural data are available [1]. These complexes crystallized in six crystal classes: monoclinic (19 examples), triclinic (10 examples), orthorhombic (2 examples), tetragonal, hexagonal and rhombohedral each (1 example). Thirty four Pt(0) complexes show a variety of stereo-chemistries about a Pt(0) atom, linear, almost linear, trigonal planar, T-shaped and tetrahedral with varying degrees of distortion. Structure of $Pt(Bu_2^tPh)_2$ is shown in **Figure 1** [6] as an example. Two unidentate bulkybdi-tert-butylphenylphosphine directly coordinated to the central Pt(0) atom whit the mean Pt(0)-P bond distances of 2.23Å and P-Pt-P bond angle is 177.0°. As can be see there is a number of Pt ... H interactions which stabilized the respective structure. The linear, almost linear as well as trigonal planar (Y shape) geometries are building up only by monodentate P-donor ligands. The mean Pt(0)-P bond distances and P-Pt-P bond angles are: 2.249 Å and 180.0° (linear); 2.240 Å and 168.7° (±8.3°) (almost linear); 2.270 Å and 120° (±5°). T-shape geometry about Pt(0) atom is created by two monodentate P-donor ligands and SO_2 ligand (PtP_2S). The Pt-P bond distance is 2.307 Å (ave) and Pt-S is 2.295(1) Å. The P-Pt-P bond angle is 165.7° and the mean P-Pt-S bond angle is 96.2°.

There are twenty five examples in which Pt(0) atoms are tetrahedrally coordinated. In fourteen of them a distorted tetrahedral environment about Pt(0) is created solely by bulky phosphine molecules (PtP_4). These can be subdivided into the four groups with four unidentate, two unidentate plus one bidentate, two bidentate and one unidentate plus one tridentate. A tetrahedral geometry occurs about the Pt(0), distorted to varying degrees depending on the ligand involved. For unidentate ligands an almost regular tetrahedral geometry is observed deviating from 109.5° by only 0.6° with the mean Pt-P bond distance of 2.254 Å. For the chelated derivatives the distortion depends on the size of the P-Pt-P bite angles of the ligands. The mean Pt-P bond distance in the series of bidentate P-donor ligands elongated with the decrease in number of atoms in the respective metallocycle: 2.248 Å (nine-PC_8P) < 2.296 Å (six-PC_3P) < 2.360 Å (three-PP). The mean P-Pt-Pt bite angle closes in the same order: 115.3° > 97.4° > 53.1° and at the same time the distortion of the respective tetrahedral increases.

There are three derivatives in which each Pt(0) atom has heterogeneous inner sphere (PtP_3S). In two of them three unidentate PPh_3 ligands with SO_2 created such sphere. The mean Pt-P and Pt-S bond distances are 2.313 and 2.384 Å, respectively. The mean P-Pt-P and P-Pt-S bond angles are 118.6° and 96.8°. In the third derivative the PtP_3S chromophore is build up by two unidentate PPh_3 ligands and one bidentate ligand with P and S donor sites. Here the Pt-PPh_3 bond distances are quite different at 2.252 and 2.387 Å because of a *trans* effect. The former is opposite S and the latter opposite of the bidentate ligand: The P-Pt-S bond angles range from 52.8(1)° (three-membered) to 160.4(1)° and the P-Pt-P bond angles from 103.5(1)° to 147.9(1)°. In another three derivatives two unidentate P donor ligands with bidentate O_2 molecule created PtO_2P_2 chromophore. Structure of $Pt(\eta^2\text{-}O_2)(PPh_3)_2 \cdot 2CHCl_3$ is shown in **Figure 2** [7] as an example. The molecule of oxygen plus two unidentate bulky triphenylphosphine ligands are coordinated to the central Pt(0) atom. The molecule has a two-fold axis of symmetry through the Pt atom and the O-O axis. The mean Pt-P and Pt-O bond distances are 2.260 and 2.01
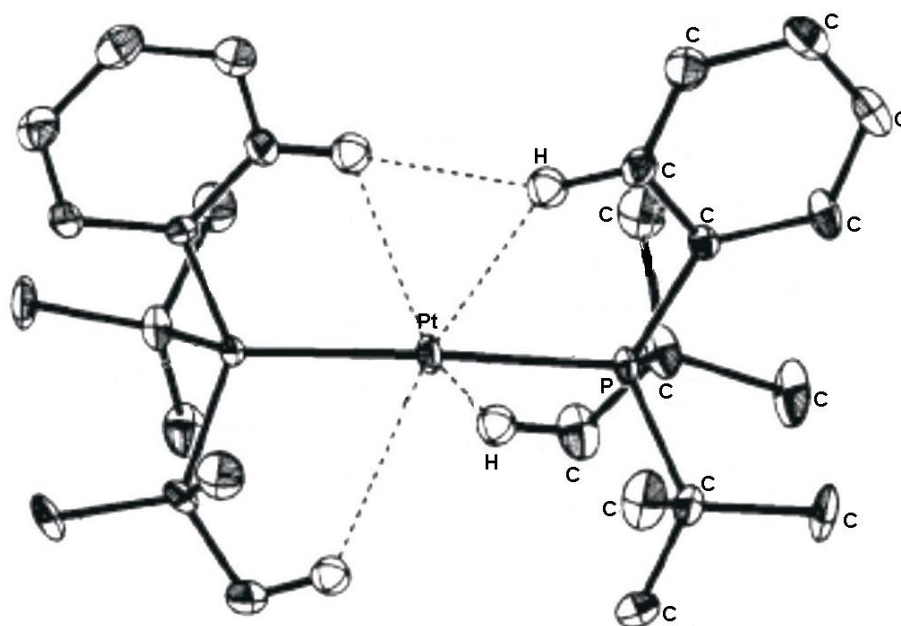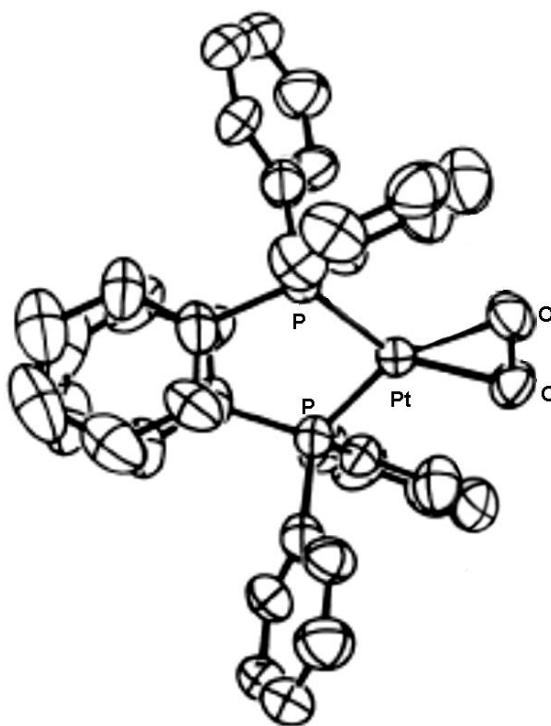
Figure 1. Structure of $Pt(Bu_2^tPh)_2$ [3].

Figure 2. Structure of $Pt(\eta^2\text{-}O_2)(PPh_3)_2$ [4].

Å. The mean O-Pt-O bite angle is 42.8°. The mean P-Pt-P and O-Pt-P bond angles are 101.2° and 107.8°.

There is an example in which pairs of PMe_2Ph and pyrazole form PtN_2P_2 chromophore with the mean Pt-N and Pt-P bond distances of 2.027 and 2.305 Å, with the mean N-Pt-P bond angle of 91.7°. In another derivative two PPh_3 ligands with two SO_2 molecule build up a distorted tetrahedral geometry about Pt(0) atom (PtS_2P_2). The mean Pt-S and Pt-P bond distances are 2.428 and 2.315 Å. The L-Pt-L bond angles open in the order: 96.3° (S-Pt-P) < 106.3° (S-Pt-S) < 158.6° (P-Pt-P).

The remaining three Pt(0) derivatives have a pair of PPh_3 ligands and heterobidentate ligand giving the following isosceles triangles: PtON angle 40.0˚, PtNS angle of 43.1˚ and PtCS angle 45.5˚. The angle increases with increasing sum of covalent radii of the ligand atoms and with increasing average Pt-L bond distance, for example: 1.48 and 2.058 Å (O + N) < 1.77 and 2.194 Å (N + S) < 1.79 and 2.196 Å (C + S). The mean Pt-P bond distance is 2.276 Å. The sum of all four Pt-L bond distances increases in the order: 8.63 Å (PtP_2ON) < 8.945 Å (PtP_2NS) < 8.98 Å (PtP_2CS). In the same order a distortion of the respective tetrahedral geometry decreases.

The most common donor atom is P. The mean Pt(0)-P bond distance for monodentate ligands elongated in the order: 2.24 Å (two-) < 2.275 Å (four-) < 2.28 Å (three-coordinate). In the four-coordinated derivatives the mean Pt(0)-L bond distance elongated in the order: 2.10 Å (η^2-O_2) < 2.03 Å (NL) < 2.275 Å (PL) < 2.29 Å (η^2-PL) < 2.41 Å (SO_2).

2.2. Pt(I) Complexes

There are two examples in which Pt(I) atom is four-coordinated. In one of the examples two 2,2'-bipyridine ligands in complex cation $[Pt(\eta^2$-bpy$)]^+$ created a distorted square-planar configuration (PtN_4). The mean Pt-N bond distance is 2.029(7) Å, and the ring N-Pt-N internal angle is 79.2(4)˚. A distorted tetrahedral geometry about the Pt(I) atom, in $Pt(PPh_3)_2(\eta^2$-1,2,3,4-tetraphenyl-1,2-dihydro-1,2-diphosphate) is created by two monodentate PPh_3 ligands and a bidentate diphosphate ligand with mean Pt-P bond distances at 2.32(I) and 2.285(I) Å, respectively. The P-Pt-P bond angles range from 82.67(3)˚ (five-membered metallocycle) to 140.95(6)˚.

2.3. Pt(II) Complexes—Four Coordinated

There are over one thousand and six hundred four-coordinated Pt(II) complexes for which structural parameters are available. Their structural parameters were detail analyzed and classified by us [2]-[5]. Therefore in this section will be only briefly summarized these structures. The inner coordination sphere about the Pt(II) atoms is very variable: PtA_4, PtA_3B, PtA_2BCD and even PtABCD. The PtA_4 derivatives include those with homogeneous or quasi-homogeneous coordination spheres (*i.e.* different ligands) but with the same donor atoms.

2.3.1. PtA_4 (A = O, N, C, Cl, S, P, Br, Se or As)

There are only four Pt(II) derivatives with PtO_4 inner coordination sphere. In each of them a pair of bidentate –O,O' donor ligands create a square planar arrangement about the Pt(II) atom. In one derivative two 3,5-di-tert-butyl-1,2-semiquinone ligands creating two five-membered metallocyclic rings with mean O-Pt-O bond angles of 81.3(2)˚. The mean derivatives a bidentate O-donor ligands (acetylacetonatate, benzoyltrifluoroacetonate) form a six-membered metallocycles with mean O-Pt-O bond angle of 94.8(6)˚. The mean Pt-O bond distance of 2.012 Å is about 0.045 Å longer than that found in the former derivative.

There are almost two hundred and sixty PtN_4 derivatives, which can be divided into the six groups: $Pt(\eta^1$-NL$)_4$; $Pt(\eta^1$-NL$)_2(\eta^2$-NL); $Pt(\eta^2$-NL$)_2$; $Pt(\eta^2$-NL$)$ $(\eta^2$-NL'$)$; $Pt(\eta^3$-NL$)$ $(\eta^1$-NL$)$ and $Pt(\eta^4$-NL$)$. The $Pt(\eta^1$-NL$)_4$ derivatives (over one hundred) can be subdivided into two main groups: (a) with a homogeneous coordination sphere (all four N-donor ligands are identical); (b) with a quasi-homogeneous coordination sphere. The (b) group can be divided into four subgroups: (b_1) three identical ligands plus one other PtN_3N'; (b_2) two pairs of identical ligands $PtN_2N'_2$; (b_3) one identical pair and two different ligands $PtN_2N'N''$; (b_4) all ligands different.

The (a) group is most often created by four amine ligands, in several other cases four alkyl N-donor ligands, or aryl N-donor ligands used. The mean Pt-N bond distances elongated in the order: 2.01 Å (N-alkyl) < 2.02 Å (N-aryl) < 2.055 Å (NH_3). The mean *cis*-N-Pt-N bond angle depart from the 90.0˚ by 1.4˚ (N-aryl) < 2.0˚ (N-alkyl) < 2.3˚ (NH_3), which indicated that the distortion of the respective square-planar geometry increases in the given order.

There are only three derivatives belonging to the (b_1) subgroup (PtN_3N'). The mean Pt-N bond distance is 2.05 Å and *cis*-N-Pt-N angle depart from 90.0˚ by 2.4˚.

The most common type subgroup is actually (b_2), $Pt(\eta^1$-NL$)_2(\eta^1$-NL'$)_2$. Practically all examples are of the composition $[Pt(NH_3)_2(\eta^1$-NL$)_2]^{2+}$ with both *cis*- (22 examples) and *trans*- (10 examples) derivatives. The mean Pt-NH_3 bond distance in the *cis*-derivatives is 2.04 Å, which is slightly shorter than in the *trans*-derivatives at 2.06 Å. The mean depart of *cis*-H_2N-Pt-NH_3 bond angle from 90.0˚ is 1.7˚. The mean *trans*-N-Pt-N bond angle in those *cis*-derivatives is 177.5˚. The depart of *trans*-H_3N-Pt-NH_3 bond derivatives in the series of *trans*-

$[Pt(NH_3)_2(\eta^1\text{-NL})_2]^{2+}$ from 180.0° is 0.3% and *cis*-H_3N-Pt-NL bond angle depart from 90.0° by 11.5°. For the composition $[Pt(MeNH_2)_2(\eta^1\text{-NL})_2]^{2+}$ only *trans*-derivatives (seven examples) are found, with a mean Pt-$N(H_2Me)$ bond distance of 2.06 Å. The mean *trans*-N-Pt-N bond angle is 176.7° and *cis*-N-Pt-N bond angle depart from 90.0 by 3.3° (mean).

Several derivatives have the (b_3) type composition $[Pt(NH_3)_2(\eta^1\text{-NL'})(\eta^1\text{-NL''})]^{2+}$ and again exhibit *cis*- (9 examples) as well as *trans*- (6 examples). The mean Pt-$N(H_3)$ bond distances for both *cis* and *trans* derivatives are the same at 2.05 Å in this case. Once again, for the compositions $[Pt(MeNH_2)_2(\eta^1\text{-NL'})(\eta^1\text{-NL''})]$ (3 examples) only *trans* derivatives are found again with mean Pt-$N(H_2Me)$ bond distances of 2.06 Å.

Finally there is only one example which belongs to the (b_4) subgroup and that is $[Pt(NH_3)(1\text{-methylcyto-}$ sine)(9-methyladenine)(9-ethylguaninate)]$^+$, $[Pt(NH_3)(1\text{-MeC})(9\text{-MeA})(9\text{-EtG})]^+$. Most of the compounds represent a hypothetical interaction of *cis*-Pt(II) with two biomolecules (nucleobases), which can be considered a model for the interaction of a transition metal with DNA in an inter- and intra-strand fashion simultaneously. The data in this section reveals the rich Pt(II) chemistry of N-donor ligands with a dominant NH_3 ligand and different nucleobases [2]. The mean Pt-N bond distances elongate in the sequence: 2.015 Å (9-EtG) < 2.02 Å (9-MeA) < 2.03 Å (1-MeC) < 2.035 Å (NL) < 2.04 Å (NH_2Me) ~ 2.04 Å (NH_3) for the *cis*-derivative. For the *trans*-derivatives the order is: 2.01 Å (9-EtG) < 2.015 Å (NL) < 2.03 Å (9-MeA) < 2.04 Å (1-MeC) < 2.05 Å (NH_3) < 2.06 Å (NH_2Me).

There are over forty derivatives of $Pt(\eta^2\text{-NL})(\eta^1\text{-NL})_2$ type: for which structural parameters are available [2]. Structure of $Pt(\eta^2\text{-4,4'-Ph}_2\text{bpy})(3,5\text{-Me}_2\text{py})_2(PF_6)_2$ is shown in **Figure 3** as an example [8]. The crystallographic asymmetric unit contains the dicationic complex of Pt(II). There are interactions with both the hexafluorophosphate anions on each axial position at a distance of 3.40(1) and 2.58(3) Å, respectively. The most common bidentate ligands are 2,2'-bipyridyl (by) and its derivatives for the unsaturated –N,N'donor ligands (8 examples), and ethylenediamine (en) and its derivatives for the saturated –N,N'donor ligands (17 examples). The mean values of Pt-N bond distance and N-Pt-N bond angle found in the *cis*-$Pt(\eta^2\text{-bpy})(\eta^1\text{-NL})_2$ derivatives of 2.005 Å and 80.5° are smaller than those found in the *cis*-$Pt(\eta^2\text{-en})(\eta^1\text{-NL})_2$ derivatives with the values of 2.04 Å and 84.0°, respectively. The mean Pt-N bond distance in the series of monodentate ligands elongate in the order: 2.005 Å (NCX) < 2.015 Å (pyridine, pyrazole) < 2.02 Å (N-nucleoside) < 2.05 Å (NH_3).

There are seventy-five examples in which a square planar arrangement created by two pairs of the same tridentate ligands $Pt(\eta^3\text{-NL})_2$ or different bidentate ligands $Pt(\eta^2\text{-NL})(\eta^2\text{-NL'})$, occurs about the Pt(II) atom with varying degrees of distortion. In $Pt(\eta^2\text{-NL})_2$ derivatives are examples in which a pair of bidentate –N,N'donor atoms giving two four-membered metallocyclic rings with the mean N-Pt-N bite angle of 63.7° and the mean Pt-N bond distance of 2.033 Å, typical of purely σ-bonding between metal and nitrogen atoms.

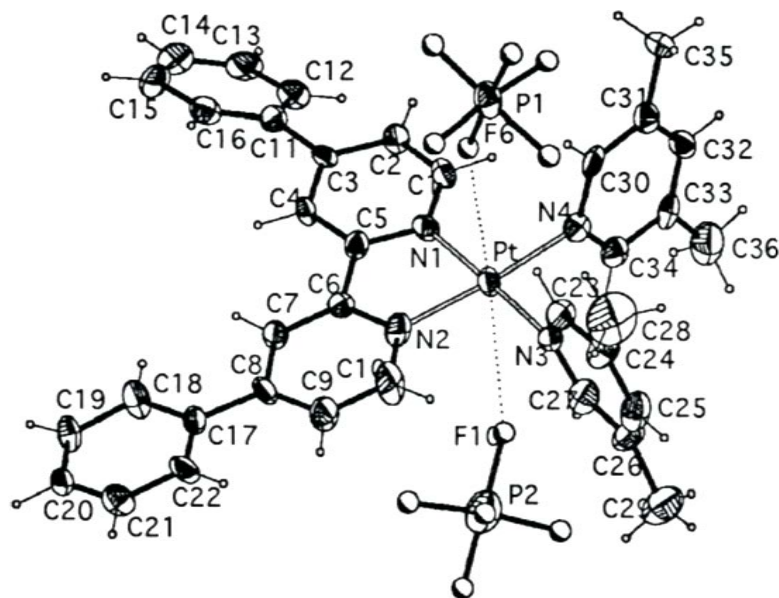**Figure 3.** Structure of $Pt(\eta^2\text{-4,4'-Ph}_2\text{bpy})(3,5\text{-Me}_2\text{py})_2(PF_6)_2$ [6].

In some derivatives with two non-equivalent N,N'-donor ligands form four- and five- in another one five- and seven- and some other six- and seven-membered metallocyclic rings, respectively, with the Pt(II) atom. The mean values of N-Pt-N bite angles are 63.5˚ (four-), 83.0˚ (five-), 92.0˚ (six-) and 87.9˚ (seven-membered). The ~4˚ closure of the seven-membered ring reflects its greater flexibility. The six-membered chelate ring is in the chair conformation.

The data in $Pt(\eta^2\text{-NL})_2$ and $Pt(\eta^2\text{-NL})(\eta^2\text{-NL})'$ indicate the most common situation with the N,N'-donor ligands and Pt(II) in the five-membered metallocyclic ring. In the unsaturated chelate ligands the mean values of the Pt-N bond distances and N-Pt-N bite angles are 1.995 Å and 78.5˚, which are smaller than those found in the saturated chelate ligands of 2.05 Å and 82.2˚. The respective mean values for the six-membered metallocyclic rings are 2.045 Å and 89.7˚.

In the series of $Pt(\eta^3\text{-NL})(NL)$ derivatives are actually two groups, one where the tridentate ligand is 2,2': 6',2''-terpyridine (5 examples) and the other, where the tridentate ligand is diethylenetriamine (11 examples). In those derivatives with terpyridine as the tridentate ligand, the central N atom is usually much closer to the Pt(II) atom than the remaining two outer N atoms, with mean values of Pt-N of 1.94 and 2.03 Å, respectively. The mean values of five-membered metallocyclic ring N-Pt-N angle is 80.8 (range 80.0˚ - 81.8˚).

In those derivatives with diethylene triamine as the tridentae ligand, the central N atom of the chelate is again closer to the Pt(II) atom than the outer N atoms are, with mean Pt-N values of 1.99 and 2.05 Å, respectively. Both of these are somewhat longer than the terpyridine case in which π-effects are believed to play a role. The mean value of the five-membered metallocyclic N-Pt-N ring angle is also slightly larger at 84.7˚ (range 84.3˚ - 85.7˚). However it does mean than these derivatives are somewhat less distorted from the ideal square-planar geometry than the terpyridine derivatives.

There are over twenty $Pt(\eta^4\text{-NL})$ derivatives in which a single tetradentate ligand provides a square-planar environment around a Pt(II) atom. These derivatives are divided into two groups, one with three metallocyclic rings (8 examples) and the other with four metallocyclic rings (15 examples). In the four derivatives of the former type of derivative, three five-membered metallocyclic rings are found with mean intra Pt-N bond distances of 1.985 Å and mean inter Pt-N bond distances of 2.045 Å. The N-Pt-N bond angles range from 78.5(3)˚ to 88.9(4)˚ with the mean value of 82.8˚. The remaining four derivatives of this type have a middle six-membered metallocycle and two outer five-member chelate rings with mean N-Pt-N values of 97.6˚ and 79.6˚, respectively. The mean Pt-N bond distances are 1.99 Å for intra-N atoms and 2.01 Å for inter-N atoms. In one derivative $[Pt(\eta^4\text{-AID seco-corrinoid})]^+$ tetradentate ligand makes three six-membered rings with N-Pt-N bond angles of 91˚ (central), 89˚ and 91˚ (outer) and mean Pt-N bond distances of 2.00 Å (metallocycle) and 2.02 Å.

In the second group with four metallocyclic rings the most common are those which form two pairs of rings, five- and six-membered in *trans* positions (7 examples). The mean N-Pt-N value for the former is 84.3˚ (range 83˚ to 85˚) and for the latter is 95.5˚ (range 95˚ to 96.4˚), as expected. The mean Pt-N bond distance is 2.04 Å (range 1.97 to 2.10 Å). In $Pt(\eta^4\text{-tetrapropylporphycene})$ has a 16-membered macrocycle which creates two pairs of metallocyclic rings, five- and seven-membered in *trans* positions with mean values of 84.9˚ and 95.1˚, respectively. In the remaining seven derivatives of this group a 16-membered macrocycle creates four six-membered metallocyclic rings with Pt(II) atoms of mean N-Pt-N value of 90.0˚ (range 88˚ to 92˚) and the mean Pt-N bond distance of 2.00 Å (range 1.97 to 2.035 Å).

There are almost thirty, mostly black, derivatives where four cyamide groups are arranged in a square planar geometry around a Pt(II) atom (PtC_4). For half of them only unit cell parameters are reported in the original papers. For the others the Pt-C(N) bond distances range from 1.93 to 2.15 Å with an average value of 1.99 Å. The *cis* and *trans* C-Pt-C bond angles range from 86˚ to 94˚/average 90˚ and 176˚ to 180˚, respectively.

In another thirty derivatives with colors from red to yellow, four chlorine atoms create a square-planar environment for the Pt(II) atom. The $[PtCl_4]^{2-}$ anions exist in the crystal state only with bulky ligand cations [2]. The mean Pt-Cl bond distance is 2.30 Å (range 2.23 zo 2.32 Å). The *cis* and *trans* Cl-Pt-Cl bond angles depart from the ideal values of 90˚ and 180˚ by 1.9˚ and 2.9˚, respectively. Thus the $PtCl_4$ anionic moiety is somewhat less distorted than the tetra-cyano analogue (vide supra). The mean Pt-Cl bond distance is about 0.3 Å longer than the Pt-C bond distance, in correlation with the respective covalent radii of the donor atoms of 0.99 Å for Cl and 0.77 Å for C.

There are more than sixty derivatives in which square-planar geometry is realized by mono-, bi- and tetradentate S-donor ligand. Thirteen derivatives have only monodentate ligands, $Pt(\eta^1\text{-SL})_4$. The Pt(II)-S bond distances range from 2.30 to 2.34 Å (average 2.32 Å). The maximum deviation of *cis* and *trans* S-Pt-S bond angles from

the ideal values of 90˚ and 180˚ are 9˚ and 10˚, respectively. Two derivatives use one bidentate and two monodentate ligand to form a distorted square planar geometry about each Pt(II) atom. In one the geometry about the Pt(II) atom is more distorted than in other. This is because of the chelate rings, which is in the former is four-membered and in the latter six-membered, with S-Pt-S bite angles of 75.6˚ and 88.6˚, respectively.

The most common derivative are those with a pair of bidentate ligands about the Pt(II) atoms. The size of the chelate rings include four-membered moieties (7 examples) with a mean Pt-S bond distance of 2.32 Å and S-Pt-S bite angle of 75.0˚ for RCS_2 ligands and 2.34 Å and 83.6˚, respectively for RPS_2 ligands. In the $[Pt(\eta^2-S_4)_2]^{2-}$ anion the mean S-Pt-S bite angle is 93.4˚.

A $[Pt(\eta^2-C_5H_9S_2)(\eta^2-C_5H_9S_3)]$ has a distorted square planar arrangement of four- (the former ligand) and five- (the latter ligand)-membered chelate rings. The S-Pt-S bite angles within the two rings are 73.0˚ and 93.6˚, respectively, and the two Pt-S bond distances are correspondingly different at 2.323 and 2.242 Å, respectively.

In thirty derivatives two bidentate ligands form two five-membered rings about the Pt(II) atoms, and represent the most common arrangement for the 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 bond angles range from 86.5˚ to 92.0˚ (average 89.3˚).

There are some derivatives (3 examples) in which a pair of bidentate ligands form two six-membered chelate rings. All three differ in the ring atoms involved with the ring angle opens in the order: 90.0˚ (SPNPS) < 92.7˚ (SCNCS) < 97.5˚ (SC_3S). In the same order the mean Pt-S bond distance shortened: 2.335 Å > 2.295 Å > 2.280 Å.

In the remaining nine derivatives a tetradentate ligand is bonded to the Pt(II) atom. In one derivative the tetradentate 1,3-bis(2-mercaptophenylthio)-2-propanol ligand forms three chelate rings, two five-membered and one six-membered, with the angles of 89.3˚ and 90.2˚, respectively. In all others a tetradentate ligand creates four chelate rings about the Pt(II) atom. In another two derivatives the macrocycles creating four five-membered rings of mean S-Pt-S bond angle of 88.9˚ and the mean Pt-S bond distance of 2.287 Å. There is also example, in which macrocycle forms four six-membered chelate rings with a mean S-Pt-S value of 98.9˚. In another derivative are present two pairs of non-equivalent chelate rings (five- and seven-) in *trans* position with an 87.5˚ angle and 92.8˚, respectively. In two derivatives tetradentate macrocycles create also pairs of non-equivalent chelate rings of six- and eight-members in *trans* related positions. Finally there is an example, with three five- and one ten-membered chelate rings.

There are forty Pt(II) derivatives mostly colorless with mono-, bi- and tetradentate P donor ligands, bidentate being most common. In eight derivatives four monodentate ligands form a square planar arrangement about the Pt(II) atom. The mean Pt-P bond distance is 2.32 Å (range 2.20 to 2.37 Å). The deviations of *cis* and *trans* P-Pt-P bond angles from ideal (92˚ and 180˚) are 4˚ and 13˚.

Four derivatives contain two bidentate ligands, both PNP, forming four-membered metallocyclic rings with a mean P-Pt-P angle of 70.4˚. The mean Pt-P bond distance is 2.298 Å. In another two derivatives two bidentate ligands, both PCP, give four-membered rings with mean P-Pt-P angle of 70.7˚ and mean Pt-P bond distance of 2.313 Å. Two dissimilar bidentate ligands are found in five derivatives with a distorted square planar geometry around the Pt(II) atoms. In each derivative there is a four-membered ring, PNP plus five-PCCP; PCP plus PCCP; PNP plus PCHCP; and PNP plus PNPNP. The bond distances and angles reflect the covalent radii of the atoms involved. Fourteen derivatives have a pair of bidentate ligands, both PCCP, given five-membered metallocyclic rings with mean P-Pt-P angles of 84.3˚ (range 82.0˚ to 86.3˚). The mean Pt-P bond distances range from 2.280 to 2.335 Å (average 2.31 Å).

Pair of six-membered metallocyclic rings is found in three derivatives with mean P-Pt-P angles of 90.0˚ (POBOP) in two derivatives, and 80.7˚ (PCNCP) in the third one. The mean Pt-P bond distance is 2.31 Å (range 2.297 to 2.314 Å).

There are three derivatives which contain a tetradentate ligand. In two of them a macrocycle forms three five-membered rings with mean P-Pt-P angle of 84.3˚. The mean Pt-P bond distance 2.266 Å for intra P atoms are shorter by 0.006 Å than those for inter P atoms (2.327 Å), as expected. In the third derivative a 14-membered macrocycle creates a five- and a six-membered chelate rings in *trans* positions about the central Pt(II) atom.

There are two examples which contain $[PtBr_4]^{2-}$ anion. The mean Pt-Br bond distance is 2.42 Å. The *cis*- and *tras* Br-Pt-Br angles depart from the ideal values (90˚ and 180˚) by 1.4˚ and 2.8˚, respectively.

There are seven derivatives with the $PtSe_4$ chromophore. In one of them four selenourea molecules form a square planar geometry about Pt(II) with mean Pt-Se bond distance of 2.44 Å. The *cis* and *trans* Se-Pt-Se bond angles deviate from ideal by 5˚ and 7˚, respectively. In another one two $(Bu^i)_2NCSe_2$ ligands provide two four-

membered chelate rings with the Pt(II) atom, the Se-Pt-Se bond angles have a mean value of 77.8° and the two pair of Pt-Se bonds are at 2.426 and 2.429 Å.

The structure of the $[Pt\{\eta^2\text{-MeSe}(CH_2)_3\text{SeMe}\}_2]^{2+}$ cation shows the Pt(II) atom occupying a crystallographic inversion centre and coordinated to an array of four Se donor ligands with Pt-Se distances of 2.414 and 2.421 Å. The angles around the central Pt(II) atom do not deviate significantly from 90° or 180°, reflecting the good match of the six-membered chelate rings formed by the diseleno ligands.

In two derivatives, where two bidentate $N(\text{SePPH}_2)_2$ ligands are bonded to a Pt(II) atom there is a moticeable distortion in the coordination geometry with ligand bite angles of 99.5° and other angles being 80.5°. Structure of $[Pt\{\eta^4\text{-[16]-aneSe}_4\}]^{2+}$ is shown in **Figure 4** [9]. The Pt(II) atom lies precisely in the Se_4 coordination plane. The Se-Pt-Se angles are all within 1.2° of the ideal values of 90° and 180°, indicating a good size match between the crown and the Pt(II) radius. In $[Pt\{\eta^4\text{-[16]aneSe}_4\}]^{2+}$ the Pt(II) atom lies precisely in the Se_4 coordination plane. The Se-Pt-Se angles are all within 1.2° of the ideal values of 90° and 180°, indicating a good size match between the crown and the Pt(II) radius.

Only one derivative exists with a $PtAs_4$ chromophore. Here the Pt(II) atom is in approximately square planar geometry, bonded to four As atoms from two o-phenylenebisdimethylarsine ligands. The five-membered ligand bite angles are 84.2° and the other angles are 97.1°. The mean Pt-As bond distance is 2.375 Å.

The overall data in 2.3 chapter includes over four hundred and thirty Pt(II) complexes (PtA_4). The frequency of examples for the donor atoms are: As(1) < Br(2) < O(4) < Se(7) < Cl(30) < CN(31) < P(41) < S(63) < N(258). The ligands range from monodentate through bi-, tri- and tetradentate. There is a tendency for Pt-L to increase in value with the covalent radius of the coordinating atom. In the N-donor ligand series it is also noted that the unsaturated ligands have smaller Pt-N bond distances than the saturated ligand as expected. The mean Pt-L bond distances of the monodentate ligands are in the sequence: 2.03 Å (N, 0.75 Å) < 2.30 Å (Cl, 0.99 Å) < 2.32 Å (S, 1.02 Å) < 2.33 Å (P, 1.06 Å) < 2.42 Å (Br, 1.14 Å) < 2.44 Å (Se, 1.16 Å). A somewhat shorter value is observed for Pt-C in the cyanide derivative of 1.99 Å. The Pt(II)-L bond distances of the bidentate (chelate) ligands are in the sequence: 2.00 Å (NL, unsaturate) < 2.03 Å (OL) < 2.04 Å (RNH_2, NH_3) < 2.05 Å (NL, saturated) < 2.30 Å (SL) < 2.32 Å (PL). The chelate L-Pt(I)-L ring angle values for four-membered opens in the order: 69.0° (PNP) < 70.8° (PCP) < 74.7° (PBP) < 75.0° (SCS) < 83.6° (SPS); for five-membered: 79.0° (NC_2N, unsaturate) < 81.3° (OC_2O) < 83.3° (NC_2N, saturate) < 84.2° (PC_2P) < 86.5° (SCPS) < 89.3° (SC_2S) < 93.4° (SS_2S) < 93.6° (SSCS); and for six-membered: 86.5° (PNPNP) < 88.5° (PCHCP) < 89.5° (NC_3N) < 91.3° (PC_3P) < 93.7° (SC_3S) < 94.8° (OC_3O). The chelate ring angles close with increasing covalent radii of the atoms involved in these rings, but opens with increasing number of atoms as expected.
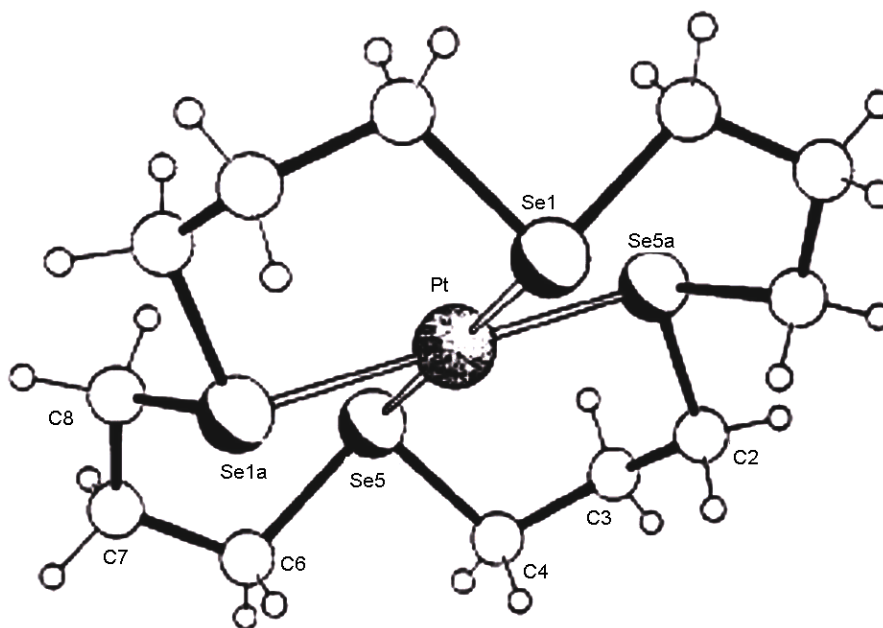
Figure 4. Structure of $[Pt\{\eta^4\text{-[16]-aneSe}_4\}]^{2+}$ [7].

There are two types of tridentate ligands, both with N-donor atoms, terpyridine and diethylenetriamine. The former is unsaturated and the latter is saturated, and the electronic effects can be seen in both the Pt-N bond distances and the N-Pt-N ring angles. In the former the Pt-N bond distances are shorter and the chelate ring angle smaller than in the latter. In both the Pt-N bond distances with the central N atom are shorter/(mean value 1.94 and 2.03 Å) than with the outer N atoms (mean values 1.99 and 2.05 Å) of the ligand. The respective N-Pt-N ring angles are 80.8° and 84.6°, respectively.

There are three types of homo-tetradentate ligands with N, S and P donor atoms. The mean Pt-N bond distances and N-Pt-N chelate ring angles are 2.01 Å, 83.8° (five-) and 93.0° (six-membered rings). The mean Pt-S and S-Pt-S values are 2.30 Å, 88.6°. The mean Pt-P and P-Pt-P values are 2.29 Å and 84.3°.

2.3.2. PtO$_3$X (X = N, P, Br or I), PtN$_3$X (X = O, C, Cl, S, Br or I)

There are over one hundred and seventy derivatives of the composition PtA$_3$B. Their structural parameters were detail classified and analyzed in [3] and therefore in this section will be only in short version outline.

Only four derivatives of PtO$_3$X composition are known. In one derivative the 2,6-pyridine dicarboxylate(-2)anion acts as a tridentate ligand via the ring N atom and an O atom from each of the carboxylate groups. The water molecule completes the square planar geometry about the Pt(II) atom. The tridentate ligand creates two five-membered metallocyclic rings with the mean O-Pt-N bite angle of 81.9Å. The central Pt-N bond distance of 1.898 Å is about 0.130 Å shorter than the outer Pt-O bonds (2.028 Å ave). The Pt-OH$_2$ bond distance is 2.053 Å.

The other three derivatives have the composition Pt(η^2-hfac)(η^1-hfac)X (X = Pcy$_3$, Br or I) and are isostructural. The mean Pt-O bond distances for bidentate hexafluoropentadionate (hfac) and 2.005 Å for monodentate (hfac). The mean value of the O-Pt-O bite angle is 92.0° (six-membered ring). The Pt-X bond distance elongated in the order: 2.232 Å (X = P) < 2.395 Å (Br) < 2.567 Å (I) which follow well covalent radii of the respective atoms.

Almost seventy derivatives have the composition PtN$_3$X. Fifteen have the PtN$_3$O chromophore. In two of them cis-[Pt(NH$_3$)$_2$(1-MeC)(OH)]$^+$ and cis-[Pt(NH$_3$)$_2$(1-MeC)·(H$_2$O)]$^{2+}$ a square planar geometry consists of four unidentate ligands. The mean Pt-NH$_3$ bond distance is 2.027 Å and Pt-N (MeC) is 2.034 Å. The Pt-O(H) and Pt-O(H$_2$) bond distances are 2.027 and 2.052 Å, respectively. The depart of the cis and trans angles from the ideal (90° and 180°) are 2.3° and 3.4°, respectively. Another six derivatives have the composition Pt(NH$_3$)$_2$\{η^2-N,O(L)\} have a cis arrangement. The bidentate ligands create a five-membered metallocyclic ring about each Pt(II) atom with mean O-Pt-N bond angles of 83.1° (range 81.0° to 85.2°). Surprisingly perhaps the mean Pt-O and Pt-N bond distances of the bidentate ligands are the same of 2.018 Å (range 1.980 - 2.055 Å (O) and 1.95 - 2.06 Å (N)).

A square planar geometry with a PtN$_3$O chromophore in one derivative is created by a bidentate ethylenediamine-N,N' molecule with a five-membered chelate ring (N-Pt-N, 84.6°) and monodentate uracylate-N and a water molecule. In the next set of derivatives (3 examples) a pair of non-equivalent bidentate ligands form a square planar arrangement about the Pt(II) atoms, with five-membered rings (N-Pt-N and N-Pt-O), in one example a five-(N-Pt-O) and six-(N-Pt-N) membered rings. Another three examples contain one tridentate (N-donor) and an O-donor ligand. Each of the tridentate ligands, terpyridine (trpy) or diethylenetriamine (dien) include the Pt(II) atom in a pair of five-membered rings with mean angles of 79.7° (trpy) and 85.7° (dien). These values reflect an electronic effect of the respective ligands, trpy-unsaturated in the first case and saturated dien in the latter two cases. This effect can, also be seen in the mean Pt-N bond distances of 1.92 and 2.07 Å (trpy), and 1.99 and 2.05 Å (dien) for the central and satellite N-atoms.

There is only one example with PtN$_3$C chromophore, build up by bidentate o-phenantroline-N,N'ligand with average Pt-N bond distance of 2.032 Å, and one monodentate o-phenanthroline (Pt-N 2.053 Å). The CN ligand completes the square planar arrangement about the Pt(II) atom (Pt-C 1.93 Å).

There are forty derivatives with the PtN$_3$Cl chromophore. In twenty five derivatives a square planar arrangement about the Pt(II) atom is created by three unidentate –N donor ligands with the mean Pt-N bond distance of 2.12 Å and a chlorine atom which completed a square-planar geometry. The mean Pt-Cl bond distance is 2.293 Å. The cis and trans angles depart from the ideal values (90° and 180°) by 2.2° and 2.9°, respectively.

There are nine derivatives [Pt(η^2-ethylenediamine)(η^1-NL)Cl]$^+$ in which bidentate –N,N' ligand with monodentate –N donor ligand and a Cl$^-$ created a distorted square planar environment about each Pt(II) atom. The mean Pt-N(en), Pt-N (monodentate) and Pt-Cl bond distances are 2.045, 2.020 and 2.308 Å. The ethylenedia-

mine created a five-membered metallocyclic ring with the mean N-Pt-N bite angle of 83.7˚.

In another four derivatives tridentate terpyridine –N,N',N" ligand with a chlorine atom created a distorted square planar geometry about Pt(II) atom. The mean Pt-N bond distances are 1.94 Å (central) and 2.02 Å (outer) with the mean five-membered ring angle (N-Pt-N) of 81.2˚. There is also an example in which diethylenetria-mine acts as a tridentate ligand with the Pt-N (central) and mean PtN (outer) distances of 2.002 and 2.063 Å, which are somewhat longer than those found for terpyridine, as expected. Also the mean N-Pt-N bite angle is somewhat more open (84.0˚).

There are two derivatives in which tridentate terpyridine ligand with monodentate –S(CH$_2$)$_2$OH ligand created a distorted square planar environment about each Pt(II) atom (PtN$_3$S). Structure of [Pt(η^3-trpy){S(CH$_2$)$_2$OH}](NO$_3$) is shown in **Figure 5** [10]. The Pt(II) atom is in slightly distorted square planar environment with the three N atoms of the terpyridine the S atom of mercaptoethanol. The average N-Pt-N angle is 80.7˚ and the average N-Pt-S angle is 99.3˚. The Pt-N bond distance to the central atom at 1.968 Å is about 0.06 Å shorter than to the outer N atoms (2.027 Å). The Pt-S bond distance is 2.303(2) Å.

In two derivatives, three N atoms of diethylenetriamine and one Br atom form a square planar geometry about the Pt(II) atom (PtN$_3$Br). The mean Pt-N bond distances are 1.98 and 2.07 Å for the central and outer N atoms, respectively. The N-Pt-N angles are 84.8˚ and N-Pt-Br angles are 95.4˚.

There are eight derivatives with a PtN$_3$I chromophore. Two of them have monodentate ligands forming the square planar environment about the Pt(II) atom. The mean Pt-N and Pt-I bond distances are 2.04 and 2.565 Å, respectively. The *cis* and *trans* angles depart from the ideal (90˚ and 180˚) by 2.5˚ and 3.9˚. In another two de-rivatives one bidentate ethylenediamine –N,N' ligand and one pyridine plus the iodine atom form an approx-imate square planar environment with five-membered chelate ring of average N-Pt-N bite angle 89.3˚. The mean Pt-N (en), Pt-N (py) and Pt-I bond distances are 2.055, 2.022 and 2.604 Å.

In the remaining four derivatives, substituted diethylenetriamine molecules coordinate in a tridentate fashion and with iodine atom complete the PtN$_3$I chromophore. The mean Pt-N bond distances are 2.01 Å (central) and 2.06 Å (outer) with mean N-Pt-N bite angles of 85.0˚ for five-membered chelate ring. The mean Pt-I bond dis-tance is 2.591 Å.

The overall data in this subgroup shows the frequency of types of chromophore increasing in the order: PtN$_3$C(1) < PtN$_3$S(2) ~ PtN$_3$Br(2) < PtO$_3$N(4) < PtN$_3$I(8) < PtN$_3$O(15) < PtN$_3$Cl(40). The mean Pt-N bond dis-tance elongated in the order: 1.98 Å (η^3-trpy) < 2.03 Å (NL, η^3-dien) < 2.04 Å (NH$_3$, η^2-NL). The chelate five-membered rings (N-Pt-N open in the order: 80.9˚ (η^3-trpy) < 83.8˚ (η^2-NL) < 85.3˚ (η^3-dien). In the series of monodentate ligands the mean Pt-L bond distance increases with increasing covalent radii of the coordinated atoms: 2.02 Å (O, 0.73 Å) < 2.03 Å (N, 0.75 Å) < 2.30 Å (Cl, 0.99 Å) < 2.42 Å (Br, 1.14 Å) < 2.59 Å (I, 1.33 Å).
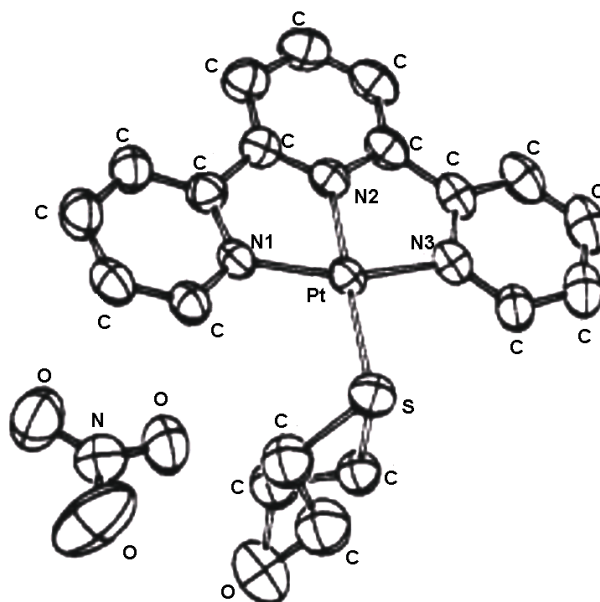

Figure 5. Structure of [Pt(η^3-trpy){S(CH$_2$)$_2$OH}](NO$_3$) [9].

2.3.3. $PtCl_3X$ (X = N, S or P), PtS_3X (X = O, N, Cl, P, As or I)

The number of $PtCl_3X$ derivatives decreases in the order: $PtCl_3N$ (30) > $PtCl_3S$ (15) > $PtCl_3P$ (2). Parts from Cl atoms, the most common monodentate ligands are N-donor nucleobases, and dimethylsulphoxide as S-donor. There is a *trans* effect on the Pt-Cl bond distances. The influence of the effect increases in the order: N< S < P, increasing the Pt-Cl distances in the same order with the mean values 2.302 Å (*trans* to N) < 2.324 Å (*trans* to S) < 2.380 Å (*trans* to P). The mean values of the Pt-Cl distances *trans* to each other are essentially the same in all three types of chromophore, at 2.30 Å. The mean Cl-Pt-X angles also follow a similar trend, opening in the order: 89.4˚ (X = N) < 91.0˚ (X = S) < 91.5˚ (X = P). The mean Pt-L bond distance elongated in the order: 2.03 Å (NL) < 2.205 Å (SL) < 2.215 Å (PL) < 2.30 Å (Cl).

There are twelve examples with PtS_3X chromophore (X = O (x2), N (x1), Cl (x3), P (x4), As nad I each (x1). There is complex, in which two 2-hydroxy-3-mercaptopyridine ligands, coordinated to Pt(II) only via the S atoms, while a third deprotonated, 2-hydroxy-3-mercaptopyridyne ligand chelates via the S and O atoms. This ambidentate behavior produced a slightly distorted square planar PtS_3O coordination arrangement, and is the only example with such a chromophore. The mean Pt-S(η^1-SL) bond distance is 2.294 Å, and Pt-L(η^2) bond distances are 2.284 Å (S) and 2.049 Å (O). The chelate ligand create five-membered metallocyclic ring with the S-Pt-O bite angle of 85.7˚.

In another derivative 2,6-bis(methylthiomethyl)pyridine acts as a tridentate SNS ligand with the S atoms in *trans* positions to each other. The fourth coordination site, *trans* to the N atom, is occupied by the S atom of a SCN group. The Pt-S, Pt-N and Pt-S(CN) bond distances are 2.285 Å (ave), 2.014 and 2.289 Å. The mean S-Pt-N angle is 85.7˚.

There are three derivatives with the PtS_3Cl chromophore. One has three monodentate S donor ligands (N-propyl-O-ethylthiocarbamate) plus the Cl atom. A second has one bi-(Et_2NCS_2) and one monodentate (MeS_2CNEt) S donor ligands plus the Cl atom. The third has one tridentate S donor ligand (2,12-dimethyl-3,7,11-trithiadecane) (dmtt) plus the Cl atom. All create a distorted square planar environment about the Pt(II) atom.

Three derivatives of the composition $[Pt(\eta^3\text{-dmtt})X]BF_4$ (X = Cl, PPh_3 or I) are isostructural. The dmtt molecule in each coordinates in a tridentate fashion and forms two six-membered chelate rings about the Pt(II) atom. In another one derivative bidentate $(EtO)_2PS_2$ and monodentate $(EtO)_2PS_2$ plus $Ph_2AsCH_2CH_2P(S)Ph_2$ ligand created about the Pt(II) atom a distorted square planar PtS_3As chromophore. The Pt-S distances *trans* to As is significantly longer (2.373 Å) than the other Pt-S distances (2.335 Å ave). The relevant S-Pt-S bite angle is 83.2˚.

The relevant data in this subgroup show that the mean Pt-S bond distance elongated in the order: 2.304 Å (η^3-SL) < 2.305 Å (η^1-SL) < 2.340 Å (η^2-SL). The mean value of the Pt-L bond distance for the monodentate ligands elongated in the order: 2.26 Å (PL) < 2.305 Å (SL) < 2.33 Å (Cl) < 2.35 Å (AsL) < 2.60 Å (I).

2.3.4. PtP_3X (X = H, F, Cl, S, Br or I), $PtBr_3X$ (X = N or S), PtI_3X (X = P or Sb)

Thirty derivatives with PtP_3X chromophores are known. Seven of them have PtP_3H chromophore. In six PtP_3H examples only monodentate PR_3 (R = Me, Et, Ph or cy) with H atom created a distorted square-planar environment about the Pt(II) atom. The Pt-P bond distances *trans* to the H atom are longer than the other, with mean values of 2.335 Å and 2.290 Å, respectively. In one example a bidentate P_7 ligand with PPh_3 plus H atom create a distorted square planar geometry about the Pt(II) atom. The P_7 ligand creates four-membered ring with the P-Pt-P bite angle of 78.2˚. A similar effect was found in this derivative with Pt-P bond distances of 2.42 Å (*trans* to H) and 2.40 Å (*trans* to P).

Colorless $[Pt(PEt_3)_3F]BF_4$ is the only example with the PtP_3F chromophore. The Pt-P bond distance *trans* to the F atom is 2.239 Å which is about 0.098 Å shorter than the other two with mean value of 2.337 Å (*trans* to P).

There are fifteen derivatives with the PtP_3Cl chromophore, by far the most common in this series. In eight of these, only monodentate ligands form a square planar environment about the Pt(II) atom. The remaining seven derivatives have one bidentate –P,P' with one monodentate P donor plus the Cl atom. There are four types of chelate ligands, those forming 4-membered PCP chelate rings (2 examples), with P-Pt-P bite angle of 71.5˚; 4-membered PN (2 exemples) with bite angle of 70.0˚; 5-membered PC_2P (2 examples) with bite angle of 85.8˚, and 6-membered PC_3P (1 example) with bite angle of 92.4˚, respectively. For the monodentate ligands, the mean Pt-P bond distance *trans* to the Cl atom is 2.24 Å. A similar trend is observed for the bidentate ligands (P,P')

with the values of 2.24 and 2.295 Å, respectively. The mean Pt-Cl bond distance, which is *trans* to the P atom, is 2.345 Å.

There are three derivatives with the PtP_3S chromophore. In one derivative three PMe_2Ph ligands plus SO_2 form a distorted square planar arrangement about the Pt(II) atom. In another one two bidentate ligands ($Ph_2PCH_2PPh_2$ –P,P', and $Ph_2PN(Et)C=N(Et)S$ –P,S) form such chromophore. The significant distortion from an ideal square planar arrangement of the donor atoms is apparently due to the P-Pt-P bite angles, 71.4˚ (PCP) and 85.7˚ (PNCS). In the third one derivative, tridentate $PhP(CH_2CH_2PPh_2)_2$ –P,P',P" ligand with monodentate Et_2NCS_2 -S donor atom created a distorted square planar geometry (PtP_3S). The tridentate ligand forms two five-membered rings with the mean P-Pt-P bite angle of 85.0˚. The *trans* influence of the S atom is not as simple as for the Cl atom. In the first PtP_3S derivative (all four ligands are monodentate) the Pt-P bond distance *trans* to S atom is 2.324 Å, which is 0.039 Å longer than the other Pt-P bonds (2.324 Å ave). Conversely, in remaining two derivatives, the former Pt-P bond is shorter than the latter (Pt-P) with mean values of 2.268 and 2.298 Å, respectively.

There also three derivatives with PtP_3Br chromophore. In two of them three monodentate ligands ($C_{13}H_{11}P$, $C_{14}H_{13}P$) plus Br atom created a distorted square planar geometry about the Pt(II) atom. In remaining one derivative, one bidentate –P,P' ($Bu_2^tPP=PBu_2^t$), one PPh_3 plus Br atom form a distorted square planar geometry at the Pt(II) atom (PtP_3Br). The mean Pt-P bond distance *trans* to the Br atom at 2.245 Å is about 0.083 Å shorter than the other Pt-P distances (2.328 Å, ave).

There is only one example in which monodentate ligands form a distorted square planar geometry at the Pt(II) atom (PtP_3I). The Pt-P bond distance *trans* to the I atom at 2.257 Å is about 0.083 Å shorter than the other Pt-P bond distances (2.343 Å, ave).

Overall, the data of PtP_3X derivatives show that the mean Pt-L bond distance elongated with the covalent radius of the donor atom (in parentheses) except Cl and S atoms in the sequence: 1.75 Å (H, 0.37 Å) < 2.04 Å (F, 0.72 Å) < 2.31 Å (P, 1.05 Å) < 2.345 Å (Cl, 0.99 Å) < 2.37 Å (S, 1.02 Å) < 2.53 Å (Br, 1.14 Å) < 2.64 Å (I, 1.33 Å).

There are seven derivatives with $PtBr_3N$ chromophore. In one derivative the MeCN molecule acts as a N-donor ligand with Pt-N bond distance of 1.98 the shortest in the $PtBr_3N$ group. The Pt-Br bond distance *trans* to NCMe ligand is 2.393 Å, which is shortest than the other Pt-Br bond distances (2.429 Å, ave). This difference of 0.036 Å is the largest in this group, indicating the larger *trans* influence of the MeCN group than that of other N-donor ligands, which have mean values of 2.420 and 2.425 Å, respectively. The Pt-N bond distances range from 2.00 to 2.02 Å and Pt-Br from 2.417 to 2.432 Å.

There are two derivatives $[PtBr_3(Et_2SO)]^-$ and $[PtBr_3(Ph_2SO)]^-$ which have the chromophore $PtBr_3S$ in a square planar geometry. The mean Pt-Br bond distance *trans* to the S atom is 2.435 Å, somewhat longer than the other values (mean 2.420 Å). The Pt-S bond distances are 2.220 Å (ave).

The largest donor atoms assemblies in this section are given by the chromophores PtI_3P and PtI_3Sb. This have square planar geometries also, with the Pt-I bond distances *trans* to P atom of 2.662 Å and *trans* to Sb atom of 2.637 Å. These are longer than the other Pt-I bond distances, which have mean values of 2.590 and 2.596 Å, respectively. The differences (0.072 Å *trans* to P and 0.041 Å *trans* to Sb) indicate a stronger *trans* effect for PPh_3 than $SbPh_3$. The Pt-P and Pt-Sb bond distances are 2.225 and 2.507 Å, respectively.

The overall of the data in 2.3.2, 2.3.3 and 2.3.4 subgroups includes over one hundred and seventy Pt(II) complexes of the composition PtA_3B. Platinum(II) is considered a soft Lewis acid, but it interacts with a large number of Lewis bases from both soft through to hard. The number of derivatives with a particular A-donor donor increases in the order: A = I(2) < O(4) < Br(9) < S(11) < P(30) < Cl(47) < N(68). The B type atoms are more variable. Noticeable, in the series of the PtA_3B type chromophores the distortion of the respective square planar geometry about the Pt(II) atom reflects the dentate of the coordinated ligands. The mean values of deviations of the *cis* and *trans* L-Pt-L bond angles from the ideal (90˚ and 180˚) are: 4.3˚ and 1.7˚ (L are monodentate) < 8.3˚ and 7.3˚ (one L forms 6-membered ring) < 13.3˚ and 7.4˚ (5-membered ring) < 20.0˚ and 8.6˚ (4-membered ring). In the same order the distortion increases as expected.

2.3.5. PtH_2P_2, PtO_2X_2 (X = N, Cl, S, P or As), PtN_2X_2 (X = C, Cl, S, P, Br or I)

There are four hundred and twenty derivatives of the composition PtA_2B_2. Their structural parameters were classified and analyzed in details [3] [4] and therefore in this chapter will be only briefly summarized.

There are three *trans* derivatives of the composition $Pt(H)_2(PL)_2$. Two pairs of monodentate H atoms and P

atoms (PR$_3$) form distorted a square planar geometry about the Pt(II) atom. Unfortunately, only for one deriva-tive are data for Pt-H and H-Pt-H are given. The mean Pt-H bond distance is 1.55 Å and the mean H-Pt-P(Pr^i)$_3$ bond angle is 95°. The mean Pt-P bond distances for remaining two (PMe$_3$) and (PBu$^t_3$) are 2.259 and 2.252 Å, respectively. The *trans*-P-Pt-P bond angle in both derivatives is exact linear, 180.0°.

There are one hundred and twenty six derivatives of the composition PtO$_2$X$_2$. The number of examples in-creases in the order of X atoms: Cl(2), As(2) < S(7) < P(45) < N(70). In this series the PtO$_2$N$_2$ the derivatives can be divided into eight subgroups by the way in which the ligands are coordinated in a square planar fashion with varying degrees of distortion. The sug-groups are four monodentate ligands (1 example); monodentate O-donor and bidentate N-donor ligands with a five-member chelate ring (5 examples); bidentate O-donor (five-membered ring) and monodentate N-donor ligands (5 examples); bidentate O-donor and N-donor ligands with five-membered rings (8 examples); bidentate O-donor with six-membered rings and bidentate N-donor ligands with five-membered chelate rings (20 examples), bidentate O-donor (six- membered ring) and bidentate N-donor (seven-membered rings (2 examples)); heterobidentate O,N-donors with five-membered rings (15 ex-amples); tridentate O,N ligand (five- and six-membered rings) plus a monodentate N-donor ligand (1 example). Structure of Pt(η^2-cbdc)(η^2-1,4-dach) is shown in **Figure 6** as an example [11]. The Pt(II) atom has a slighly distorted square planar geometry with two adjacent corners being occupied by two N atoms of cis-1,4-dach (diaminocyclohexane) ligand. The remaining two corners are occupied by O atoms of the cbdc (1,1-cyclobutane dicarboxylate). The dach moiety is in a twist boat configuration. The data of 1,4-dach forms seven and the cbdc forms six membered rings with N-Pt-N 98.8(4)° and O-Pt-O of 89.2(3)°. The mean value of the Pt-L bond dis-tances elongated in the order: 1.97 Å (η^2-N, unsaturated) < 2.04 Å (η^1-OL). The mean values of the Pt-O vs Pt-N bond distances in heterobi- and heterotridentate ligands are: 2.02 vs 2.00 Å and 2.00 vs 2.02 Å, respectively. The chelate rings (N-Pt-N) open in the order: 80.5° (five-membered, unsaturated) < 83.8° (five-membered satu-rated) < 92.8° (six-membered) < 98.7° (seven-membered). For O-Pt-N the values are: 81.3° (five-) < 93.0° (six-membered).

Two examples are only derivatives of the PtO$_2$Cl$_2$ type. In one two derivative monodentate O-donor ligands and two Cl atoms in *trans* position form an almost ideal square planar geometry about the Pt(II) atom. In the other the oxalate ligand is a bidentate O-donor, giving a distorted square-planar arrangement with two Cl atoms in *cis* positions. The mean Pt-O and Pt-Cl bond distances are: 2.02 Å (η^1-OL) < 2.035 Å (η^2-OL) < 2.286 Å (Cl). The O-Pt-O bite angle is 82.8(1)°.

In another seven derivatives a distorted square planar environment about the Pt(II) atom has a PtO$_2$S$_2$ chro-mophore. Four molecules of dimethylsulphoxide (dmso) form a *cis* configuration about Pt(II) so that two of the ligands are O-donors while the other two, as is more common in platinum chemistry, act as S-donor ligands. In another case a pair of NO$_3$ groups act as O-donors while a pair of dmso molecules act as S-donors. Two more derivatives have a bidentate O-donor ligands and monodentate S-donor ligands. The remaining three examples have a pair of heterobidentate, O- and S-donor ligands. The mean Pt-L bond distance elongated in the order: 2.025 Å (η^2-OL) < 2.048 Å (η^1-Odmso) < 2.214 Å (η^1-Sdmso) < 2.329 Å (SCN). The O-Pt-O and O-Pt-S bite angles are 88.3° and 94.4°, respectively. The mean Pt-O and Pt-S values (for heterobidentate) are 2.00 nd 2.24 Å, respectively.
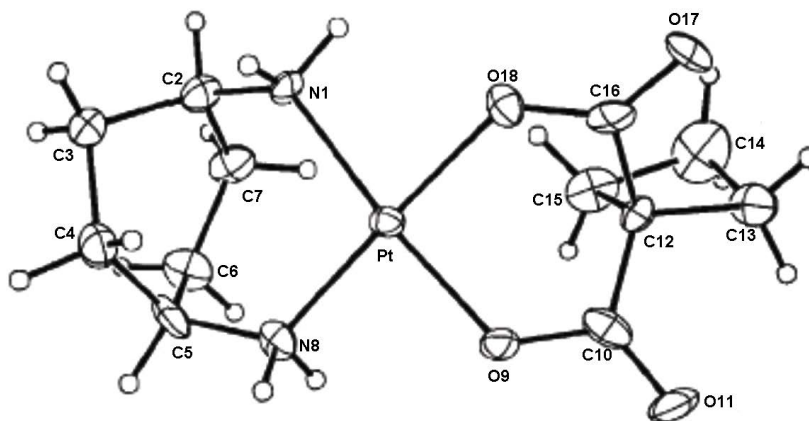
Figure 6. Structure of Pt(η^2-cbdc)(η^2-1,4-dach) [11].

There are forty five derivatives with the PtO_2P_2 square planar chromophore. A wide range of examples are found with various degrees of distortion from ideal geometry. Four monodentate ligands are used (2 examples); or one bidentate O-donor ligand, with two monodentate P-donor ligands, including four-membered chelate ring (8 examples), five-membered chelate ring (11 examples) or six-membered chelate ring (2 examples). Similarly, there are examples with a bidentate P-donor ligand plus two monodentate O-donor ligands: four-membered (1 example), or five-membered chelate ring (3 examples). Several examples have a bidentate O-donor plus a bidentate P-donor ligand: both five-membered chelate rings (3 examples); four-membered O-donor chelate ring plus a six-membered P-donor chelate ring (2 examples); seven-membered O-donor ring and five-membered P-donor ring (1 example), and eight-membered O-donor ring plus five-membered P-donor ring (1 example). Also there are mixed examples: two hetero-O,P-donor ligands with five-membered rings (seven examples), and a tridentate O,P,P'-donor ligand with five- and six-membered rings, O-Pt-P (1 example).

The most common ligands is the RCO_2 group (four-membered chelate rings) and PPh_3. The mean Pt-L bond distance elongated in the sequence: 2.06 Å (η^2-OL) < 2.11 Å (η^1-OL) < 2.21 Å (η^2-PL) < 2.24 Å (η^1-PL). The four-membered chelate rings open in the order: 65° (OCO) < 71.2° (OPO) < 74° (PCP) < 74.3° (OSeO). For the five-membered chelate rings the order is: 78.0° (ONNO) < 80.5° (OCNO) < 81.8° (OCCO) < 84.2° (OCCP) < 85.5° (ONPP) < 87.0° (PCCP). The six-membered chelate rings are 86.0° (OC_3P) and 95.8° (PC_3P).

Two derivatives are found for the PtO_2As_2 square planar chromophore. In both examples only monodentate ligand are involved with mean Pt-O and Pt-As bond distances of 2.05 and 2.33 Å, respectively.

There are three hundred PtN_2X_2 (X = C (x7), N (x190), S (x34), P (x40), Br (x10), I (x19) for which structural parameters are available. There are only seven derivatives with the PtN_2C_2 chromophore and a square-planar geometry. In only one derivative two monodentate N-donor ligands with two CN groups create a square-planar geometry about Pt(II) atom. The Pt-N and the mean Pt-C bond distances are 2.045 Å (NH_3), 2.047 Å (NH_2Me) and 1.978 Å (CN). In the remaining six derivatives a pair of bidentate N-donor ligand (mostly 2,2'-bipyridine) with two CN groups create a distorted square planar geometry about the Pt(II) atom. The mean Pt-N and Pt-C bond distances are 2.035 and 1.95 Å. The five-membered chelate rings have the mean N-Pt-N bite angles of 80.0°.

There are over one hundred and eighty derivatives with the PtN_2Cl_2 chromophore. Those derivatives can be divided into two main types, the first with only monodentate ligands with both *cis* and *trans* arrangements (112 examples) and the second with bidentate N,N'-donor ligands.

There are three types of bidentate ligands, the majority giving a five-membered chelate ring with Pt(II) atom (65 examples), some with a six-membered ring (10 examples) and a few with a seven-membered ring (4 examples). With such a high number (over 180) of derivatives especially those with a PtN_2Cl_2 chromophore, one of the main goals has been a search for a soluble less toxic analogue of *cis* platin. The establishment of a relationship between structure and antitumor activity and the bonding possibilities to nucleic acid derivatives, have also been major objectives in the synthesis and characterization of these new Pt(II) compounds.

The mean Pt-N bond distances for monodentate N-donor ligands are somewhat shorter in *cis* than in *trans* derivatives, with values 1.990 vs 1.995 Å (NL-unsaturated); 2.05 vs 2.06 Å (NL, saturated). On the other hand the mean Pt-Cl values are 2.295 vs 2.290 Å. These values are somewhat shorter than those for Pt-Cl bonds found in *cis* derivatives involving a bidentate N,N'-donor ligand. The mean Pt-Cl bond distance elongated with a closing of the bidentate chelate ring angle as a result of steric interactions: 2.295 Å (seven-) < 2.315 Å (six-) < 2.340 Å (five-membered chelate ring). The mean Pt-N bond distances and the N-Pt-N bite angles reflect both steric and electronic effects. The mean values are 2.00 Å and 80° (NL, unsaturated, 2.05 Å and 83.8° for NL-saturated), both with five-membered chelate ring. The values for six- and seven-membered chelate rings are 2.03 Å and 90.5°, and 2.01 Å and 88.5°, respectively.

There are over thirty derivatives with the PtN_2S_2 chromophore. The types of ligand situations found in these derivatives can be separated into the following: mono N-donors with mono S-donor ligands (5 examples); mono N-donor with bidentate S-donor lignds (four-membered) (2 examples); bidentate N-donor (five-) and bidentate S-donor (four-membered); (2 examples); bidentate N-donor and bidentate S-donor (both five-membered) (5 examples); heterobidentate N,S-donors (five-membered) (7 examples); tri-derivative S, N, S donor (six-membered) plus monodentate N donor (2 examples); tetra-derivative S, N, N, S-donor (five-membered rings) (1 example); tetra N, N, S, S (five- and eight-membered) (1 example), and tetra derivative N,N,S,S (six- and eight-membered) (1 example).

There are *cis* (24 examples) and *trans* (9 examples). The mean Pt-N bond distances are 2.057 Å (η^1-NL) and

2.06 Å (η^2-NL). The mean Pt-S bond distances are 2.245 Å (η^2-SL, five-) and 2.270 Å (η^2-SL, four-membered chelate ring). For heterobidentate N,S the mean Pt-N and Pt-S bonds are 1.98 and 2.29 Å). The mean values for tridentate NS_2 ligands, Pt-N vs Pt-S bonds are 1.99 vs 2.29 Å. The mean values for *cis* tetradentate N_2S_2 (Pt-N vs Pt-S) are 1.97 vs 2.25 Å. For *trans* tetradentate (N_2S_2) the values are 2.02 vs 2.29 Å. The mean values of the L-Pt-L bite angles open in the order: 77.0° (SCS) < 91.5° (NCCN) < 82.5° (NNCS) < 85.3° (NCCS) < 89.0° (SCCS) < 92.0° (NCCCN) < 102.4° (SC_2SC_2S).

There are thirty six derivatives with the PtN_2P_2 chromophore. Each Pt(II) atom has a square planar environment with varying degree of distortion. The ligand arrays can be subdivided into several groups: all monodentate ligands (14 examples); monodentate N-donors and bidentate P-donors with five-membered rings (3 examples); the same but six-membered rings (4 examples); bidentate (five-membered N-donors with bidentate (five-membered ring) P-donors (4 examples); heterobidentate N,P-donors with five-membered rings (6 examples), and the same with six-membered rings (1 example). Structure of Pt{η^2-(HN)$_2$SO$_2$(PMePh$_2$)$_2$ is shown in **Figure 7** [12] as an example. The PtN$_2$S ring is essentially planar with a maximum deviation of 0.03Å from the plane, the O$_2$ atoms lying equidistant above and below the plane. The ring is rotated about 5° with respect to the P(1)-Pt-(P(2) plane. The mean Pt-L bond distances for monodentate ligands (*cis* vs *trans*) are 2.08 vs 2.00 (L = N) and 2.27 vs 2.34 Å (L = P). While the Pt-N bond distance is shorter in *cis* than *trans*, the opposite is true for the Pt-P bonds. The mean Pt-L bond distances for homobidentate ligands are 2.068 Å (η^2-NL) and 2.255 Å (η^2-PL). For heterobidentate –N,P ligands (*cis* vs *trans*) are 2.08 vs 2.01 Å (N) and 2.240 vs 2.285 Å (P). The men N-Pt-N bite angles open in the order: 72.0° (NSN) < 76.5° (NN$_2$N) < 79.0° (NC$_2$N) < 85.0° (NC$_3$N) < 88.7° (NSNSN) < 89.5° (NCNPN). The mean P-Pt-P bite angles open in the order: 85.0° (PC$_2$P) < 94.2° (PC$_3$P); and the mean N-Pt-P bite angles in the order: 79.5° (NCNP) < 83.5° (NC$_2$P) < 89.0° (NNC$_2$P).

There are ten derivatives with PtN$_2$Br$_2$ chromophore. Seven of these have only monodentate ligands in a square planar array around Pt(II) atoms. Some derivatives have a *cis* arrangement (3 examples) and remaining four a *trans* arrangement. The mean Pt-N bond distances (*cis* vs *trans*) are equal at 2.02 Å, where as the Pt-Br bond distances are at 2.405 vs 2.430 Å, respectively. The *trans* derivatives are less distorted tha n the *cis*. The mean L-Pt-L bond distances departs from the ideal (90° and 180°) (*trans* vs *cis*) by 0.7° and 0.0° vs 4.4° and 3.0°, respectively.

Remaining three derivatives have a bidentate N-donor ligand with a five-membered chelate ring plus two Br atoms in a distorted square planar geometry about the Pt(II) atoms. The mean Pt-N bond distance for the bidentate ligands is 2.045 Å and the mean N-Pt-N bite angle is 811.4°.

There is nineteen examples with the PtN$_2$I$_2$ chromophore, which can be subdivided by ligand type as follows: monodentate N-donor ligands (8 examples); bidentate N-donor ligands with five-membered chelate rings (7 examples); bidentate N-donor with six-membered rings (3 examples), and bidentate N-donors with twelve-membered ring (1 example). There are derivatives which have *cis* (3 examples) or *trans* (5 examples) configurations for the monodentate N-donor systems, the bidentate N-donors being all *cis* as expected.
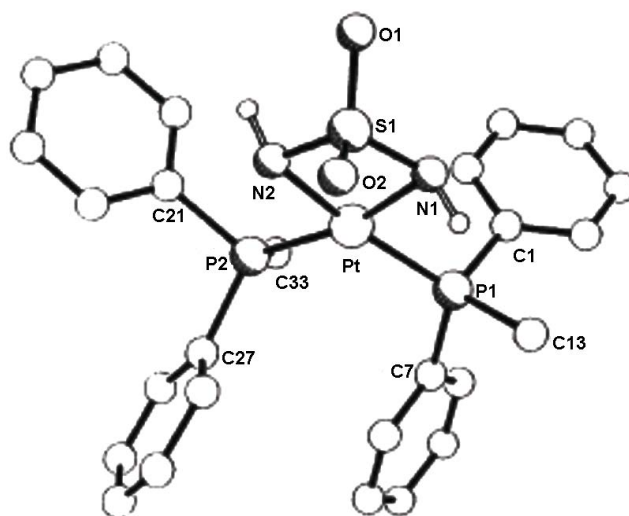

Figure 7. Structure of Pt{η^2-(HN)$_2$SO$_2$(PMePh$_2$)$_2$ [12].

The mean Pt-N bond distances are 2.04 Å (η^1-NL, *trans*) < 2.055 Å (η^2-NL, five-membered ring) < 2.07 Å (η^2-NL, six-membered ring) < 2.075 Å (η^1-NL, *cis*). The mean Pt-I bond distances are 2.600 Å (*trans*) and 2.585 Å (*cis*). The mean N-Pt-N bite angles are 77.3° (five-) and 91.4° (six-membered ring).

2.3.6. PtC$_2$X$_2$ (X = Cl, S, P or I), PtB$_2$P$_2$, PtCl$_2$X$_2$ (X = S, P, Se or As)

A *cis*-Pt(CNPh)$_2$Cl$_2$ complex is only example where two PhNC ligands with a pair of Cl atoms create a square planar environment around the Pt(II) atom, PtC$_2$Cl$_2$. The mean Pt-L bond distances are 1.89 Å (L = C) and 2.308 Å (Cl). The *cis*- and *trans* bond angles departs from the ideal values (90° and 180°) by 1.9° and 2.1° respectively.

In another *cis*-Pt(CNMe)$_2$(η^2-mnt), (mnt = 1,2-dicarbomethoxyethylene-1,2-dithiolate), two CNMe ligands with a bidentate η^2-mnt (S,S') ligand to give a distorted square plane (PtC$_2$S$_2$). The chelating ligand forms a five-membered metallocycle which is mostly responsible for the observed distortion. The mean Pt-C and Pt-S bond distances are 1.95 Å and 2.279 Å.

There are six examples with the PtC$_2$P$_2$ chromophore. In five *trans*-Pt(CN)$_2$(PL)$_2$ complexes only monodentate ligands create a square planar arrangement about the Pt(II) atom. The mean Pt-L bond distances are 1.98 Å (L = CN) and 2.320 Å (PL). The remaining example is *cis*- in which a pair of CN groups with bidentate P,P' (bis (diphenylphosphine)-methylamine) create a highly distorted square planar arrangement about the Pt(II) atom (PtC$_2$P$_2$). The mean Pt-C and Pt-P bond distances are 1.98 and 2.270 Å, respectively. The five-membered metallocycle has P-Pt-P bite angle of 70.7°.

In two *cis*-derivatives two CNR lignds plus two I atoms form a square plane about Pt(II) to give a PtC$_2$I$_2$ chromophore. The mean Pt-L bond distances are 1.96 and 2.600 Å (I), respectively.

There are eleven PtB$_2$P$_2$ derivatives with a square planar geometry about the Pt(II) atom and only with a *cis* configuration. In nine of the derivatives only monodentate ligands are involved, PPh$_3$ and two B-donor ligands (mostly B(catecholate)). In the remaining two examples, one has a bidentate five-membered ring 1,2-bis(di-phenylphosphine)ethane-(dppe) P,P' ligand and the other a seven-membered ring, 1,4-bis(diphenylphosphine)butan (dppb) ligand. The mean B-Pt-B and P-Pt-P bond angles are 76.5° and 100.7°, which are comparable with those found in derivatives in which only monodentate ligands are involved, mean values being 77.0° (range 73.3° - 80.0°) and 103.0° (range 99.3° - 107.3°), respectively. However, in the η^2-dppe derivative the P-Pt-P bite angle is reduced to 85.4° and B-Pt-B angle opens to 81.0° as a result of five-membered metallocyclic ring. The mean Pt-P bond distance elongated in the order: 2.320 Å (η^2-dppe) < 2.340 Å (η^2dppb) < 2.360° (PPh$_3$). The mean Pt-B bond distance is 2.055 Å.

There are almost forty compounds with the PtCl$_2$S$_2$ chromophore. More then half have monodentate S-donor ligands and many of these have *cis*-configuration. The remainders have a bidentate (S,S') ligand bonded to the Pt(II) atom. Bidentate chelate ligands, forms four-, five-, six- and even eleven-membered metallocycles. Each P(II) atom has a square planar environment with a different degree of distortion. The mean S-Pt-S bite angles are 76.3° (four-) < 87.0° (eleven-) < 90.0° (five-) < 100.5° (six-membered). Clearly the conformation of the largest, eleven-membered, ring is fairly rigid at an angle of 87.0°

The mean Pt-Cl bond distance of 2.300 Å in these derivatives with a *trans* configuration is shorter than that found for the *cis*-configuration (2.309 Å for monodentate ligands and 2.317 Å for bidentate ligands). The mean Pt-S bond distances show an opposite trend. Here the *trans*-configuration value of 2.302 Å for monodentate ligands is longer than that found for *cis*-configuration, 2.255 Å for monodentate and 2.540 Å for bidentate.

Overall, the sum of all Pt-L bond distances (2x Pt-Cl plus 2x Pt-S) are somewhat smaller for *cis* than *trans* derivatives, 9.126 vs 9.204 Å (monodentate) and 9.112 Å (bidentate). The S-Pt-S bond angles in monodentate *cis*-derivatives range from 87° to 94.5° (average 91.5°), which is larger than the Cl-Pt-Cl bond angles in this series (87° - 90.5° average 88.5°). The *cis*-Cl-Pt-Cl bond angles in the bidentate series are larger, at 90° to 93.5° (average 91.5°).

There ate over one hundred and twenty examples with the PtCl$_2$P$_2$ chromophore. For the PtCl$_2$P$_2$ derivatives the most common is a predominantly *cis*-arranged pair of monodentate P-donor ligand (84 examples). For the remainder, bidentate P-donor ligands are involved with four-membered chelate rings (2 examples), five-membered (11 examples), six-membered (2 examples), seven-membered (7 examples), eight-membered (2 examples), nine-membered (2 examples), twelve-membered (3 examples), fifteen-membered (2 examples), seventeen-membered (1 example) and even twenty-membered metallocyclic rings (2 examples). Each Pt(II) atom has a square planar environment with varying degrees of distortion. The *cis* derivatives (91 examples) tend to be more crowded than the *trans* derivatives (34 examples) as seen by comparing the sum of the Pt-L bond distances at 9.16 Å and 9.24

Å, respectively. The mean Pt-Cl and monodentate Pt-P bond distances are 2.347 and 2.332 Å, respectively for *cis*, and 2.308 and 2.313 Å respectively, for *trans*. For bidentate P-donor ligands the respective values are 2.350 and 2.231 Å for *cis*, 2.309 and 2.307 Å for *trans*.

There are at least two contributing factors to the size of the L-Pt-L bond angles, both ligand based. One of the steric constraints imposed on the ligand and the other is the need to a accommodate bidentates where appropriate. Comparing the bidentate P-Pt-P angles it is seen that it there is an increase in value as the size of the metallocyclic ring increases. This parallels an increase in Pt-P bond distance: 74.0° and 2.230 Å (six-) < 97.0° and 2.235 Å (seven-) < 102.2° and 2.240 Å (eight-membered metallocyclic ring). For the *cis* monodentate derivatives the P-Pt-P bond angles range from 87° to 107° (average 97°) and Cl-Pt-Cl bond angles from 82° to 92° (average 88°).

Five derivatives contain the $PtCl_2Se_2$ chromophore with a square planar geometry. In three of these, one *cis* and two *trans*, two monodentate Se-donor ligands are involved. The other two examples are *cis* with a bidentate Se donor ligand as before, the *cis* derivatives are less crowded than the *trans* derivatives as evidenced by the sum of the Pt-L distances of 9.385 and 9.445 Å, respectively. The mean Se-Pt-Se bite angle of five-membered metallocyclic ring at 82.2° is somewhat smaller than found in the bidentate P-donor case (86.7°). The mean L-Pt-L bite angle of the five-membered chelate rings open with decreasing covalent radius of the donor ligand in the sequence: 82.2° (Se, 1.16 Å) < 86.7° (P, 1.06 Å) < 90.0° (S, 1.02 Å).

One *trans*-$PtCl_2(\eta^2$-$As_2L)$ molecule has a slightly distorted square planar arrangement with two chlorine atoms and two As atoms from bidentate As donor ligand with a twelve-membered metallocyclic ring. The As-Pt-As bite angle is 174.1°. The mean Pt-As bond distance of 2.375 Å is about 0.082 Å longer than found in similar P-donor derivatives (2.293 Å), in which a twelve-membered metallocyclic ring is also found with the P-Pt-P bite angle of 177.1°. The small differences reflect the relevant covalent radii of the donor atoms (As, 1.20; P, 1.06 Å).

2.3.7. PtS_2X_2 (X = P, Br, I or As), PtP_2X_2 (X = Br, Se, Si, I or Te), $PtBr_2Se_2$ and PtI_2X_2 (X = As or Te)

There are over sixty PtS_2X_2 (X = P (x56), Br (x4), I (x6), As (x2)) derivatives. They are predominantly yellow in color. The phosphorus containing derivatives are quite varied from a ligand point of view. Five derivatives (two *cis*- and three *trans*) have pairs of unidentate ligands creating a slightly distorted square planar environment about the Pt(II) atoms. Thirty two *cis*-derivatives have a bidentate-S,S' donor ligand and two unidentate P-donor ligands (predominantly PPh_3) give a distorted square planar environment, with four-, five-, six- and seven-membered metallocyclic rings. Another three derivatives have a pair of unidentate S-donors with a bidentate P-donor ligand to create the distorted square planar environment, with four- and five-membered metallocyclic rings. Bidentate S-donor and bidentate P-donor ligands are found in seven derivatives with distorted *cis*-square planar geometry. The chelates form four-S-Pt-S with five P-Pt-P membered; five S-Pt-S with five P-Pt-P membered, and six-S-Pt-S with four P-Pt-P membered metallocyclic rings.

Hetero (S,P) ligands are found in four examples with *cis* and *trans* square planar geometry. The size of the metallocyclic rings are five- and seven-membered. The remaining four examples have tetradentate (S_2P_2) ligands forming distorted square planar environments about the Pt(II) atoms. Macrocyclic ligands form five-membered SPtS and PPtP rings; five SPtP, six SPS and PPtP rings; five SPtP and six SPtP rings; and six SPtP-membered rings.

The mean Pt-L (unidentate) bond distances, *cis* versus *trans* are 2.355 vs 2.30 Å for S and 2.285 vs 2.33 Å for P. The mean Pt-L (bidentate) bond distances for *cis* derivatives are 2.335 Å for S and 2.29 Å for 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 angle opens in the sequence (mean values): 73.5° (SCP) < 75.0° (SCS) < 81.0° (SSS) < 91.7° (SPS). In the five-membered rings the sequence is: 88.0° (SC_2S) < 90.0° (SSNS) < 90.0° (SS_2S). For the six-membered rings the sequence is: 87.0° (SC_3S) < 92.5° (SC_3P) < 96.0° (SPNPS).

There are three derivatives in which pair of unidentate S-donor ligands with two Br atoms is found (PtS_2Br_2). In another one a chelate (S,S') is found with two Br atoms. All have a distorted square planar geometry about the Pt(II) atom. The mean Pt-L bond distance elongated in the order: 2.25 Å (bi-S) < 2.26 Å (uni-S) < 2.43 Å (Br).

In another five *trans*-derivatives a pair of unidentate S-donor ligands and two iodine atoms create square planar geometry (PtS_2I_2). A *cis*-derivative has a bidentate S-donor ligand, forming a six membered metallocycle with S-Pt-S bite angle of 91.0°, plus two iodine atoms. The mean Pt-S and Pt-I bond distances in the *trans* deriv-

atives are 2.30 and 2.61 Å, while in the *cis*-derivative the values are 2.265 and 2.60 Å, respectively.

In two *trans*-derivatives a pair of hetero (S,As) ligands create a slightly distorted square planar environment for Pt(II). The mean Pt-L bond distances are 2.30 Å (S) and 2.366 Å (As), with the mean five-membered S-Pt-As metallocyclic ring angle of 87.4°.

There are over thirty Pt(II) derivatives with the chromophores PtP_2X_2 (X = Br (x6), Se (x7), Si (x5), I (x11) or Te (x2)), $PtBr_2Se_2$ (x2), $PtAs_2I_2$ (x1) and PtI_2Te_2 (x1)). Six derivatives with the PtP_2Br_2 chromophore have a slightly distorted square planar geometry about each Pt(II) atom, utilizing a pair of monodentate P-donor ligands (3 examples) and remaining three a bidentate P-donor ligand. In the former three *cis*-derivatives, the mean Pt-P (monodentate) and Pt-Br bond distances are 2.300 and 2.446 Å, respectively. In another two *cis*-derivatives the mean Pt-P (bidentate) and Pt-Br bond distances are 2.229 and 2.489 Å, respectively. The bidentate P-donor ligands create five-membered metallocyclic rings with the P-Pt-P bite angles of 86.3°. In one *trans*-derivative with the mean Pt-P (bidentate) and Pt-Br bond distances are 2.319 and 2.429 Å. The bidentate P-donor ligand forms a twelve-membered metallocycle with the P-Pt-P bite angle of 179.5°. The Pt-P as well as Pt-Br bond distances are somewhat shorter in the *cis* derivatives than in the *trans*. This suggests a greater *trans* influence of P compared to Br.

Seven species with the PtP_2Se_2 chromophore have two *trans* and five *cis* examples. Two unidentate P-donor ligands are found in one *trans* configurations, giving a slightly distorted square planar geometry about the Pt(II) atom. In another example a bidentate P-donor ligand with two unidentate PhSe ligands form a *cis*-configuration derivative with four-membered metallocycle P-Pt-P bite angle of 73.1°. In *cis*-Pt(PPh$_3$)$_2$(η^2-Se$_2$CH$_2$) derivative the bidentate Se ligand forms a four-membered metallocycle (Se-Pt-Se, 77.1°). Two other *cis*-derivatives have a pair of homobidentate P,P' and Se,Se'-donor ligands, with the mean P-Pt-P and Se-Pt-Se bite angles of 89.0° and 90.0°. Remaining two derivatives, one *cis* and another one *trans*, contain a pair heterobidentate P,Se ligands with the mean P-Pt-Se bite angle of 90.3°. The mean Pt-P bond distances in the *cis* derivatives are about 0.002 Å shorter, and the Pt-Se distances about 0.045 Å longer than in the *trans* which strongly suggests a created *trans* influence for P than Se.

Here are five *cis*-derivatives of the chromophore PtP_2Si_2. In one derivative two unidentate PPh$_3$ ligands with a bidentate Si-ligands created a distorted square planar geometry about the Pt(II) atom. In another one two unidentate Si-ligands with a bidentate P-ligand are found with the five-membered metallocycle (P-Pt-P, 84.8°). Two homobidentate ligands with five-membered ring (P-Pt-P, 84.5°) and four-membered ring (Si-Pt-Si, 65.0°) form a distorted square planar geometry about the Pt(II) atom. There is also example in which monodentate –P, monodentate –Si with heterobidentate –P,Si ligand form a distorted square planar geometry with P-Pt-Si bite angle of 70.7° (four-membered). A pair of heterobidentate ligands gives a square planar environment in the last example with two five-membered metallocycles with the mean P-Pt-Sr bite angle of 83.3°.

There are eleven derivatives with the PtP_2I_2 chromophore. In eight of them *cis* (2 examples) and *trans* (6 examples), only unidentate ligands are involved. In the remaining three examples a bidentte –P donor ligand is involved, giving five-membered metallocycles with mean P-Pt-P bite angle of 85.4°. The mean Pt-L bond distances *cis* versus *trans*, are 2.235 vs 2.329 Å for Pt-P and 2.658 vs 2.608 Å for Pt-I. The Pt-P bond lengths in the *cis* derivatives are about 0.094 Å shorter and the Pt-I bond lengths about 0.005 Å longer than in the *trans* derivatives, indicating a greater *trans* influence for P than I.

In *cis*-Pt(PPh$_3$)$_2$(η^2-1,2-Te$_2$C$_6$H$_4$) a homobidentate Te-ligand forms a five-membered metallocycle with the Te-Pt-Te bite angle of 88.4°. In another *trans* derivative a pair of heterobidentate –P,Te donor ligands form a five-membered metallocycle (mean P-Pt-Te, 88.5°).

There are *cis*- (1 example) and *trans* (1 example) with two Br ligands and two Se-atoms ($PtBr_2Se_2$). In the *cis* derivative the Se atoms are part of a bidentate Se-donor ligand, while in the *trans*-derivative two 1,4-oxyselenate molecules are involved to give somewhat distorted square planar geometrics.

There is *trans*-derivative in which pair of iodine atoms with a pair of AsPh$_3$ ligands forming a square planar geometry about the Pt(II) atom ($PtAs_2I_2$). Finally, in another *trans* derivative a pair of iodine atoms and pair of methylphenyl telluride molecules give a slightly distorted square-planar geometry about the Pt(II) atom (PtI_2Te_2).

The mean Pt-L bond distances in this 2.5.6 subgroup in the series of *cis*-derivatives elongated in the order: 2.25 Å (L = η^2-PL) < 2.295 Å (η^1-PL) < 2.37 Å (η^1-SiL) < 2.47 Å (η^1-SeL) < 2.485 Å (Br) < 2.66 Å (I). For the *trans*-derivatives the order is: 2.313 Å (η^2-PL) < 2.325 Å (η^1-PL) < 2.405 Å (η^1-AsL) < 2.425 Å (η^1-SeL) < 2.43 Å (Br) < 2.58 Å (η^1-TeL) < 2.61 Å (I). The mean Pt-P versus Pt-L (*trans*) are: 2.215 vs 2.49 Å (Br); 2.24 vs 2.66

Å (I); 2.24 vs 2.465 Å (Se) and 2.33 vs 2.36 Å (Si). The mean Pt-P bond distance in the *cis*-derivatives of 2.275 Å indicates that a *trans* influence is only significant in the case of Si.

In this series of bidentate chelating ligands the effect of both electronic and steric effects can be seen in the opening of the L-Pt-L bite angles of the respective metallocycles. For example, in the four-membered metallo-cyclic rings the L-Pt-L angles open in the order: 65° (SiCSi) < 70.7° (PCSi) < 73.7° (PCP) < 77.0° (SeCSe) < 85.3° (SePSe). In the five-membered rings the order is: 83.5° (PC$_2$Si) < 85.5° (PC$_2$P) < 88.4° (TeC$_2$Te) < 88.5° (PC$_2$Te) < 90.4° (PNPSe).

Overall of the data in Chapter 2.5 cover almost eight hundred and twenty Pt(II) derivatives of the composition PtA$_2$B$_2$. The mean Pt-L bond distance for monodentate ligands, elongated in the order: 1.65 Å (H) < 1.965 Å (CN) < 1.99 Å (NL, unsaturated) < 2.03 Å (OL) < 2.06 Å (BL) < 2.28 Å (SL) < 2.29 Å (PL) < 2.32 Å (Cl) < 2.425 Å (Br) < 2.349 Å (SeL) < 2.59 Å (I). For bidentate ligands the mean Pt-L bond distance elongated in the order: 2.02 Å (η^2-NL, unsaturated) < 2.045 Å (η^2-NL, saturated) < 2.29 Å (η^2-SL) < 2.27 Å (η^2-PL) < 2.39 Å (η^2-SeL) < 2.37 Å (η^2-AsL) < 2.58 Å (η^2-TeL) < 2.66 Å (η^2-SiL).

For heterobidentate ligands, the mean values are: O + N, 2.02 and 2.00 Å; O + S, 2.00 and 2.04 Å; N + S, 1.98 and 2.29 Å; N + P, 2.06 and 2.25 Å; S + P, 2.32 and 2.305 Å; S + As, 2.308 and 2.356 Å; P + Te, 2.306 and 2.575 Å. For heterotridentate ligands, the mean values are: 2O + N, 1.995 and 2.02 Å; O + 2P, 2.15 and 2.22 Å; N + 2S, 1.99 and 2.29 Å; and for tetradentate, 2N + 2S, 1.985 and 2.265 Å.

There are rich variations of metallocyclic rings. The mean L-Pt-L bite angle open in the orders: 65.0° (OCO) < 70.7° (PCSi) < 71.5° (OPO) < 72.4° (PCP) < 74.3° (OSeO) < 77.0° (SCS); 76.4° (NN$_2$N) < 78.0° (ON$_2$O) < 79.5° (NC$_2$N, unsaturated) < 79.7° (NCPN) < 80.6° (OCNO) < 81.5° (OC$_2$N) < 82.2° (OC$_2$O) < 82.5° (NNCS, NCSN) < 83.7° (OC$_2$P) < 83.8° (NC$_2$N, saturated) < 84.2° (NC$_2$S) < 84.8° (NC$_2$P) < 85.0° (NC$_2$S) < 86.3° (PC$_2$P) < 86.7° (OPNP) < 87.7° (SC$_2$P) < 88.5° (PC$_2$Te) < 89.0° (SC$_2$S); 88.7° (NSNSN) < 89.0° (NCPCN) < 90.3° (PC$_3$Se) < 91.5° (NC$_3$N) < 93.0° (OC$_3$O) < 94.5° (PC$_3$P); 88.5° (NC$_4$N, unsaturated) < 89.7° (OC$_4$O) < 98.8° (NC$_4$N, saturated) < 100.7° (PC$_4$P).

Some mean Pt-L bond distances are longer for the PtA$_3$B (Chapter 2.4) than in the PtA$_2$B$_2$ (Chapter 2.5) types, especially for H, Cl, η^1-SL, η^2-SL, η^1-PL and Br, probably because of the steric reasons. Some chelate rings in the PtA$_3$B type are a little more open than in the PtA$_2$B$_2$ type, for example, NC$_2$N, OC$_2$N and NC$_3$N; but the reverse is true for the other examples, such as PCP, CSCS, PC$_2$P, NC$_2$S and PC$_3$P.

2.3.8. PtA$_2$XY and PtABXY Derivatives

There are over two hundred and seventy such derivatives in which each Pt(II) atom has a square planar environment with a different degree of distortion. These derivatives were detail characterized, classified and analyzed [4] and therefore here will be shortly summarized and discussed.

There are almost forty such derivatives; five of them have a PtO$_2$XY chromophore. In *cis*-PtO$_2$NCl a heterobidentate –O,N ligand with water molecule and chlorine atom form a slightly distorted square planar geometry about the Pt(II) atom. The bidentate ligand creates a six-membered metallocycle with the O-Pt-N bite angle of 93.7°. In *trans*-PtO$_2$NCl a heterotridentate –O,O'N ligand with chlorine atom created a distorted square planar geometry about the Pt(II) atom. The heterotridentate ligand forms two five-membered metallocycles with the mean O-Pt-N bite angles of 81.1°.

In *trans*-PtO$_2$NP another heterotridentate –O,O',N ligand with PPh$_3$ molecule form a distorted such geometry. The heteroligand forms one five- and another one six-membered metallocycles with the O-Pt-N bite angle values of 82.4° and 94.8°, respectively. In another *trans*-PtO$_2$NI a heterotridentate –O,O',N ligand with iodine atom created a similar square-planar geometry like in *trans*-PtO$_2$NCl. The heterotridentate ligand forms a five-membered metallocycles with the O-Pt-N bite angles of 83.2°. In *cis*-PtO$_2$ClS a bidentate –O,O' ligand with chlorine atom and dmso-S ligand form a square-planar geometry about the Pt(II) atom. The O-Pt-O bite angle is 89.9° in the six-membered metallocycle.

There are six derivatives with PtN$_2$OCl chromophore. In two *trans*-derivatives a bidentate –O,N chelating prolinate ligand a chlorine and pyridine, or α-methylbenzylamine create a distorted square planar geometry about the Pt(II) atom with the mean O-Pt-N bite angles of 83.3° in the five-membered metallocycle. In *cis*-derivatives (4 examples) a tridentate, N,N',O-chelating ligand and a chlorine atom form such chromophore (PtN$_2$OCl). In one derivative are two types of metallocycles five-membered rings, N-Pt-N and O-Pt-N with the bite angles of 84.3° and 82.6°, respectively. In the remaining two *cis* derivatives only six-membered metallocycles are involved. The N-Pt-N and O-Pt-N bond angles are 93.6° and 94.4°, respectively.

There are five *cis* derivatives with the PtN$_2$OS chromophore. In three of them a bidentate N,N'-chelating ligand, a unidentate O- and unidentate S-donor are involved. The chelating (N,N') ligand forms five-membered metallocyclic rings with a mean N-Pt-N bite angle of 83.5˚. The remaining two derivatives have a bidentate (N,N') chelate and a bidentate (O,S) chelate. The chelating ligands form five-membered metallocyclic rings with N-Pt-N and O-Pt-S angles of 82.6˚ and 85.4˚, in one example, and in the other one a five-membered (N,N') and six-membered (O,S) rings with values of 83.7˚ and 95.3˚.

Thirteen derivatives have the PtN$_2$ClS chromophore. Two *trans* derivatives have unidentate ligands, two NH$_3$ ligands, a chlorine atom and the S atom of dmso, with the mean N-Pt-N bond angles of 173.5˚. Eight of the *cis* derivatives have a distorted square planar arrangement created by a N,N' chelate, a chlorine atom and a S-donor ligand. Structure of *cis*-[Pt(η^2-mbda)(Cl)(dmso)]Cl.EtOH is shows in **Figure 8** [13] as an example. The structure showing the eight membered ring to have rigid elongated chain conformations, forcing one of the two bridging methylene hydrogen atoms (endo) in close proximity to the metal centre. The bidentate2,2'-methylene-bis(5-(dimethylamino)aniline) (N,N') ligand, with chlorine atom and unidentate S donor atom of dimethysuphoxide created a distorted square planar geometry about the Pt(II) atom. Five-membered chelate rings are found in the four derivatives with mean N-Pt-N bond angle of 82.2˚. The one derivative has a six-membered metallocycle (88.9˚), the other one a seven-membered (86.0) and one even an eight-membered (89.5˚). A tridentate (N$_2$S) ligand and a chlorine atom forms the distorted square planar geometry in three other *cis* derivatives. In them the chelate ligand forms a five-membered (N,N') ring (80.6˚) and a six-membered (N,S) ring (85.4˚).

Four *cis*-derivatives have a distorted square plane created by a bidentate (N,N') chelate, a chlorine atom and a P-donor ligand give the PtN$_2$ClP chromophore. In two of them chelating (N,N') ligand forms a five-membered rings (N-Pt-N, 81.3˚) and in another two derivatives a six-membered rings (N-Pt-N, 88.8˚).

In *cis*-derivative a tridentate (N,N'',S) dianion ligand with PPh$_3$ to create a distorted square planar environment about Pt(II) to give the PtN$_2$SP chromophore. The chelate forms two five-membered metallocycles with N-Pt-N and N-Pt-S bond angles of 78.5 and 81.6˚, respectively. The structure of another *cis*-derivative is similar with a tridentate N,N',Se dianion ligand a PPh$_3$ molecule with five-membered metallocycles N-Pt-N and N-Pt-Se bite angles of 78.7˚ and 82.3˚. In other *cis*-derivative two CN groups with a bidentate N,S-ligand forms a distorted square plane about the Pt(II) atom (PtC$_2$NS).
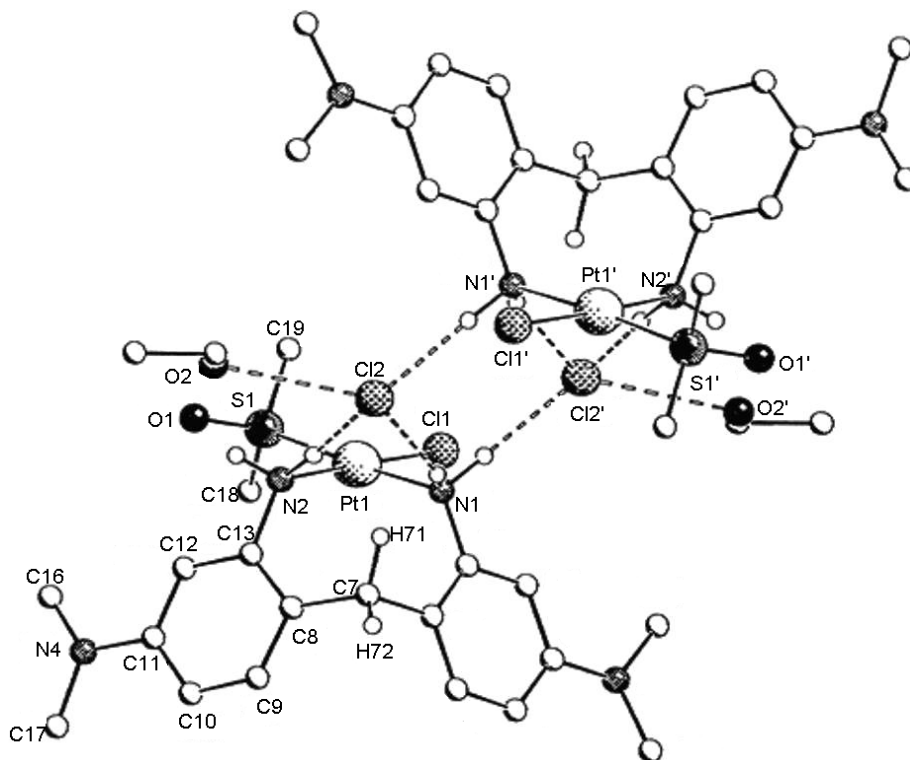
Figure 8. Structure of cis-[Pt(η^2-mbda)(Cl)(dmso)]Cl.EtOH [13].

The data of PtA_2XY (A = O, N or C) reveals homo, uni- and bidentate donor ligands. Of these only Cl, uni-SL and uni-PL types are found in both *cis-* and *trans* positions with mean Pt-L bond distances of *cis* versus *trans* of 2.31 vs 2.295 Å (Cl), 2.25 vs 2.26 Å (PL) and 2.22 vs 2.20 Å (SL). Unidentate O-donor ligands are found only in *cis* positions with the mean Pt-O bond length of 2.03 Å. Unidentate N-donor ligands and iodine are found only in *trans* positions with mean Pt-L bond lengths of 2.06 Å (N) and 2.583 Å (I), respectively. Homobidentate (O,O') and (N,N') ligands occupy only *cis* positions with mean Pt-L bond lengths of 1.97 Å (O) and 2.04 Å (N), respectively. There are two types of heterobidetate ligands with O plus N, or O plus S donor atoms. The former is found in both *cis* and *trans* positions with mean Pt-O and Pt-N bond lengths of 1.98 and 1.97 Å (*cis*); 2.01 and 2.05 Å (*trans*). There are four types of heterotridentate ligands: 2O plus N; O plus 2N, S plus 2N, and Se plus 2N sites, with the like atoms *cis*.

The effects of both electronic and steric hindrance of the coordinated atoms can be seen in the opening of the L-Pt-L bond angles of the respective metallocycles. For the five-membered rings the mean L-Pt-L intra-ligand angles are: 81.3° (N + N) < 82.2° (N + O) < 82.4° (N + Se) < 83.5° (N + S) < 85.5° (O + S). For the six-membered rings the mean L-Pt-L angles are: 90.0° (O + O) < 90.5° (N +N) < 94.3° (O + N) < 95.3° (O + S) < 99.3° (N + S).

There are over seventy Pt(II) derivative of $PtCl_2XY$ chromophores in which a Pt(II) atom are in a square planar environment with a different degrees of distortion. There are five derivatives, one *trans-* and four *cis* with $PtCl_2ON$ chromophore. The *trans* derivative is the only example in which only unidentate ligands are involved. In *cis* derivatives ($PtCl_2ON$) a bidentate O,N ligands form in three derivatives a five-membered metallocyclic rings (O-Pt-N, 83.6°) and in the fourth one a six-membered metallocycle (O-Pt-N, 90.9°). The mean Pt-Cl bond lengths are 2.303 Å (*cis*) and 2.297 Å (*trans*).

Two chlorine atoms plus water and dmso molecule form cis-$PtCl_2OS$. A slightly distorted square planar $PtCl_2OP$ chromophore uses water and a PPh_3 molecule.

There are over thirty derivatives in which two chlorine atoms and N and S donor ligands are found in a $PtCl_2NS$ square planar array. In twenty of these (ten *cis* and ten *trans*) only unidentate ligands are involved. The remaining eleven are *cis* derivatives with bidentate (N,S) chelating ligands. In four of these a chelating ligands forms a five-membered metllocyclic ring with mean N-Pt-S bite angle of 87.3°, and in seven derivatives a six-membered metallocycle is found with mean N-Pt-S bite angle of 94.8°. The mean *cis* versus *trans* Pt-L bond lengths are: 2.03 vs 2.055 Å (NL) < 2.21 vs 2.22 Å (SL) < 2.305 vs 2.295 Å (Cl). The mean Pt-N and Pt-S bond lengths for heterobidentate ligands are: 2.06 and 2.215 Å, respectively.

Twenty five species have a distorted square planar arrangement about the Pt(II) atom with the $PtCl_2NP$ chromophore. Two *cis* and twenty *trans* contain only unidentate ligands. The remaining three are *cis* derivatives with bidentate (N,P) chelating ligands. In two the chelating ligand forms five-membered metallocyclic ring with mean N-Pt-P bite angle of 87.3°, and the third forms a six-membered metallocycle with bite angle of 95.7°. The mean Pt-L bond distances *cis* vs *trans*, elongated in the order: 2.03 vs 2.13 Å (NL) < 2.225 vs 2.230 Å (PL) < 2.335 vs 2.295 Å (Cl).

In *cis* derivative two chlorine atoms with a bidentate N,Se ligand forms $PtCl_2NSe$ chromophore and the N-Pt-Se bite angle is 90.3°. In another two derivatives, two chlorine atoms, a unidentate N-donor and $AsEt_3$ ligand forms $PtCl_2NAs$ chromophore. In cis-$PtCl_2NTe$ derivative a bidentate –N,Te ligand forms six-membered metallocycle with N-Pt-Te bite angle of 89.9°. The Pt-Cl bond length of 2.351 Å opposite the Te atom is about 0.058 Å longer than the Pt-Cl distance opposite to the N atom indicating the larger *trans* influence of Te over N.

In six *cis*-derivatives a slightly distorted square planar arrangement has the $PtCl_2SP$ chromophore. In three of those, only unidentate ligands are involved. The other three involve bidentate (S,P) chelating ligands all of which form five-membered metallocyclic rings with mean S-Pt-P bite angle of 88.1°. The mean Pt-Cl bond lengths *trans* to the P atom at 2.360 Å are about 0.045 Å longer than that *trans* to S, which suggests a greater *trans* effect of P over S.

A finally, there is derivative in which two chlorine atoms and a bidentate (S,Te) chelating ligand to give the square planar $PtCl_2STe$ chromophore. The chelating ligand forms a five-membered metallocycle with S-Pt-Te bite angle of 91.5°.

The data in this section (2.6.2) reveal the mean Pt-L (unidentate) bond distances for *cis* derivatives to elongated in the order: 2.00 Å (NL) < 2.08 Å (OL) < 2.24 Å (PL) < 2.315 Å (Cl) < 2.375 Å (SL). The mean Pt-O vs Pt-L (*trans*) bond lengths are: 2.05 vs 2.01 Å (N) and 2.12 vs 2.245 Å (P), suggesting a somewhat stronger *trans* effects in the order N < O < P. The mean Pt-N vs Pt-L (*trans*) bond lengths are 2.055 vs 2.220 Å (S) < 2.13 vs 2.345 Å (As) < 2.135 vs 2.230 Å (P) indicating a greater *trans* influence of P over As. The mean Pt-Cl bond

lengths (*trans* to L) elongated in the order: 2.29 Å (L = O) < 2.30 Å (N) < 2.315 Å (S) < 2.32 Å (Se) < 2.345 Å (Te) < 2.36 Å (P). These results suggest a *trans* influence in the order of Se < Te < P. For comparison, the mean Pt-Cl bond length in the *cis* geometry is 2.315 Å.

There are a series of heterobidentate ligands O/N, N/S, N/P, N/Se, N/Te, S/P and S/Te. These chelates form metallocyclic rings in which the effects of both steric and electronic factors can be seen in the opening of the L-Pt-L bond angles. For the five-membered metallocyclic rings the mean L-Pt-L bite angles are: 83.5˚ (O/N) < 87.3˚ (N/S) and (N/P) < 87.6˚ (S/P) < 90˚ (N/Te) < 90.3˚ (N/Se) < 90.5˚ (SPNP) < 91.50˚ (S/Te). For the six-membered rings the respective values are: 91˚ (O/N) < 94.8˚ (N/S) < 95.7˚ (N/P).

There are ten species with chromophores of the PtS_2XY type a *trans* configuration about Pt(II) is created by a terdentate (S,S',N) ligand plus a chlorine atom (PtS_2NCl) and it is only example with such chromophore. The ligand forms two five-membered metallocycles with mean N-Pt-S angle of 87.2˚. A similar structure has tran-PtS_2NBr derivative, here a terdentate (S,S,N) ligand also forms two five-membered metallocycles (N-Pt-S, 85.7˚). In another two *trans* derivatives a distorted square planar environment about the Pt(II) atom is formed by a bidentate (S,N) chelate with a unidentate S-donor ligand and a PPh_3 molecule (PtS_2NP). The chelating ligand forms a four- in one example and five- in another one, membered metallocycle with N-Pt-S angles of 78.3˚ and 84.9˚, respectively. Therefore the former is more distorted than the latter.

There are three *cis* PtS_2XY derivatives in which both X and Y are halogen atoms (Cl + I, Br + I). The chelating (S,S") ligand forms a five-membered metallocycle with the Pt(II) atom in each case at a mean S-Pt-S angle of 91.0˚.

There are six *trans* derivatives with the PtP_2HO chromophore, created by two unidentate P-donor ligands, a hydrogen atom and a unidentate O-donor ligand. The *trans* P-Pt-P angle ranges from 166.1˚ to 170.7˚. Another nine derivatives have the PtP_2HM chromophore involving also only unidentate ligands. The *trans* P-Pt-P angles range from 161.4˚ to 170.9˚ with a mean value of 166.8˚ which is about 1.0˚ smaller than the O-donor analogues.

Another seven *trans* derivatives contain the PtP_2HCl chromophore with P-Pt-Pt angles ranging from 165.7˚ to 176.2˚, mean value 170.5˚. Two *trans* derivatives also with unidentate ligands have the PtP_2HS chromophore. Here the P-Pt-P angles are 161.1˚ and 162.6˚, respectively. A PtP_2HBr chromophore with unidentate ligand is found in two examples with P-Pt-P angle of 163.9˚.

There are six derivatives with the PtP_2HSi chromophore, both *trans* (2 examples) and *cis* (4 examples). The *trans* derivatives have unidentate ligands with *trans* P-Pt-P angle of 166.2˚. Two of the *cis* derivatives have only unidentate ligands and the remainders have a bidentate (P,P') ligand with an H atom and a S-donor ligand. The chelating ligand forms a seven-membered metallocycle with *cis*-P-Pt-P bond angles of 102.3˚ and 103.5˚, respectively. Two PPr_3^i molecules in *trans* positions, a H atom and a phenyl iodide ligand form a distorted square plane about Pt(II) (PtP_2HI) with a *trans* P-Pt-Pt angle of 163.7˚.

In the *trans* derivatives with the PtS_2HY chromophore there is a relationship between the *trans* P-Pt-Pt angle and the *cis*-X-Pt-Y angles, the former opening as the *trans* closes, in the order: 161.8˚ vs 98.8˚ (Y = S); 163.7˚ vs 98.7˚ (I); 163.9˚ vs 98.0˚ (Br); 166.2˚ vs 96.7˚ (Si); 166.8˚ vs 96.1˚ (N); 167.8˚ vs 95.8˚ (O); 170.5˚ vs 94.7˚ (Cl). The mean Pt-Y (*trans* to H) distance elongated in the order: 2.11 Å (Y-N) < 2.165 Å (O) < 2.355 Å (Si) < 2.385 Å (S) < 2.400 Å (Cl) < 2.572 Å (Br) < 2.696 Å (I). The mean Pt-H and Pt-P bond lengths found in the *trans* derivatives are 1.50 (±0.02) Å and 2.290 (±0.03) Å, respectively.

There are over twenty species with the PtP_2OY chromophore. Ten of them are *cis* with Y = N. In eight of these there is a hetero-bidentate (O,N) divalent anionic ligand with two PPh_3 molecules. In seven of these the chelate forms a five-membered metallocycle with mean O-Pt-N angle of 79.3˚. In the other case, there is a six-membered metallocycle with angle of 87.1˚. In the other two derivatives of *cis*-PtP_2ON type there are two chelate ligands, one homo-bidentate (P,P') and the other hetero-bidentate (O,N). Five-membered metallocyclic rings are found with P-Pt-P and O-Pt-N angles of 86.4˚ and 80.2˚. The mean Pt-P (*trans* to O) and Pt-P (*trans* to N) distance are 2.25 and 2.28 Å, respectively.

Four examples have a PtP_2OCl chromophore formed by a hetero-bidentate (O,P) ligand a Cl atom and a P donor ligand. Each chelate ligand forms a five-membered metallocycle with the mean O-Pt-P angle of 84.8˚ (OPNP) and 84.2˚ (OC_2P). The mean Pt-Cl (*trans* to O) and Pt-P (*trans* to P) bond lengths are 2.295 and 2.350 Å, respectively, suggesting a larger *trans* effect for P than O.

Five *cis*-derivatives contain the PtP_2OS chromophore created by a hetero-bidentate (O,S) ligand with two PPh_3 molecules. In four derivatives there are heterobidentate (O,S) chelating ligands, three with five-membered

metallocyclic rings with angles 82.7˚ (OCNS), and 84.2˚ (OC$_2$S). In the fourth case the 1,2-SC$_6$H$_4$COO divalent anion forms a six-membered metallocycle with O-Pt-S angle of 84.7˚. The mean Pt-P (*trans* to O) and Pt-P (*trans* to S) bond lengths are 2.247 and 2.302 Å, respectively. In another derivative a hetero-bidentate (O,P) ligand, a unidentate P-donor and a bromine atom form a *cis*-PtP$_2$OBr chromophore. The O-Pt-P angle of a five-membered metallocycle is 83.11˚. *cis*-PtP$_2$OSi chromophore in other derivative is created by a bidentate (P,P') ligand, a unidentate O-donor ligand and a unidentate Si-ligand.

The mean Pt-P (*trans* to Y) and Pt-P (*trans* to P) bond length change in the order: 2.22 and 2.09 Å (Y = O) < 2.24 and 2.35 Å (Cl) < 2.255 and 2.04 Å (N) ~ 2.25 and 2.455 Å (Br) < 2.302 and 2.31 Å (S) < 2.38 and 2.40 Å (Si). In the five-membered metallocyclic rings the O-Pt-L angle opens in the sequence (mean values): 79.5˚ (OC$_2$N) < 81.8˚ (OCNS) < 83.6˚ (ONCS) < 83.8˚ (OC$_2$P) < 84.5˚ (OPNP).

The most common Pt(II) derivatives are those with the general inner coordination sphere of PtP$_2$NY, with 30 (Y = Cl), 22 (S), 2 (Br), 5 (Se) and 1 (I). In the Cl derivatives fourteen are *cis* and four *trans* with only unidentate ligands using PPh$_3$ or PEt$_3$. In another nine *cis* derivatives there are hetero-bidentate (N,P) ligands with a PMe$_3$, PEt$_3$ or PPh$_3$ ligand and the Cl atom, forming metallocyclic rings with varying numbers of ring atoms, four-N-Pt-P angle 70.8˚ (NCP); five-80.1˚ (NCNP) and 84.2˚ (NC$_2$P); six-89.4˚ (NCN$_2$P) and 94.5˚ (NC$_2$NP). There are three PtP$_2$NCl derivatives in which hetero-tridentate (P,P',N) ligand with a Cl atom forms a such chromophore. In one of these (*trans*) a heterotridentate ligand forms two almost equal five-membered metallocycles with N-Pt-P angles of 84.2˚ and 84.9˚. In another *trans* derivative, the hetero-tridentate ligand forms a five-(N-Pt-P) and six-(N-Pt-P) metallocycles with angle of 80.7˚ and 91.3˚, respectively. In the third one (*cis*) the respective ligand created a five-(N-Pt-P) and six-(P-Pt-P) membered rings for which the data are not available.

In the derivatives (PtP$_2$NCl) with unidentate ligands, the mean values of the Pt-P (*trans* to N) and Pt-N (*trans* to P) bond lengths are 2.265 and 2.07 Å. The Pt-P (*trans* to Cl) and Pt-Cl (*trans* to P) bond lengths are 2.250 and 2.350 Å. When heterobidentate (N,P) ligands are involved the mean Pt-P and Pt-N (mutually *trans*) bond lengths are at 2.255 and 2.120 Å, and the Pt-P and Pt-Cl (mutually *trans*) are 2.205 and 2.360 Å. When hetero-tridentate (P,P',N) ligand are involved, the Pt-P and Pt-N (mutually *trans*) bond lengths are 2.298 and 2.165 Å, while the mutually *trans* Pt-P and Pt-Cl values are 2.245 and 2.393 Å, and the mutually *trans* Pt-N and Pt-Cl values are 2.03 and 2.307 Å.

The effects of both electronic and steric factors can be seen in the opening of the L-Pt-L bond angles of the respective metallocyclic rings. The five-membered metallocycles open in the sequence: 80.1˚ (NCNP) < 83.5˚ (NC$_2$P). For the six-membered rings the sequence is: 86.4˚ (NC$_2$NP) < 89.4˚ (NCN$_2$P) < 91.2˚ (NNC$_2$P) < 94.5˚ (NC$_2$OP).

There are twenty two derivatives with the PtP$_2$NS inner coordination sphere, one is *trans* and remainders are *cis*. In the *trans* and two *cis*-derivatives only unidentate ligands are involved. In eighteen *cis*-derivatives a heterobidentate (N,S) chelating ligand and two unidentate P-donor ligands create the distorted square planar arrangement around the Pt(II) atom (PtP$_2$NS). Four-membered (3 derivatives), five-membered (13 derivatives), and six-membered (2 derivatives) metallocycles are involved for which the mean N-Pt-S bond angles are: 70.0˚ (NCS), 84.8˚ (NSNS), 88.4˚ (NC$_2$NS) and 93.3˚ (NCNCS), respectively. In remaining *cis*-derivative the PtP$_2$NS chromophore is created by hetero-terdentate (P,N,S) ligand and PPh$_3$ molecule. The terdentate ligand forms two metallocyclic rings four-(N-Pt-S) and five-(N-Pt-P) membered rings with the bond angles of 69.5˚ and 83.5˚, respectively.

The data for the PtP$_2$NS derivatives with unidentate ligands shows the mean Pt-P (*trans* to N) and Pt-N (*trans* to P) lengths are 2.255 and 2.05 Å, respectively. The mutually *trans* Pt-P and Pt-S values are 2.285 and 2.365 Å. The bidentate (N,S) ligands the mutually *trans* Pt-P and Pt-N values are 2.264 and 2.05 Å, and the Pt-P and Pt-S values are 2.300 and 2.297 Å.

There are two *cis*-derivatives with PtP$_2$NBr inner coordination sphere, one with unidentate ligands and the other with a hetero-bidentate (N,P) ligand plus a PPh$_3$ molecule and bromine atom. In the latter there is a three-membered metallocyclic ring with N-Pt-N bite angle of 51.0˚.

In five *cis*-derivatives the inner coordination sphere about the Pt(II) atom contains a hetero-bidentate (N,Se) ligand with a pair of unidentate P-donor ligands (4 derivatives), or two bidentate ligands (P,P' and N,Se) (1 derivative). In three derivatives a bidentate ligand forms a five-membered with a N-Pt-Se angle of 87.1 (NSeNSe) (2 derivatives) and 85.8˚ (NSNSe) (1 derivative). A six-membered ring with angle 93.9˚ (NC$_2$NSe) is found in one derivative. Two bidentate ligands in the last example form two five-membered metallocycles with P-Pt-P

and N-Pt-Se angles of 84.8° and 83.8° (NCNSe).

One *trans*-derivative has an inner coordination sphere with a hetero-terdentate (P,N,P') ligand and an iodine atom (PtP$_2$NI). The terdentate ligand forms two metallocycles, five-membered (N-Pt-P) 83.3° and six-membered (P-Pt-P) 89.2°. In *cis*-derivative two PMe$_2$Ph molecules and a hetero-bidentate (N,Te) form a distorted square plane (PtP$_2$NTe). The bidentate ligand forms a five-membered metallocycle with N-Pt-Te angle of 84.9°.

In the PtP$_2$NY derivatives the mean Pt-P (*trans* to P) and Pt-Y (*trans* to P) bond lengths are 2.254 and 2.07 Å (Y = N); 2.242 and 2.505 Å (Br); 2.285 and 2.399 Å (Se), and 2.131 and 2.552 Å (Te). The mutually *trans* Pt-N and Pt-I bond lengths are 2.062 and 2.609 Å. The N-Pt-Y angles open in the order: 51.0° (NCP) < 83.3° (NC$_2$P) < 83.8° (NCNSe) < 84.9° (NSNTe) < 85.5° (NSNSe) < 87.2° (NC$_2$Se) < 89.2° (NC$_3$P) < 93.9° (NC$_2$NSe).

Two derivatives *trans*- and *cis*, contain the PtP$_2$BCl inner coordination sphere. While the *cis*-derivative has only unidentate ligands, the *trans* derivative has a hetero-bidentate (P,B) ligand a unidentate P-donor ligand and a chlorine atom. Bidentate ligand forms a four-membered metallocycle (Pt pB) with P-Pt-B angle of 73.6°.

Four species have an inner coordination sphere PtP$_2$ClS. One *cis*- and one *trans*-derivative contain only unidentate ligands. In another two *trans*-derivatives a hetero-bidentate (P,S) or a hetero-terdentate ligand are involved. In the former, heterobidentate ligand forms a five-membered metallocycle with P-Pt-S angle of 91.0° (PCPS), and in the latter, hetero-terdentate ligand forms two five-membered metallocycles for which data are not available.

There are five derivatives with the PtP$_2$ClSi inner coordination sphere, four *trans*- and one *cis*. In three of *trans*, only unidentate ligands are involved. The fourth *trans*-derivative has a hetero-terdentate (P,P',Si) ligand and a chlorine atom to form the distorted square plane. There are two five-membered metallocycles with P-Pt-Si angles of 89.4° and 89.9°, respectively. The *trans*-Pt(PEt$_3$)$_2$(Br)(SiMe$_3$) has an inner coordination sphere of PtP$_2$BrSi another *trans*-derivative PtP$_2$SiTe.

The data for the derivatives with PtP$_2$BCl, PtP$_2$ClS, PtP$_2$ClSi, PtP$_2$BrSi and Pt$_2$SiTe show the mean variation in *trans* influenced Pt-L bond lengths are: 2.235 Å (L = P) vs 2.382 Å (Cl); 2.286 Å (P) vs 2.320 Å (S); 2.326 Å (P) vs 2.423 Å (Si); 2.330 Å (Cl) vs 2.233 Å (S); 2.430 Å (Cl) vs 2.08 Å (B); 2.605 Å (Br) vs 2.33 Å (Si), and 2.35 Å (Si) vs 2.764 Å (Te).

In *cis* PtBr$_2$(MeCN)(dmso) an unidentate ligands created a slightly distorted square planar arrangement about the Pt(II) atom (PtBr$_2$NS). In *trans*-PtBr$_2$Cl(PPh$_3$) also unidentate ligands created a somewhat distorted square plane about the Pt(II) atom (PtBr$_2$ClP). Another *trans*-derivative has the PtSe$_2$NP chromophore made up from a hetero-bidentate (N,Se) ligand, a unidentate Se-ligand and a PPh$_3$ molecule. The N-Pt-Se angle of the four-membered metallocycle is 78.2°. Another *trans*-derivative has a hetero-terdentate (As$_2$S) ligand and a chlorine atom giving the PtAs$_2$ClS chromophore. The hetero-terdentate ligand forms two six-membered metallocycles with mean S-Pt-As angle of 93.0°.

Trans-PtI$_2$(3,5-Me$_2$py)(dmso) has only unidentate ligands giving a slightly distorted square planar environment (PtI$_2$NS). There are two derivatives with PtI$_2$NP chromophore, one *cis* and one *trans*. The *cis* derivative has two iodine atoms and a hetero-bidentate (N,P) ligand with a N-Pt-P angle of 88.3°. The *trans* derivative involves only unidentate ligands. In *cis*-derivative the PtI$_2$SP chromophore is build up by two iodine atoms and a hetero-bidentate (S,P) ligand with S-Pt-P angle of 86.9°.

The Pt-N (*trans* to Y) versus Pt-Y (*trans* to N) bond lengths have the values: 1.985 vs 2.395 Å (mean) (Y = Br), 2.05 vs 2.306 Å (Cl); 2.054 vs 2.586 Å (I); 2.08 vs 2.233 Å (S); and 2.168 vs 2.232 Å (P). The Pt-Cl (*trans* to Y) vs Pt-Y (*trans* to Cl) bond lengths have the values 2.231 vs 2.438 Å (mean) (Y = S), 2.168 vs 2.232 Å (P). The Pt-S (*trans* to Y) vs Pt-Y (*trans* to S) bond lengths the values are: 2.314 vs 2.428 Å (mean) (Y = Br) and 2.280 vs 2.598 Å (I). The mean Pt-P (*trans* to I) vs Pt-I (*trans* to I) the values are: 2.230 vs 2.657 Å. In the PtP$_2$XY derivatives with bidentate or terdentate ligands the L-Pt-L angles open in the order: 78.1° (NPSe) < 86.9° (SC$_2$P) < 88.3° (NC$_3$P) < 88.5° (mean) (NC$_2$Te) < 93.0° (SC$_3$As).

There are thirteen derivatives with the chromophore PtABXY in a distorted square planar geometry. Five species have the inner coordination sphere of PtONClS. All have a hetero-bidentate (O,N) ligand, a chlorine atom and dimethylsulphoxide molecule. Four derivatives have a five-membered metallocyclic ring and one has a six membered with the mean O-Pt-N angles of 81.5° and 90.8°, respectively.

Four derivatives have the PtONClP chromophore. Three of these contain a heterobidentate (O,N) ligand, a chlorine atom and PR$_3$ molecule. A five-membered metallocycles have the mean O-Pt-N angle of 80.3°. There is example, in which hetero-terdentate (O,N,P) with a chlorine atom forms a distorted square plane (PtONClP). This ligand forms two six-membered metallocycles with values of the O-Pt-N and N-Pt-P angles of 93.3° and

94.2˚ respectively.

In another Pt(II) derivative a hetero-terdentate (N,S,P) and a chlorine atom forms PtNClSP chromophore. The terdentate ligand forms five- (NNCS) and six (NC_3P) membered metallocycles with the N-Pt-S and N-Pt-P angles of 84.9˚ and 95.8˚.

Another two derivatives contain a hetero-bidentate (N,S) ligand, plus PMe_2Ph molecule and a bromine or iodine atom. The chelating ligand forms a five-membered metallocycle with N-Pt-S angle of 85.4˚ (PtNSPBr) and 85.5˚ (PtNSPI). Another derivative with PtNSPI chromophore has a hetero-terdentate (N,S,P) ligand and iodine atom. The chelating ligand forms two six-membered metallocycles N-Pt-S and N-Pt-P angles of 93.2˚ and 89.1˚, respectively.

In the PtABXY derivatives the mean Pt-O (*trans* to Y) vs Pt-Y (*trans* to O) bond lengths are: 1.995 vs 2.287 Å (Y = Cl); 2.017 vs 2.185 Å (S); and 2.14 vs 2.206 Å (P). The Pt-N (*trans* to Y) vs Pt-Y (*trans* to N) bond lengths are: 2.00 vs 2.313 Å (Y = Cl); 2.05 vs 2.238 Å (P); and 2.055 vs 2.520 Å (I). The Pt-S (*trans* to Y) vs Pt-Y (*trans* to S) are 2.222 vs 2.475 Å (Y = Br); 2.228 vs 2.635 Å (I); and 2.331 vs 2.247 Å (P).

2.4. Pt(II) Complexes—Five Coordinated

Detail analyzed of the structures of penta coordinated Pt(II) complexes was done [4]. Therefore, only briefly view of the structures will be outline here. There are only seven such derivatives and in all each Pt(II) atom has a trigonal bipyramidal arrangement. In three of them a tetradentate-P_4 ligand with hydride forms such arrangement. The trigonal plane is build up by three P atoms of the respective tetradentate ligand and the fourth P-atom occupied with hydride atom an axial positions. The mean Pt-P_{eq} bond distance of 2.315 Å is somewhat longer than the mean Pt-P_{ax} bond (2.210 Å). The Pt-H_{ax} bond distances are not available. The terdentate P_4 ligand forms three five-membered metallocycle with the mean P-Pt-P angles of 85.6˚. In another derivative, a tetradentate P_4 ligand with a unidentate P-donor ligand created a trigonal-bipyramidal arrangement about the Pt(II) atom (PtP$_5$). In this case also three P atoms of the chelating ligand created trigonal plane and the fourth P atom with a unidentate P-atom occupied an axial positions. The mean Pt-P_{eq} bond distances of 2.372 Å are longer than remaining two Pt-P_{ax} bond distances (2.298 Å). The tetradentate ligand created three five-membered metallocycles with the mean P-Pt-P angles of 83.4˚.

There is an example in which hetero-tetradentate (P_3N) ligand with an unidentate $PHEt_2$ ligand build up a trigonal-bipyramidal environment about the Pt(II) atom. An equatorial plane is occupied by three P atoms of the chelating ligand and an N atom of the respective ligand with $PHEt_2$ ligand occupied an axial positions. The mean P-Pt-N "bite" angles are 84.2˚. The Pt-L bond distance elongated in the order: 2.196 Å (Pt-N_{ax}) < 2.256 Å (Pt-P_{ax}) < 2.695 Å (Pt-P_{eq}). In other derivative a tetradentate (P_3N) ligand with an unidentate $AsPh_2$ ligand forms a trigonal-bipyramid about the Pt(II) atom. Three P atoms of the chelating ligand created a trigonal plane and axial positions are occupied by N atom and As atom. The Pt-L bond distance elongated in the order: 2.276 Å (Pt-N_{ax}) < 2.350 Å (Pt-P_{eq}) < 2.457 Å (Pt-As_{ax}). The mean N-Pt-P "bite" angle is 84.0˚. Finally, there is a derivative in which a tetradentate-As_4 ligand with iodine atom created a trigonal-bipyramid about the Pt(II) atom. Unfortunately, the crystal data are not available.

3. Pt(III) Complexes

Detail analyzed of crystallographic and structural data of Pt(III) complexes are in [5]. Therefore, in this part will be given only a briefly view on the structures. There are fifteen Pt(III) derivatives for which structural data are available. A pair of diphenylglyoximate-N,N' chelating anion create a distorted square-planar geometry about the Pt(III) atom with PtN_4 chromophore and it is only one such example. Each of the chelating ligand forms five-membered metallocycle with the N-Pt-N bond angle of 77.0˚. The mean Pt-N bond distance is 1.95 Å. The next twelve Pt(III) derivatives have a pair of bidentate-S,S' donor chelating ligands to make a square-planar geometry about Pt(III) atom (PtS$_4$). The Pt-S bond distances range from 2.25 to 2.30 Å (ave 2.27 Å). The five-membered metallocycles with S-Pt-S bite angles range from 88.5˚ to 91.5˚ (ave 89.5˚).

There is also example, in which a pair of chelating-Se,Se' ligands form a square-planar geometry about the Pt(III) atom (PtSe$_4$). The mean Pt-Se bond distance is 2.367 Å. Each of the chelating ligand forms a five-membered metallocycle with the Se-Pt-Se bite angle of 90.3˚.

In PtCl$_3$(η^2-en) complex the Pt(III) atom has a square-pyramidal geometry (PtCl$_3$N$_2$). The two chlorine atoms

with two N atoms of chelating ethylenediamine created square plane and remaining chlorine atom occupied an axial position. The Pt-L bond distance elongated in the order 2.04 Å (Pt-N_{eq}) < 2.313 Å (mean) (Pt-Cl_{eq}) < 2.376 Å (Pt-Cl_{ap}). The N-Pt-N bite angle is 84.6˚.

A pair of bidentate maleonitriledithiolate dianion-S,S' chelating ligands in the respective complex anion form a distorted square-planar geometry about Pt(III) atom (PtS_4). The mean Pt-S bond distance is 2.269 Å and the mean S-Pt-S bite angle is 90.3˚.

4. Pt(IV) Complexes

4.1. PtA_4 (A = N or S), PtA_6 (A = O, N, Cl, S, P, Se or I)

There are only three derivatives in which Pt(IV) atoms are in a square-planar environment with PtN_4 (2 examples) and PtS_4 (1 example). In one PtN_4 four unidentate N-donor ligands and another PtN_4 chromophore is created by terdentate ligand and a unidentate ligand. In the former the mean Pt-N bond distance is 2.036 Å. For the latter derivative only unit cell dimensions are available. In the third example a pair of bidentate-S,S' ligand forms a square-planar geometry about the Pt(IV) atom (PtS_4). The mean Pt-S bond distance is 2.241 Å. Each of the chelating ligand forms a five-membered metallocycle with the S-Pt-S bite angle of 88.0˚.

There are over sixty Pt(IV) derivatives, where each Pt(IV) atom is, six-coordinated by equivalent donor atoms. Two derivatives contain a PtO_6 inner coordination sphere. One has a centrosymmetric trans-$[Pt(\eta^2$-ox$)_2(OH)_2]^{2-}$ anion connected via hydrogen bonds from its OH groups to the aqua ligands of two protonated complex anions trans-$[Pt(\eta^2$-ox$)_2(OH)(H_2O)]^-$. While the divalent anion has six almost equal Pt-O bond lengths (four at 1.993 and two at 1.994 Å) the monovalent anion has four distances at 1.992 Å and the other two are 1.958 and 2.034 Å. This indicates a higher degree of distortion with 4:1:1 arrangement in the monovalent anion. In another Pt(IV) derivative a pentadentate oxygen donor ligand plus a hydroxide group form a distorted octahedral geometry about the Pt(IV) atom. The pentadentate ligand forms four six-membered metallocycles with a mean O-Pt-O bite angle of 95.5˚. The Pt-OH bond distance of 2.039 Å is somewhat longer than the mean Pt-O bond distance (2.006 Å).

Six derivatives have the PtN_6 chromophore. In two of them a pair of bidentate chelating ligands plus two NH_3 molecules forms the coordination sphere. In one derivative the 1-methylcytosinate ligands form a four-membered metallocycles with the N-Pt-N bite angles of 63.9˚. In another one a pair of 2,4-pentanediiminate ligands form a six-membered metallocycles with the N-Pt-N bite angles of 90.3˚. In both derivatives a pair of the chelating ligands create the plane while NH_3 molecules occupy the axial sites, to give a somewhat elongated tetragonal bipyramidal geometry about the Pt(IV) atom. Another PtN_6 derivative has a terdentate anion with two unidentate NO_2^- anions and a pyridine to give somewhat elongated tetragonal bipyramidal geometry. The NO_2^- anions occupy axial positions, and the terdentate divalent anion forms two five-membered metallocycles with mean N-Pt-N bite angle of 82.7˚. In the remaining the PN_6 species a hexadentate ligand is involved. The ligands make both five- and six-membered metallocycles with mean N-Pt-N bite angles of 84.5˚ and 92.2˚, respectively. The mean Pt-N bond distance elongated in the order 2.02 Å (bidentate) < 2.035 Å (ter-) < 2.07 Å (uni-) < 2.075 Å (tetradentate). The mean N-Pt-N bite angle opens in with increasing number of atoms as expected: 64˚ (NCN) < 92˚ (NC_2N) < 94˚ (NC_3N).

There are forty examples with the PtCl_6 chromophore. The geometry in each case is octahedral with varying degrees of distortion. The Pt-Cl (equatorial) distances range from 2.21 to 2.34 Å (ave. 2.31 Å) which is only slightly shorter than that of the Pt-Cl (axial) range from 2.29 to 2.35 Å (ave. 2.32 Å).

Six derivatives contain a PtS_6 inner coordination sphere. In three of them, six thiocyanate groups form a pseudo-octahedral environment about Pt(IV). The Pt-S bond distances range from 2.355 to 2.396 Å (ave. 2.375 Å). Another two contain $[Pt(\eta^2$-$S_5)_3]^{-2}$ anion. The S_5^{-2} ligands are coordinated to Pt(IV) in a bidentate fashion, forming three six-membered rings around it. The bonding parameters of the anions in both compounds are very similar. The mean S-Pt-S bite angle is 91.2˚ (range 90.5˚ - 92.1˚). In another derivative the inner coordination sphere consists of three S_6^{-2} ligands, which form three seven-membered metallocycles with mean S-Pt-S bite angle of 99.9˚. The mean Pt-S bond length of 2.376 Å is about 0.021 Å shorter than in the $Pt(\eta^2$-$S_5)_3]^{-2}$.

Structure of $[Pt(\eta^3$-$P_3)(\eta^3$-triphos$)]^+$ is shown in **Figure 9** [14]. The Pt(IV) atom is six-coordinated by the cyclo-P_3 group and the triphos P atoms, giving a distorted octahedral environment. The mean Pt-P bond distances are 2.435 Å (P_3) and 2.339 Å (triphos). There are two type of metallocycle, one three-(P_3) and one six-(triphos) membered with P-Pt-P bite angles of 52.6˚ and 90.0˚, respectively.
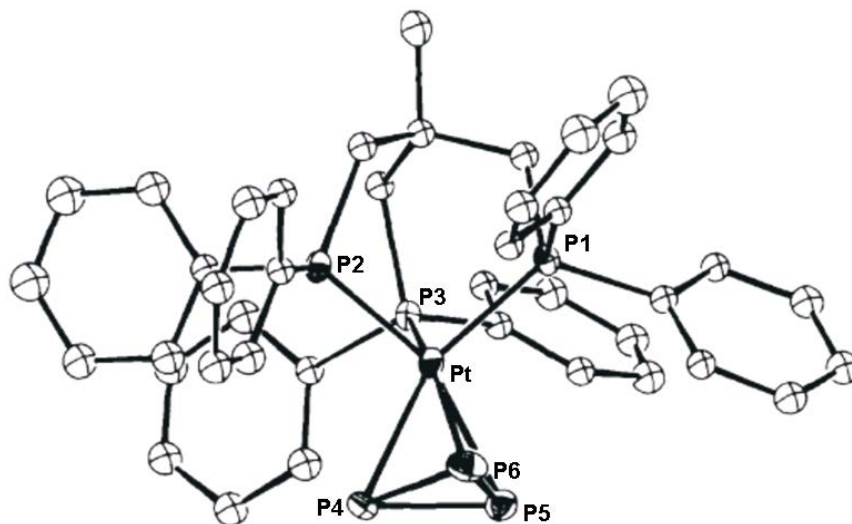
Figure 9. Structure of $[Pt(\eta^2\text{-}P_3)(\eta^2\text{-tripos})]^+$ [14].

Six bromine atoms form an octahedral geometry about the Pt(IV) in another derivative (PtBr$_6$) with the mean Pt-Br bond length of 2.456 Å. Three derivatives contain a $[Pt(\eta^2\text{-Se}_4)_3]^{-2}$ complex anion. The S_4^{-2} ligands are coordinated to Pt(IV) atom in a bidentate fashion forming three five-membered metallocycles. The mean Pt-Se bond distance is 2.486 Å and Se-Pt-Se bite angle is 99.4°. Six iodine atoms form an octahedral arrangement about Pt(IV) atom with mean Pt-I bond distance of 2.665 Å which is about 0.210 and 0.352 Å longer than those for Pt-Br and Pt-Cl.

4.2. PtA$_5$X, PtA$_4$X$_2$, PtA$_3$X$_3$, PtA$_4$XY

There are seventeen examples of PtA$_5$X type. In one derivative the five fluorine atoms and one chlorine atom form an unsymetrical tetragonal bipyramid about the Pt(IV) atom (PtF$_5$Cl). Four of the F atoms, with a mean Pt-F bond distance of 1.929 Å (1.926 - 1.932 Å), are in one plane, while the fifth F atom occupies and axial position (Pt-F 1.957 Å) and the Cl atom occupies the other (Pt-Cl 2.258 Å). As noted, the Pt-F (axial) distance is about 0.028 Å longer than the Pt-F (equatorial) which is a result of the Cl atom *trans* effect.

In two divalent anions $[Pt(NH_3)_2(\eta^2\text{-mec})(\eta\text{-mec})(OH)]^{-2}$ and $[Pt(\eta^2\text{-bpy})(\eta^3\text{-tachH}_2).(H_2O)]^{-2}$, the Pt(IV) atoms have five N atoms and one O atom as donors. In the first anion three unidentate ligands and one bidentate group donate N atoms, and together with a hydroxide group form a pseudo-octahedral environment about the Pt(IV) atom (PtN$_5$O). The chelating ligand forms a four-membered metallocyclic ring with the N-Pt-N bite angle of 65.0°. The other anion has ter- and bidentate N donor ligands, which together with a water molecule form a pseudo-octahedron (PtN$_5$O).

There are four derivatives in which inner coordination sphere about the Pt(IV) centre consists of five N atoms and one chlorine atom (PtN$_5$Cl). In two of these, three unidentate N donor ligands with one bidentate N donor and together with Cl atom create a distorted octahedral environment. In a third example two bidentate N-donor ligands are found, and in the fourth terdentate and unidentate ligands provide the N atoms. Together with the Cl atom in each case a similar geometry is found with mean Pt-N bond length of 2.09 Å and mean Pt-Cl bond length of 2.34 Å. The bi- and terdentate ligands form five-membered metallocycles with mean N-Pt-N bite angle of 81.0° (range 77.8 - 84.0).

Five chlorine atoms plus a O donor ligand form an octahedral environment around Pt(IV) in three derivatives. The mean Pt-Cl (equatorial) bond distance of 2.315 Å (range 2.30 - 2.33 Å) is about 0.035 longer than the Pt-Cl (axial) distance (2.280 Å), which is *trans* to the O atom, and the Pt-O (axial) distance range from 2.06 to 2.084 Å (ave. 2.07 Å).

There are three derivatives which have five chlorine atoms and one N atom in the inner coordination sphere (PtCl$_5$N). The mean Pt-Cl (equatorial) distance of 2.315 Å is only about 0.001 Å longer than the Pt-Cl (axial) distance, which is *trans* to a N atom, and the Pt-N bond distances have the mean value of 2.045 Å.

Two other derivatives have five chlorine atoms with an S atom giving an octahedral environment (PtCl$_5$S).

The mean Pt-Cl (axial) distance *trans* to the S atom is 2.340 Å, and is about 0.025 Å longer than the Pt-Cl (equatorial) distance. The mean Pt-S (axial) distance is 2.335 Å.

In [PtCl$_5$(PEt$_3$)]$^-$ complex anion the mean Pt-Cl (axial) bond distance (*trans* to the P atom) is 2.425 Å which is about 0.110° longer than the Pt-Cl (equatorial) mean value of 2.315 Å. The Pt-P (axial) length is 2.307 Å. In [PtBr$_5$(PPh$_3$)]$^-$ complex anion the mean Pt-Br (equatorial) distance of 2.468 Å which is about 0.065 Å shorter than the Pt-Br (axial) value *trans* to the P atom. The Pt-P (axial) bond distance is 2.364 Å.

The data in PtA$_5$X derivatives show the Pt-Cl (*trans* to Y) distance increasing in the order: 2.26 Å (Y = F) < 2.28 Å (OL) < 2.325 Å (NL) < 2.340 Å (SL) < 2.425 Å (PL). This follows the *trans* effect of the donor atom Y. The mean Pt-X (equatorial) versus Pt-X (axial) elongated in the order: 1.93 vs 1.96 Å (F, 0.72 Å) < 2.315 vs 2.333 Å (Cl, 0.99 Å) < 2.468 vs 2.533 Å (Br, 1.14 Å). The hetero-*trans* X-Pt-Y angles range from 164.9 to 179.8° (ave. 176.6°).

There are ninety examples with PtA$_4$X$_2$ type. Two derivatives contain [PtF$_4$Cl$_2$]$^{-2}$ anions, one *cis* and the other *trans* with the sum of all six Pt-X bond distances of 12.31 and 12.37 Å, respectively, indicating a *trans* influence of the Cl atom on the Pt-F distance. The mean Pt-F vs Pt-Cl (*trans*) bond distances of 1.96 and 2.26 Å differ from the latter longer (2.30 Å). This indicates that Cl has the larger *trans* effect over F.

Eleven derivatives have an inner coordination sphere of PtO$_4$N$_2$. In two of these four unidentate OH$^-$ or CH$_3$COO$^-$ groups with a bidentate-N,N' donor ligand form a distorted octahedron about the Pt(IV) atom. The chelating ligand form a five-membered metallocycle with mean N-Pt-N bite angle of 84.5°. In another example a pair of heterobidentate (O,N) ligands and two OH$^-$ units form the distorted octahedron with two five-membered metallocycles with mean O-Pt-N bite angle of 84.5°. Two more derivatives have a pairs of OH$^-$ and NH$_3$ ligands with a bidentate-O,O' ligand, or a pairs of CH$_3$COO$^-$ and NH$_3$ ligands with a bidentate-O,O' ligand.. Each chelating ligand forms a six-membered metallocycle with O-Pt-O bite angles of 94.3° and 91.3°, respectively.

The remaining six examples use a pair of OH$^-$ groups or CH$_3$COO$^-$ groups plus two bidentate ligand one O,O' and the other N,N´ donor, to give PtO$_4$N$_2$ chromophore. The chelating-O,O' ligands created a six-membered metallocycle with the mean O-Pt-O bite angle of 92.3° and chelating N,N' ligands a five-membered with the mean N-Pt-N bite angle of 84.5°. The mean Pt-O vs Pt-N (*trans*) bond lengths 2.01 and 2.02 Å, respectively. The values for both homo-*trans* situations are 2.00 and 2.05 Å, respectively.

A pair of oxalate or acetylacetonate groups form a plane about the Pt(IV) with two chlorine atoms (in axial) positions to give tetragonal bipyramidal environment (PtO$_4$Cl$_2$). The chelating ligands form five-membered metallocycles in the former with the mean O-Pt-O bite angle of 83.2° and in the latter a six-membered (O-Pt-O) 95.9°. A similar structure is found with two bidentate acetylacetonate ligands forming a PtO$_4$ plane with two CNS groups in axial positions (PtO$_4$S$_2$) with equivalent O-Pt-O bite angles of 96.3°.

Two derivatives Pt(η^2-ox)$_2$Br$_2$ and Pt(η^2-acac)$_2$Br$_2$ are isostructural with their chloro analogues. The mean Pt-Br (axial) lengths of 2.453 Å are longer than the Pt-Cl (axial) lengths by about 0.138 Å, as would be expected from the covalent radii of Br and Cl. Another two derivative Pt(η^2-ox)$_2$I$_2$ and Pt(η^2-acac)$_2$I$_2$ are isostructural with Br and Cl analogues. The mean Pt-I (axial) bond lengths is 2.661 Å. This again is longer than the Pt-Br length, as expected. The *trans*-Pt(py)$_4$F$_2$ has a Pt(IV) atom in a squashed tetragonal bipyramidal environment, with four equal in plane Pt-N(py) distances (2.008 Å) and Pt-F (axial) at 1.941 Å.

Another seven derivatives have PtN$_4$O$_2$ inner coordination sphere. Six of these have a *trans*-configuration of which five have only unidentate ligands. The other one has a terdentate (N,N',N") ligand, one unidentate N donor ligand and two OH$^-$ groups. The *cis*-derivative has four unidentate N-donor ligands plus OH$^-$ and water.

Nineteen derivatives have PtN$_4$Cl$_2$ inner coordination sphere. In four of them only unidentated ligands are involved. In another three derivatives one bidentate-N,N' ligand with unidentate ligands. The chelating ligands form a five-membered metallocycle with mean N-Pt-N bite angle of 83°. In another two derivatives a bidentate-N,N' ligand forms a six-membered metallocycles or two bidentate-N,N' ligand each forming a six-membered metallocycle. In the remaining six derivatives, tetradentate N-donor ligands are involved. The mean Pt-L bond distances in the PtN$_4$Cl$_2$ derivatives elongated in the order: 2.05 Å (tetra-NL) < 2.06 Å (uni-NL) < 2.065 Å (bi-NL) < 2.305 Å (Cl). It is noted that the mean Pt-N vs Pt-Cl (*trans*) and hetero-*trans* bond distances are the same at 2.06 and 2.31 Å, respectively. The mean N-Pt-N bite angles are 83.5° (five-) and 95.4° (six-membered).

There are four derivatives with four N atoms in plane and two bromine atoms in axial positions to give a tetragonal bipyramidal geometry about the Pt(IV) atom (PtN$_4$Br$_2$). Six derivatives have a similar geometry with iodine atoms in axial positions (PtN$_4$I$_2$). Tetragonal bipyramidal geometry is also formed by four in-plane CN$^-$ groups with two NH$_3$ ligands in axial positions (PtC$_4$N$_2$). In another derivative four Cl atoms and two O donor

ligands form a pseudo-octahedron ($PtCl_4O_2$). Sixteen derivatives have four Cl atoms and two N-donor ligands ($PtCl_4N_2$). There are eleven of those with *trans*-configurations and four with *cis*, using only unidentate ligands. The remaining five have bidentate (N,N') ligands which form five- (3 examples), six- (1 example) and seven- (1 example)-membered metallocycles with mean bite angles of 83°, 92° and 98.5°, respectively. The mean Pt-N vs Pt-Cl (*trans*) bond lengths are 2.05 and 2.31 Å, respectively, which are almost the same as for homo-*trans* situation at 2.05 and 2.315 Å, respectively.

There are one *cis*- and three *trans*-derivatives, involving only unidentate ligands forming a $PtCl_4S_2$ chromophore. The mean Pt-Cl vs Pt-S (*trans*) bond lengths at 2.315 and 2.365 Å, respectively, differ from hetero-*trans* values of 2.360 and 2.340 Å, suggesting a greater *trans* influence of S over Cl. In *cis*-$PtCl_4(PEt_3)_2$ the mean Pt-Cl vs Pt-P (*trans*) bond lengths are 2.394 and 2.335 Å, respectively. The former is about 0.073 Å longer than that for the homo-*trans* value of 2.321 Å, indicating a greater *trans* effect of P over S, as expected. In another derivative a bidentate-Se,Se' ligand with four chlorine atoms form a pseudo octahedral geometry about the Pt(IV) atom ($PtCl_4Se_2$). The chelating ligand forms a five-membered metallocycle (Se-Pt-Se, 87.6°). The mean Pt-Cl vs PtSe (*trans*) bond lengths are 2.343 and 2.437 Å, the former being shorter in the homo-*trans* situation at 2.315 Å indicating a greater *trans* influence of the Se over Cl. In $[Pt(\eta^3\text{-}As_2S_5)_2]^{2-}$ anion the Pt(IV) atom has PtS_4As_2 chromophore (**Figure 10**) [15]. There are two types of metallocycles, a pair of five-membered (SAsSAs) rings and a pair of six-membered (SAsSAsS) rings with mean S-Pt-As and S-Pt-S bite angles of 91.4° and 99.1°. There are also two types of Pt-S bond distance with mean values of 2.428 Å (*trans* to As) and 2.355 Å otherwise. This indicates a greater *trans* effect for As over S. The *trans* Pt-As bond length is 2.454 Å.

In *cis*-derivative a pair of bidentate-S,S' ligands with two iodine atoms form a tetragonal bipyramidal geometry about the Pt(IV) atom (PtS_4I_2). The chelating ligands form four-membered metallocycles (S-Pt-S, 73.5°). There are two types of Pt-S bond distance, 2.34 Å (*trans* to I) and 2.355 Å (*trans* to S). The mean Pt-I bond distance is 2.659 Å.
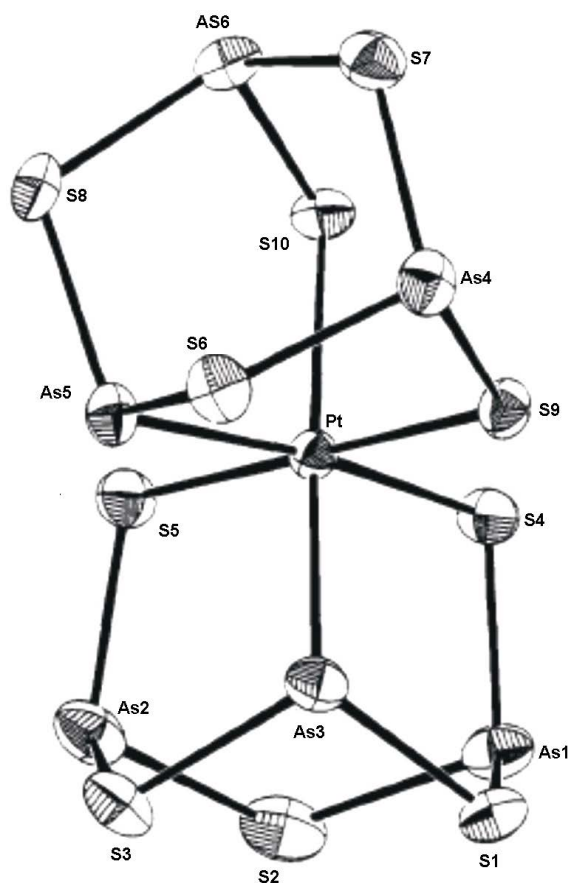

Figure 10. Structure of $[Pt(\eta^3\text{-}As_2S_5)_2]^{2-}$ [15].

Two *cis*-derivatives PtBr$_4$(η^2-en) and PtBr$_4$(η^2-1,3-pn) are isostructural, having a plane containing two bromine atoms and two N atoms from bidentate ethylenediamine in the former and 1,3-propanediamine in the latter. The mean Pt-Br and Pt-N bond lengths are 2.452 and 2.045 Å, respectively. The axial positions contain the remaining two Br atoms to give distorted octahedron about the Pt(IV) atoms (PtBr$_4$N$_2$). The mean Pt-Br length (*trans* to Br) is 2.457 Å, which is about 0.005 Å longer than the value for Br *trans* to N. Each of the chelating ligands form a metallocycle, five-membered (en) or six-membered (1,3-pn) with the N-Pt-N bite angles of 83.1˚ and 95˚, respectively.

Four Br atoms located in a plane about Pt(IV) in *trans*-derivative with two Me$_2$S ligands in axial positions (PtBr$_4$S$_2$). The mean Pt-Br length is 2.471 Å and the mean Pt-S value is 2.363 Å, giving compressed tetragonal bipyramidal geometry. In another *trans*-derivative a compressed tetragonal bipyramidal environment about Pt(IV) consisting of a tetradentate (Se$_4$) ligand in plane with two axial Cl atoms. The mean Pt-Se distance is 2.499 Å and the mean Pt-Cl value is 2.315 Å. The Se-Pt-Se bite angle is 88.4˚ (six-membered ring).

A similar structure is found in another *trans*-derivative formed by two unidentate Si ligands plus one bidentate (Si,Si) ligand in plane and Bu^{t}NC ligands in axial positions (PtSi$_4$C$_2$). The mean Pt-Si bond length is 2.47 Å and the Si-Pt-Si bite angle value is 68.6˚ (four-membered ring). The mean Pt-C value is 1.91 Å. A distorted *cis*-octahedral geometry is found in a derivative with a pair of bidentate (Si,Si') ligands and two PEt$_3$ molecules. Each bidentate ligand forms a five-membered metallocycle with mean Si-Pt-Si bite angle of 83.2˚. The mean Pt-Si bond length (*trans* to P) is 2.429 Å, about 0.049 Å longer than those *trans* to Si atom (2.380 Å) indicating a greater *trans* influence for P over Si.

There are two *trans*-derivatives have a pair of bidentate-As,As' ligands in a plane with mean Pt-As bond length 2.452 Å. The Cl or I atoms occupy axial positions to complete tetragonal bipyramidal geometry (PtAs$_4$Cl$_2$; PtAs$_4$I$_2$). In four *cis*-PtI$_4$(η^2-NL) complexes one bidentate-N,N'-ligand with four iodine atoms form a pseudo-octahedral geometry about the Pt(IV) atom (PtI$_4$N$_2$). There are two different Pt-I distances, mean value 2.667 Å (*trans* to I) and 2.609 Å (*trans* to N), indicating a larger *trans* influence for I over N, as expected. The mean Pt-N bond lengths are 2.10 Å and the mean N-Pt-N bite angle is 79.7˚ (four-membered ring).

Inpection of the data in PtA$_4$X$_2$ type derivatives showed several types of chromophore: PtF$_4$Cl$_2$; PtO$_4$X$_2$ (X = N, Cl, S, Br or I); PtN$_4$X$_2$ (X = F, O, Cl, Br or I); PtCl$_4$X$_2$ (X = O, N, S, P or S); PtS$_4$X$_2$ (X = As or I); PtBr$_4$X$_2$ (X = N or S); PtSe$_4$Cl$_2$; PtSi$_4$C$_2$; PtAs$_4$X$_2$ (X = Cl or I) and PtI$_4$N$_2$. The ligands are uni-, bi-, ter- and tetradentate. The effect of both steric and electronic factor can be seen in the opening of the L-Pt-L bond angles of the metallocycles which they form. The five-membered metallocyclic rings open in the order: 83.2˚ (OC$_2$O) ~ (NC$_2$N) ~ (SiC$_2$Si) < 84.5˚ (OC$_2$N) < 87.6˚ (SeC$_2$Se) < 99.5˚ (SAsSAs). For six-membered rings the order is: 88.5˚ (SeC$_3$Se) < 91.5˚ (SAsSAsS) < 94.3˚ (NC$_3$N) < 95˚ (OC$_3$O).

There are ten derivatives with PtA$_3$X$_3$ chromophores. Two derivatives *fac*- and *mer*-[PtF$_3$Cl$_3$]$^{2-}$, have three F and three Cl atoms creating an octahedral environment about Pt(IV) atoms. The sum of all six Pt-L bond distances in the *fac*-derivative is 12.74 Å, somewhat higher than in the *mer*-derivative at 12.71 Å. In the former the mean Pt-F and Pt-Cl distances, all hetero-*trans* are 1.977 and 2.272 Å, respectively. In the *mer*-derivative there are two types of Pt-L bond distance, hetero-*trans* (F-Pt-Cl) and homo-*trans* (e.g. F-Pt-F), with mean values of 1.972 Å (F) and 2.271 Å (Cl); in the former and 1.937 Å (F) and 2.298 Å (Cl) in the latter.

There are five derivatives with a PtN$_3$Cl$_3$ inner coordination sphere, four with *mer*- and one with *fac*-arrangement of donor atoms. In three of *mer*- only unidentate ligands are involved, and in a fourth *mer*- a bidentate ethylenediamine, unidentate N ligand and three Cl atoms are involved. The bidentate ligand forms five-membered metallocycle (N-Pt-N, 83.4˚). In the *fac*-derivative a terdentate diethylenetriamine ligand and three Cl atoms are found, and the terdentate ligand forms two five-membered metallocycles (N-Pt-N, 84.4˚). The sum of all six bond distances in the *mer*-derivative is 13.14 Å somewhat smaller than the value for the *fac*-derivative at 13.17 Å. The mean Pt-N bond distance elongated in the order: 2.045 Å (bi-) < 2.068 Å (uni-) < 2.075 Å (terdentate). The mean Pt-Cl distance is 2.322 Å. One *fac*-derivative has a terdentate diethylene-triamine ligand with three iodine atoms around a Pt(IV) atom (PtN$_3$I$_3$). The mean N-Pt-N bite angle is 82.9˚, with mean Pt-N and Pt-I bond distances of 2.10 and 2.629 Å, respectively.

Another two derivatives *mer*- and *fac*- have PtCl$_3$S$_3$ chromophore and only unidentate ligands. In the *mer*-derivatives two different Pt-Cl and Pt-S bond distances are present with mean values of 2.318 and 2.376 Å, respectively, for the homo-*trans* positions, and 2.346 and 2.329 Å for the hetero-*trans* positions. The mean Pt-Cl and Pt-S bond distances for the *fac*-derivative are 2.359 and 2.361 Å. The sum of all six bond distances is 14.16 Å for the *mer*- and 14.01 Å for the *fac*-derivative.

Two derivatives contain $[Pt(\eta^2\text{-en})_2(CN)X]^{+2}$ cations (X = Br or I) in which pair of ethylenediamine ligands with two five-membered metallocycles form a plane. The CN and X ligands are in axial positions completing an asymmetrical tetragonal bipyramid about the Pt(IV) atom (PtN_4CBr, PtN_4CI).

There are three derivatives in which the Pt(IV) atom has a $PtCl_4ON$ inner coordination sphere. In addition to four Cl atoms the distorted octahedron is completed by heterobidentate (O,N) ligand. Each derivative has three types of Pt-Cl location with bond distances 2.306 Å (*trans* to O), 2.308 Å (*trans* to N) and 2.316 Å (*trans* to Cl). The chelating ligand forms five-membered in two derivatives and six-membered in the third one with the O-Pt-N bite angles of 84.0° (ave.) and 89.9°, respectively. Another two derivatives have four Cl atoms plus N and S atom about Pt(IV) to give the $PtCl_4NS$ chromophore. In one only unidentte ligands are involved and in the other one a heterobidentate-N,S donor ligand forming a five-membered metallocycle (N-Pt-S, 86.9°). There are also three types of Pt-Cl bond distances 2.307 Å (*trans* to N), 2.356 Å (*trans* to S) and 2.312 Å (*trans* to Cl). In another derivative four bromine atoms with hetero-bidentate (O,N) ligand forms a $PtBr_4ON$ chromophore. The heterobidentate ligand forms a five-membered metallocycle (O-Pt-N, 85.6°). Three different Pt-Br bond lengths elongated in the order: 2.405 Å (*trans* to O) < 2.439 Å (*trans* to N) < 2.462 Å (*trans* to Br).

4.3. PtA_3X_2Y, $PtA_2X_2Y_2$, $PtCl_3ONS$, PtA_2X_2YZ

A derivative with inner coordination sphere of PtO_3N_2Cl contains three unidentate O-donor ligands, a bidentate (N,N') ligand and a Cl atom. The bidentate ligand forms a six-membered metallocycle with N-Pt-N angle of 91.6°. Two chelating ligands, one bidentate (N,N') and the other terdentate (N,O,O') plus a Cl atom give a pseudo-octahedron about the Pt(IV) (PtN_3O_2Cl). There are three five-membered metallocycles with N-Pt-N angle of 82.7° and two O-Pt-N angles of 83.7° (ave). A homo-terdentate diethylenetriamine ligand plus a Cl atoms and S-donor ligand create a distorted octahedron about the Pt(IV) (PtN_3Cl_2S). There are two equal five-membered metallocycle (N-Pt-N, 83.4°). In another derivative a heteroterdentate (N,N',S) ligand forms two five-membered metallocycles (N-Pt-N and N-Pt-S) and with three Br atoms create a distorted octahedron about Pt(IV) ($PtBr_3N_2S$). There are two Pt-Br locations with the bond distances of 2.456 Å (average *trans* to N) and 2.477 Å (*trans* to S), indicating a greater *trans* influence of S over N as might be anticipated.

In $[PtBr_3(\eta^3\text{-}S_4N_4)]^-$ anion the Pt(IV) atom is facially coordinated by three Br atoms together with two S atoms and one N atom from $S_4N_4^{-2}$ ligand (**Figure 11**) [16]. The five-membered ring (NSNS) is essentially planar with N-Pt-S bite angle of 89.9°, whereas the six-membered rings (SNSNS) is planar except for the coordinated S atom common to both rings, with S-Pt-S bite angle of 98.8°. The Pt-Br bond lengths are 2.476 Å (*trans* to N) and 2.495 Å (average *trans* to S).
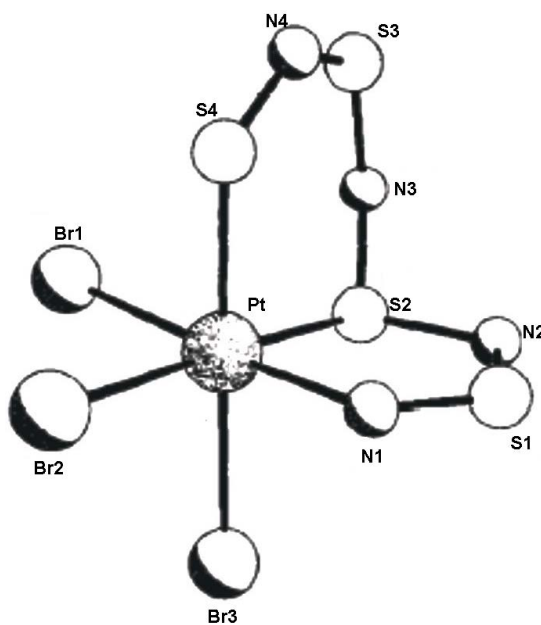

Figure 11. Structure of $[PtBr_3(\eta^3\text{-}S_4N_4)]^-$ [16].

Another derivative has three unidentate Si donor ligands, a bidentate (P,P') ligand and a hydrogen atom about the Pt(IV) atom (PtSi$_3$P$_2$H). The homobidentate ligand forms a five-membered metallocycle (P-Pt-P, 84.9˚). The Pt-Si bond distances of 2.375 Å (mean *trans* to P) and 2.406 Å (*trans* to H) strongly suggests a greater *trans* influence of H over P.

Eighteen derivatives contain a PtO$_2$N$_2$Cl$_2$ inner coordination sphere. Six of these use only unidentate ligands, with the two O-donor ligands *trans* to each other and the N-donor ligands *trans* to chlorine. Another four derivatives utilize a homobidentate (N,N') ligand with the other ligands unidentate, O *trans* to O and N *trans* to Cl. Heterobidentate (N,O) ligands plus two Cl atoms create a distorted octahedral arrangement about the Pt(IV) atom in another six derivatives. In the above derivatives there are three types of Pt-Cl bond distance with the mean values of 2.307 Å (*trans* to Cl), 2.288 Å (*trans* to O) and 2.313 Å (*trans* to N). The mean Pt-O distances are: 2.02 Å (*trans* to O) and 2.02 Å (*trans* to N). The mean L-Pt-L bite angles open in the order: 83.6˚ (OC$_2$N) < 84.7˚ (NC$_2$N) < 97.0˚ (OC$_3$O) ~ (NC$_3$N) < 98.7˚ (NC$_4$N).

A chelating ethylenediamine (N,N'), two unidentate acetate (O) units and two iodine atoms form a distorted octahedron about the Pt(IV) atom (PtO$_2$N$_2$I$_2$). There are two hetero-*trans* axes (N-L) with mean Pt-N and Pt-I bond lengths of 2.090 and 2.627 Å, respectively. Both O-atoms are *trans* oriented with a mean Pt-O bond distance of 2.029 Å. The N-Pt-N bite angle is 82.3˚. Another distorted octahedral environment is found with heterobidentate (N,S) ligands and two Cl atoms (PtN$_2$Cl$_2$S$_2$) for which only unit cell dimensions are available. A similar arrangement is found in PtCl$_2$(PEt$_3$)$_2$Br$_2$, with three homo-*trans* axis.

There are four derivatives which contain four different hetero atoms in the inner coordination sphere. One derivative contains three Cl atoms, a hetero-bidentate (O,N) ligand and S-donor ligand (PtCl$_2$ONS). There are two hetero-*trans* axes O-Cl and N-S, and one homo-*trans* axes (Cl-Cl). The Pt-Cl bond lengths are 2.314 Å (*trans* to Cl) and 2.323 Å (*trans* to O). The O-Pt-N bite angle is 91.6˚.

In PtCl$_2$(η^3-S$_4$N$_4$)(PMe$_2$Ph), the terdentate meridional S$_4$N$_4$ divalent anion coordinated via two S atoms and one N atom. The anion forms two metallocycles, five- and six-membered, with N-Pt-S and S-Pt-S bie angles of 85.0˚ and 90.1˚, respectively. There are two hetero-*trans* axes, N-S and S-P, with the Pt-S bond distances of 2.335 Å and 2.394 Å, respectively. The Cl atoms are *trans* oriented with mean Pt-Cl bond length of 2.322 Å. In [Pt(PMe$_2$Ph)$_2$Br$_2$\{η^2-N(H)SNS\}]$^+$ cation the chelating ligand forms a five-membered metallocycle with N-Pt-S bite angle of 84.7˚. The mean Pt-P bond distances are 2.327 Å (*trans* to N) and 2.346 Å (*trans* to Br). The mean Pt-Br bond distances are 2.496 Å (*trans* to S) and 2.556 Å (*trans* to P). The mean Pt-N length is 2.096 Å (*trans* to P) and the Pt-S length is 2.327 Å (*trans* to Br).

5. Isomers

The huge area of almost two thousand monomeric platinum coordination compounds has been surveyed [2]-[5] with over 200 isomeric examples, which were detailed analyzed by us [17]. The platinum oxidation state in these isomers are found in the oxidation state of zero, +2 (the more common), +3 and +4. In this section will be briefly outline view of the isomers. Isomers can be broadly classed into two major categories, structural and stereoisomers. The former can be divided into ionization, hydrate, coordination, linkage and polymerization subcategories, and the latter can be divided into geometric (*cis-trans*, *fac-mer*), optical and distortion isomerism. The analyzed of the isomers to show that stereoisomers are more common than structural isomers, and surprisingly, that distortion isomerism is more common that the better known *cis-trans* isomerism. Platinum(II) has a strongly preference for square-planar coordination geometry. The kinetic inertness of these compounds has allowed their extensive use in the characterization of geometrical isomerism and reaction mechanistic.

5.1. Distortion Isomerism

The coexistence of two or more species differing only by degree of distortion of M-L bond distances and L-M-L bond angles is typical of the general class of distortion isomers [18]. The Pt(PPh$_3$)$_3$ and Pt(η^2-dppp)$_2$ complexes are only examples of Pt(0) distortion isomers. In the former three Ph$_3$ ligands form about Pt(0) atom trigonal planar geometry about the Pt(0) atom to give triclinic and monoclinic forms. The Pt-P bond distances range from 2.26 to 2.28 Å in triclinic, and from 2.26 to 2.27 Å in monoclinic, and the P-Pt-P bond angles from 11.5˚ to 122˚, and from 117˚ to 128˚, respectively. In two monoclinic Pt(η^2-dppp)$_2$ isomers a pair of bis(diphenylphosphino)propane ligands create a square-planar geometry (PtP$_4$) about the Pt(0) atom. The mean Pt-P bond distances and the mean P-Pt-P bond angles within the six-membered rings are 2.292 Å and 97.9˚ (in one isomer),

and 2.296 Å and 97.7° (in another one).

There are over 125 Pt(II) distortion isomers which can be divided into several subgroups. The *trans*-PtCl$_2$\{P(Bu^t)$_2$Ph\}$_2$ exists in three isomeric forms, two monoclinic and one orthorhombic. There are over thirty examples exsist in two isomeric forms with homo- as well as hetero-crystal classes. In twenty derivatives both isomeric classes belong to the homo-monoclinic (10 examples), orthorhombic (6 examples) and triclinic (4 examples). The remaining examples differ from each other not only by degree of distortion but also by crystal class. In six of these one isomer is monoclinic and the other triclinic. In three examples one is monoclinic and the other orthorhombic. Of the remainder the mixture is monoclinic and tetragonal, triclinic and orthorhombic, orthorhombic and trigonal.

Over seventy five examples contain two crystallographically independent molecules within the same crystal. Another six derivatives contain three such molecules, and three derivatives have four such molecules. There is even example (NH$_4$)[Pt(η^2-oxp)$_2$]H$_2$O which contains five such molecules within the same crystal. There are several examples in Pt(II) chemistry which exist in two isomeric forms where one form contains two crystallographically independent molecules (8 examples), three such molecules (1 example) and four such molecules (2 examples).

Two Pt(III) derivatives contain three such molecules within the same crystal. In the chemistry of Pt(IV) there are twenty derivatives do this class of isomerism. Nine exist in two isomeric forms, orthorhombic (4 examples), triclinic (3 examples), and monoclinic (2 examples). Ten Pt(IV) derivatives contain two crystallographically independent molecules within the same crystal. One examples, PtCl$_4$(η^2-dach), contains three such molecules. The *trans*-Pt(η^2-bcd)$_2$I$_2$ exists in two isomeric forms, one of which contain two crystallographically independent molecules within the same crystal. The isomeric forms as well as the respective molecules differ from each other by degree of distortion. In this series of distortion isomers the predominant square-planar configuration about the platinum atom is *cis* rather than *trans*.

5.2. *Cis-Trans* Isomerism

There are almost thirty examples of Pt(II) complexes which exist in two isomeric forms, *cis* and *trans*. Some pair of isomers belongs to the monoclinic class (8 examples), orthorhombic (2 examples) or the triclinic class (3 examples). The remaining derivatives differ in crystal class. Six examples have monoclinic *cis* isomers and triclinic *trans* isomers. Two examples have monoclinic *cis* and orthorhombic *trans*, three have orthorhombic *cis* and monoclinic *trans*, and two have triclinic *cis* and monoclinic *trans*.

5.3. Mixes Isomerism (*Cis-Trans* and Distortion)

Two Pt(II) complexes belong to this unusual combination of isomerism. The PtCl$_2$(py)(dmso) complex exists as monoclinic *cis* and triclinic *trans* isomers. In addition, the *trans* isomer contains two crystallographically independent molecules. Each Pt(II) atom has a square-planar geometry (PtCl$_2$NS) with different degree of distortion. The mean Pt-Cl (mean), Pt-N and Pt-S bond distances in the *cis* isomer are 2.313, 2.027 and 2.209 Å, respectively. In the *trans* isomer the values are 2.288, 2.052 and 2.224 Å (molecule 1) and 2.300, 2.061 and 2.225 Å (molecule 2), respectively.

The Pt(MeNH$_2$)$_2$Cl$_2$ exists in three different *cis* isomeric forms and in a *trans* form. Two of the *cis* forms are monoclinic and one is orthorhombic. The *cis* isomers are differ from each other. One of the monoclinic forms contains a single molecule while the other contains three crystallographicaly independent molecules. The orthorhombic *cis* form contains two such molecules. The differences are found in the degrees of distortion.

5.4. Ligand Isomerism

There are five Pt(II) complexes which exhibit this type of isomerism Pt(η^2-4,4'-Me$_2$bpy)(NCO)$_2$; and Pt(η^2-5,5'-Me$_2$bpy)(NCO)$_2$; Pt(η^2-3,3'-Me$_2$bpy)Cl$_2$ and Pt(η^2-5,5'-Me$_2$bpy)Cl$_2$; Pt(η^2-3,3'-Bu$_2$bpy)Cl$_2$ and Pt(η^2-5,5-Bu$_2$bpy)Cl$_2$; *trans*-PtCl$_2$(2,3-Me$_2$pyr). (PMe$_2$Ph) and PtCl$_2$(2,5-Me$_2$pyr)(PMe$_2$Ph). Each Pt(II) atom has a square-planar geometry with differing degrees of distortion. The mean Pt-N (R$_2$bpy) bond distance reflects the position of the R$_2$bpy group and elongated in the order: 1.985 Å (5,5-) < 2.011 Å (3,3'-) < 2.030 Å (4,4'-). The mean Pt-N (Me$_2$pyr) bond distance also reflects the position of the Me$_2$R group, elongated in the order: 2.120 Å (2,5-) < 2.133 Å (2,4-) < 2.153 Å (2,3-).

6. Conclusions

The coordination chemistry of platinum covers a huge field, as shown by a recent survey covering the crystallographic and structural data of almost two thousand monomeric examples [2]-[5]. About 10% of these complexes exist as isomers and were detail analyzed [17]. In this review the respective data are briefly summarized. Therefore, the reviews [2]-[5] cover almost two thousand references with over six hundred pages whit almost 2000 references cited therein. In this review we prefer without detail references (see the reviews for detail data and references).

Monomeric platinum coordination complexes crystallized in wide variations of crystal classes: rhombohedral (0.1%) < cubic and trigonal each (0.2%) < hexagonal (0.3%) < tetragonal (2.5%) < orthorhombic (18%) < triclinic (24.7%) < monoclinic (54%). The platinum exists in oxidation states zero, +1, +2, +3 and +4, from which +2 by far prevails.

In the chemistry of monomeric coordination complexes of "soft" platinum is found a wide variety of uni-, bi-, ter- and tetradentate ligands forming variable inner coordination spheres about the platinum.

The Pt(0) atoms are two-(PtP_2) linear or almost linear; three-(PtP_3, PtP_2S), Y-shape; and four-(PtP_4, PtP_3S, PtO_2S_2, PtN_2P_2, PtS_2P_2, PtP_2ON, PtP_2NS and PtP_2CS; mostly tetrahedral), coordinated.

The Pt(I) atoms are four-(PtN_4 and PtP_4, square-planar), coordinated.

The Pt(II) atoms are four-PtA_4 (A = O, N, C, Cl, S, P, Br, Se or As); PtO_3X (X = N, P, Br or I); PtN_3S (X = O, C, Cl, S, Br or I); $PtCl_3X$ (X = N, S or P); PtS_3X (X = O, N, Cl, P, As or I); PtP_3X (X = H, F, Cl, S, Br or I); $PtBr_3X$ (X = N, Cl, S, P or As); PtO_2X_2 (X = N, Cl, S, P or As); PtN_2X_2 (X = C, Cl, S, P, Br or I); PtC_2X_2 (X = Cl, S, P or I); PtB_2P_2; $PtCl_2X_2$ (X = S or P); PtS_2X_2 (X = P, Br, I or As); PtP_2X_2 (X = Br, Se, Si, I or Te), $PtAs_2I_2$; PtI_2Te_2; PtO_2NX (X = Cl, P or I) PtO_2ClS; PtN_2OX (X = Cl or S); PtN_2ClX (X = S or P); PtN_2SP; PtN_2PSe; PtC_2NS; $PtCl_2OX$ (X = N, S or P); $PtCl_2NX$ (X = S, P, Se, As or Te); $PtCl_2SX$ (X = P or Te); PtS_2NX (X = Cl, P or Br); PtS_2ClX (X = P, Br or I); PtS_2CI, PtS_2BrI; PtS_2HX (X = O, N, Cl, S, B, Si or I); PtP_2OX (X = N, Cl, S, Br or Si); PtP_2NX (X = Cl, S, Br, Se, I or Te); PtP_2BCl; PtP_2ClX (X = S, Si or Te); PtP_2BrSi; PtP_2SiTe; $PtBr_2NS$; $PtBr_2NP$, $PtBr_2ClP$, $PtSe_2ClP$, $PtAs_2ClS$, PtI_2NX (X = S or P), PtI_2SP, $PtTe_2NCl$; $PtONClS$, $PtONClP$, $PtNClSP$, $PtNSPBr$, $PtNCClP$ and $PtNSPI$—distorted square planar, coordinated; and five-PtP_5, PtP_4X (X = H or N), $PtAs_4I$, $PtCl_3S_2$, PtP_3NAs—trigonal-bipyramidal coordinated.

The Pt(III) atoms are four-PtA_4 (A = N, S or Se) and $PtCl_3N$—square-planar coordinated.

The Pt(IV) atoms are four-PtA_4 (A = N or S)—square-planar coordinated; and six-PtA_6 (A = O, N, Cl, S, P, Br, Se or I); PtF_5Cl, PtN_5X (X = O or Cl); $PtCl_5X$ (X = O, N, S or P), $PtBr_5Cl$; PtF_4Cl_2; PtO_4X_2 (X = N, Cl, S, Br or I); PtN_4X_2 (X = F, O, Cl, Br or I); PtC_4N_2, $PtCl_4X_2$ (X = O, N, S, Se or As); PtS_4I_2; $PtBr_4X_2$ (X = N or S), $PtSe_4Cl_2$, $PtSe_4C_2$; $PtAs_4X_2$ (X = Cl or I); PtI_4N_2; PtF_3Cl_3; PtN_3X_3 (X = Cl or I), $PtCl_3S_3$; PtN_4CX (X = Br or I), $PtCl_4ON$, $PtCl_4NS$, $PtBr_4ON$, PtO_3N_2Cl, PtN_3O_2Cl, PtN_3Cl_2S, $PtBr_3N_2S$, $PtBr_3S_2N$, $PtSe_3P_2H$, $PtO_2N_2Cl_2$, $PtN_2Cl_2S_2$, $PtCl_2P_2Br_2$, $PtCl_3ONS$, $PtCl_2S_2NP$ and PtP_2Br_2NS—pseudo-octahedral coordinated.

One can see already from the inner coordination sphere how rich the platinum chemistry is. There is wide variety not only of unidentate ligands: H, F, OL, NL, CN, Cl, SL, PL, SeL, Br, SiL, I, TeL, from which by far prevail P and N donor ligands. The bi-, ter- and tetradentate (homo- as well as hetero-donors) are very rich which can be see from the wide variety of metallocycles and the effects of both steric and electronic factors can be seen from the values of the L-Pt-L bite angles. The mean L-Pt(0)-L bite angle opens in the orders: 40.0˚ (ON) < 42.0˚ (OO) < 43.0˚ (NS) < 45.5˚ (CS) < 52.8˚ (SP) < 53.0˚ (PP); 79.2˚ (NC_2N, unsaturated) < 82.7˚ (PC_2P) < 96.8˚ (PC_3P) < 115.3˚ (PC_6P).

The mean L-Pt(II)-L bite angle opens in the order: 65.0˚ (OCO, SCSi) < 70.0˚ (NCS) < 70.2˚ (NCP) < 70.4˚ (PNP) < 70.7˚ (PCSi) < 71.5˚ (OPO) < 72.8˚ (PCP) < 73.4˚ (SCP) < 73.6˚ (PCB) < 74.3˚ (OSeO) < 74.5˚ (SCS) < 74.7˚ (PBP) < 77.0˚ (SeCSe) < 78.0˚ (NCSe) < 78.2˚ (PPP) < 81.0˚ (SSS) < 82.2˚ (SPS) < 85.3˚ (SePSe) < 88.2˚ (TeCTe) < 88.5˚ (PCTe);

76.4˚ (NN_2N) < 78.0˚ (ON_2O) < 79.7˚ (NCPN) < 79.8˚ (NC_2N, unsaturated) < 80.0˚ (NONP) < 80.6˚ (OCNO) < 81.5˚ (OC_2N) < 81.7˚ (OC_2O, NCON) < 82.2˚ (SeC_2Se) < 82.5˚ (NCSN) < 82.6˚ (OCNS, OC_2P) < 83.3˚ (PC_2Si) < 83.5˚ (ONCS) < 83.8˚ (NCNSe) < 84.2˚ (NC_2N), saturated) < 84.8˚ (NSNTe) < 85.0˚ (PC_2P) < 85.2˚ (NSNS, OC_2S) < 85.5˚ (NSNSe) < 85.7˚ (NC_2S, PCNS, OPNP) < 86.5˚ (NCNP, SCPS, NC_2Se) < 87.0˚ (SC_2P, NSeNSe) < 87.4˚ (SC_2As) < 89.0˚ (SC_2S), SP_2S, NC_2Te) < 89.8˚ (SSNS) < 90.4˚ (PC_2Se, SPNP) < 91.0˚ (SPCP) < 91.3˚ (SS_2S) < 91.5˚ (SC_2Te);

79.6˚ (PNCNP) < 86.5˚ (NC_2NP, NC_3Se, PNPNP) < 88.3˚ (NSNSN) < 88.5˚ (NC_2NS), PCHCP) < 89.0˚ (SC_3P, NCPCN) < 89.4˚ (NC_2NP) < 89.7˚ (PC_3Si, NCNPN) < 90.0˚ (OC_3S) < 91.0˚ (NC_3N, NNC_2P) < 91.5˚

(NC$_2$NS) < 91.8˚ (OC$_3$O, NC$_3$P) < 92.3˚ (OC$_3$N, PC$_3$P) < 93.0˚ (SC$_3$As) < 93.3˚ (NCNCS) < 93.5˚ (SC$_3$S) < 94.0˚ (NC$_3$Se) < 96.3˚ (SPNPS);

87.3˚ (NC$_4$N, unsaturated) < 89.7˚ (OC$_4$O) < 92.2˚ (SC$_4$S) < 98.8˚ (NC$_4$N, saturated) < 99.0˚ (PC$_4$P); 89.5˚ (NC$_5$N) < 90.3˚ (PC$_5$P) < 102.4˚ (SC$_2$SC$_2$S); 87.0˚ (SC$_8$S) < 95.0˚ (PC$_6$P) < 99.0˚ (PC$_{15}$P, PC$_{17}$P) < 104.9˚ (PC$_9$P) < 174.2˚ (AsC$_9$As) < 175.8˚ (PC$_{11}$P) < 176.2˚ (PC$_9$P).

The mean L-P(III)-L bite angle opens in the order: 77.0˚ (NC$_2$N, unsaturated) < 84.6˚ (NC$_2$N, saturated) < 89.5˚ (SC$_2$S) < 90.2˚ (SeC$_2$Se). The mean L-Pt(IV)-L bite angle opens in the orders: 52.6˚ (PP) < 64.8˚ (NCN) < 68.6˚ (SiCSi) < 73.5˚ (SCS); 80.8˚ (NC$_2$N, unsaturated) < 83.2˚ (OC$_2$O, SiC$_2$Si) < 83.8˚ (NC$_2$N, saturated, OC$_2$N) < 84.8˚ (NC$_2$S) < 85.0˚ (PC$_2$S) < 87.7˚ (SC$_2$S, SeC$_2$Se) < 91.4˚ (SAsSAs) < 94.9˚ (SeSe$_2$Se) < 99.0˚ (NSNS); 90.0˚ (PC$_3$P) < 90.8˚ (OC$_3$N) < 91.2˚ (SC$_3$S) < 92.8˚ (NC$_3$N) < 93.7˚ (OC$_3$O) < 99.0˚ (SNSNS, SAsSAsS).

Noticeable, the oxidation state of the platinum also influence on the L-Pt-L bite angle as well. In the series of the metallocycles: SCS, NC$_2$N, OC$_2$N, NC$_2$S, SC$_2$S, OC$_3$N, SC$_3$S, PC$_3$P and PC$_6$P, the respective L-Pt-L bite angle closses with an increasing oxidation state of platinum, however in the series: PP, OC$_2$O, PC$_2$P, NSNS, SeC$_2$Se, OCl$_3$O and NC$_3$N, opposite is true.

As can be seen chelating homo- as well as hetero-donor ligands form metallocyclic rings with varying atoms and number of atoms in the ring. The homo-chelating ligands have the mean L-Pt(0)-L bite angles open in the sequence: 47.5˚ (three-) < 80.9˚ (five-) < 96.8˚ (six-) < 115.3˚ (nine-membered rings). However the mean L-Pt(0)-L' bite angle is 45.3˚ (three-membered rings). The homo-chelating ligands have the mean L-Pt(II)-L bite angles open in the sequence: 76.5˚ (four-) < 83.6˚ (five-) < 89.7˚ (six-) < 93.4˚ (seven-) < 94.0˚ (eight-) < 95.0˚ (nine-membered rings). In the hetero-chelating ligands the sequence is: 73.7˚ (four-) < 86.0˚ (five-) < 90.8˚ (six-membered rings). The mean L-Pt(IV)-L bite angles open in the order: 52.6˚ (three-) < 69.0˚ (four-) < 85.8˚ (five-) < 94.3˚ (six-) < 98.0˚ (seven-membered rings) for homo-ligands; and 89.2˚ (five-) < 90.8˚ (six-membered rings) for hetero-ligands.

There are at least two contributing factors to the size of the L-Pt-L chelate bond angles, bond ligand based. One is the steric constraint imposed on the ligand and the other is the need to accommodate the imposed ring size. Comparing the bidentate P-Pt(II)-P angles, there is an increase in the value of the angle as the number of ring atoms increasis. This parallels an increase in the Pt(II)-P bond distance: 74.0˚ and 2.218 Å (four-) < 86.7˚ and 2.220 Å (five-) < 95.6˚ and 2.230 Å (six-) < 97.0˚ and 2.235 Å (seven-) < 102.2˚ and 2.240 Å (eight-membered ring).

Although platinum preferentially bond to "soft" donor ligands such as H, C, S, P, As, I, it can also be found bonded to "borderline" (e.g. bromide) and "hard" donor atoms (F, O, N, Cl). In general the "soft" atoms have a larger *trans* effect than the borderline or hard atoms [2]-[5]. The Pt-L values for soft and bordeline ligands are observed to increase with covalent radius of the donor atom. A similar trend is observed for the hard ligands, but there is no overlap.

In the series of two thousand of monomeric platinum coordination complexes for which structural parameters are available were analyzed [2]-[5] and in this part only shortly outline. About 10% of these complexes exist as isomers and were detail analyzed [17] and shortly outline in this part of paper. There are at least four types of isomerism: distortion (65%), *cis-trans* (30%), mixed isomers and ligand isomers. Distortion isomers, differing only by degree of distortion in Pt-L and L-Pt-L angles, are the most numerous. They are also spread over a wide range of oxidation state of platinum (zero, +2, +3 and +4), than *cis-trans* isomers (+2 and +4 only), or mixed isomers (+2 only) and ligand isomerism (+2 only).

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