Structural Aspects of Monomeric Platinum Coordination Complexes

Milan Melník, Peter Mikuš

Department of Pharmaceutical Analysis and Nuclear Pharmacy, Faculty of Pharmacy, Comenius University in Bratislava, Bratislava, Slovak Republic
Email: qmelnik@stuba.sk

Received 6 April 2014; revised 11 April 2014; accepted 3 May 2014

Copyright © 2014 by authors and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY).
http://creativecommons.org/licenses/by/4.0/

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 PtCl₂(NH₃)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 briefly 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 stereochemistries about a Pt(0) atom, linear, almost linear, trigonal planar, T-shaped and tetrahedral with varying degrees of distortion. Structure of Pt{Bu₃Ph₂} [7] as an example. Two unidentate bulky triphenylphosphine directly coordinated to the central Pt(0) atom with the mean Pt-P bond distance of 2.23 Å and Pt-P-P-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 as well as trigonal planar (Y shape) geometries are building up only by monodentate P-donor ligands. The mean Pt-P-P-P bond distances and P-Pt-P-P bond angles are: 2.249 Å and 180.0° (linear); 2.240 Å and 168.7° (almost linear); 2.270 Å and 120° (±5°). T-shape geometry about Pt(0) atom is created by two monodentate P-donor ligands and SO₂ ligand (PtP₃S). 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 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 (PPh₃). 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 Pt-Pt-P bite angles of the ligands. The mean Pt-P bond distance in the series of bidentate Pt-donor ligands elongated with the decrease in number of atoms in the respective metallocycle: 2.248 Å (nine-PC₃P) < 2.296 Å (six-PC₃P) < 2.360 Å (three-PP). The P-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 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 stereochemistries about a Pt(0) atom, linear, almost linear, trigonal planar, T-shaped and tetrahedral with varying degrees of distortion. Structure of Pt{Bu₃Ph₂} [7] as an example. Two unidentate bulky triphenylphosphine directly coordinated to the central Pt(0) atom with the mean Pt-P bond distance of 2.23 Å and Pt-P-P-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 as well as trigonal planar (Y shape) geometries are building up only by monodentate P-donor ligands. The mean Pt-P-P-P bond distances and P-Pt-P-P bond angles are: 2.249 Å and 180.0° (linear); 2.240 Å and 168.7° (almost linear); 2.270 Å and 120° (±5°). T-shape geometry about Pt(0) atom is created by two monodentate P-donor ligands and SO₂ ligand (PtP₃S). 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 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 (PPh₃). 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 Pt-donor ligands elongated with the decrease in number of atoms in the respective metallocycle: 2.248 Å (nine-PC₃P) < 2.296 Å (six-PC₃P) < 2.360 Å (three-PP). The P-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 three derivatives in which each Pt(0) atom has heterogeneous inner sphere (PtP₂S). In two of them three unidentate PPh₃ ligands with SO₂ 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 PtP₂S chromophore is build up by two unidentate PPh₃ ligands and one bidentate ligand with P and S donor sites. Here the Pt-PPh₃ 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 O₂ molecule created PtO₂P₂ chromophore. Structure of Pt(O²)=O(PPh₃)₂2CHCl₃ 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
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$_2$Ph and pyrazole form PtN$_2$P$_2$ 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$_2$P$_2$). 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 PPh3 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 (PtP2ON) < 8.945 Å (PtP2NS) < 8.98 Å (PtP2CS). 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 (η2-O2) < 2.03 Å (NL) < 2.275 Å (PL) < 2.29 Å (η2-PL) < 2.41 Å (SO2).

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(η2-bpy)]+ created a distorted square-planar configuration (PtN4). 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(PPh3)2(η2-1,2,3,4-tetraphenyl-1,2-dihydro-1,2-diphosphate) is created by two monodentate PPh3 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: PtA4, PtA3B, PtA2BCD and even PtABCD. The PtA4 derivatives include those with homogeneous or quasi-homogeneous coordination spheres (i.e. different ligands) but with the same donor atoms.

2.3.1. PtA4 (A = O, N, C, Cl, S, P, Br, Se or As)
There are only four Pt(II) derivatives with PtO4 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 of bidentate O-donor ligands (acetylacetonate, 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 PtN4 derivatives, which can be divided into the six groups: Pt(η1-NL)4; Pt(η1-NL)(η2-NL); Pt(η2-NL)2; Pt(η1-NL)2(η2-NL’); Pt(η2-NL) (η1-NL) and Pt(η2-NL). The Pt(η1-NL)4 derivatives (over one hundred) can be subdivided into three 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: (b1) three identical ligands plus one other PtN3N’; (b2) two pairs of identical ligands PtN2N’N”; (b3) one identical pair and two different ligands PtN2N’N”; (b4) 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 (NH3). The mean cis-N-Pt-N bond angle depart from the 90.0° by 1.4° (N-aryl) < 2.0° (N-alkyl) < 2.3° (NH3), which indicated that the distortion of the respective square-planar geometry increases in the given order.

There are only three derivatives belonging to the (b1) subgroup (PtN3N’). 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 (b2), Pt(η1-NL)(η1-NL’)2. Practically all examples are of the composition [Pt(NH3)4(η1-NL)(η1-NL’)2]2+ with both cis- (22 examples) and trans- (10 examples) derivatives. The mean Pt-NH3 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-H2N-Pt-NH3 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-H2N-Pt-NH3 bond derivatives in the series of trans-
Several derivatives have the \((b_3)\) type composition \([\text{Pt}(\text{NH}_3)_2(\eta^1-\text{NL})\text{NL'])_2\]^2+ and again exhibit \(cис\)- (9 examples) as well as \(транс\)- (6 examples). The mean \(Pt-N\) bond distances for both \(cис\) and \(транс\) derivatives are the same at 2.05 Å in this case. Once again, for the compositions \([\text{Pt}(\text{MeNH}_2)_2(\eta^1-\text{NL})\text{NL'})_2\]^2+ only \(транс\)-derivatives (seven examples) are found, with a mean \(Pt-N(\text{H}_2\text{Me})\) bond distance of 2.06 Å. The mean \(транс\)-N-Pt-N bond angle is 176.7° and \(cис\)-N-Pt-N bond angle depart from 90.0° by 3.3° (mean).

Finally there is only one example which belongs to the \((b_4)\) subgroup and that is \([\text{Pt}(\text{NH}_3)(1\text{-methylcytosine})(9\text{-methyladenine})(9\text{-ethylguaninate})]_2^2+\), \([\text{Pt}(\text{NH}_3)(1\text{-MeC})(9\text{-MeA})(9\text{-EtG})]_2^2+\). Most of the compounds represent a hypothetical interaction of \(cис\)-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 \(\text{NH}_3\) 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\(_2\)Me) < 2.04 Å (NH\(_3\)) for the \(cис\)-derivatives. For the \(транс\)-derivatives the order is: 2.01 Å (9-EtG) < 2.015 Å (NL) < 2.02 Å (9-MeA) < 2.04 Å (1-MeC) < 2.05 Å (NH\(_3\)) < 2.06 Å (NH\(_2\)Me).

There are over forty derivatives of \(Pt(\eta^2\text{-N,L})(\eta^1\text{-N,L})_2\) type: for which structural parameters are available [2]. Structure of \(Pt(\eta^2\text{-4,4\text{-Ph}}_2\text{bpy})(3,5\text{-Me}_2\text{py})_2(\text{PF}_6)_2\) is shown in Figure 3 as an example [8]. The crystallographic asymmetric unit contains the dicatonic 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 \(Pt-N\)-bond angle found in the \(cис\)-\(Pt(\eta^2\text{-bpy})(\eta^1\text{-N,L})_2\) derivatives of 2.005 Å and 80.5° are smaller than those found in the \(cис\)-\(Pt(\eta^2\text{-en})(\eta^1\text{-N,L})_2\) 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 \(Pt(\eta^3\text{-N,L})_2\) or different bidentate ligands \(Pt(\eta^2\text{-N,L})(\eta^2\text{-N,L’})\), occurs about the Pt(II) atom with varying degrees of distortion. In \(Pt(\eta^3\text{-N,L})_2\) derivatives are examples in which a pair of bidentate –N,N’donor atoms giving two four-membered metalloccyclic 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.

\(\text{Figure 3. Structure of } Pt(\eta^2\text{-4,4\text{-Ph}}_2\text{bpy})(3,5\text{-Me}_2\text{py})_2(\text{PF}_6)_2 \) [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 metalloccyclic 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(η²-NL)₂ and Pt(η²-NL)(η²-NL) indicate the most common situation with the N,N'-donor ligands and Pt(II) in the five-membered metalloccyclic 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 metalloccyclic rings are 2.045 Å and 89.7˚.

In the series of Pt(η²-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 metalloccyclic ring N-Pt-N angle is 80.8˚ (range 80.0˚ - 81.8˚). In those derivatives with diethylene triamine as the tridentate 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 metalloccyclic N-Pt-N ring angle is also slightly larger at 84.7˚ (range 84.3˚ - 85.7˚). However it does mean that these derivatives are somewhat less distorted from the ideal square-planar geometry than the terpyridine derivatives.

There are over twenty Pt(η²-NL) derivatives in which a single tetradeinate ligand provides a square-planar environment around a Pt(II) atom. These derivatives are divided into two groups, one with three metalloccyclic rings (8 examples) and the other with four metalloccyclic rings (15 examples). In the four derivatives of the former type of derivative, three six-membered metalloccyclic rings are found with mean inter 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(η⁴-AID seco-corrinoid)]⁺ tetradeinate 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 metalloccyclic 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(η⁴-tetrapropylporphycene) has a 16-membered macrocycle which creates two pairs of metalloccyclic 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 metalloccyclic 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 2.05 Å).

There are almost thirty, mostly black, derivatives where four cyamide groups are arranged in a square planar geometry around a Pt(II) atom (PtC₄). 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 [PtCl₄]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 to 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 PtCl₄ 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 tetradeinate S-donor ligand. Thirteen derivatives have only monodentate ligands, Pt(η¹-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 RCS₂ ligands and 2.34 Å and 83.6°, respectively for RPS₂ ligands. In the [Pt(η²-S₄)₂]²⁻ anion the mean S-Pt-S bite angle is 93.4°.

A [Pt(η²-C₆H₆S₂)(η²-C₆H₅S₂)] 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 PtS₄ 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 ranges 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° (SC₃S). 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 tetradeinate ligand is bonded to the Pt(II) atom. In one derivative the tetradentate 1,3-bis(2-mercaptopenylthio)-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 tetradeinate 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 tetradeinate 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 metalloccyclic rings with a mean P-P bond 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-P bond 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 metalloccyclic rings with mean P-P bond 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 Â).

Pair of six-membered metalloccyclic rings is found in three derivatives with mean P-P bond angles of 90.0° (POBOP) in two derivatives, and 80.7° (PCNCPS) 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 tetradeinate ligand. In two of them a macrocycle forms three five-membered rings with mean P-P bond 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 [PtBr₃]²⁻ anion. The mean Pt-Br bond distance is 2.42 Å. The cis and trans 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 PtSe₄ 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)₂NCSe₂ 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(η²-MeSe(CH₂)₂SeMe₂)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(SePPH₂)₂ ligands are bonded to a Pt(II) atom there is a noticeable distortion in the coordination geometry with ligand bite angles of 99.5˚ and other angles being 80.5˚. Structure of [Pt(η⁴-[16]-aneSe₄)]²⁺ is shown in Figure 4 [9]. The Pt(II) atom lies precisely in the Se₄ 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(η⁴-[16]aneSe₄)]²⁺ the Pt(II) atom lies precisely in the Se₄ 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 PtAs₄ 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 (Pt₄L₄). 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 (RNH₂, NH₃) < 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˚ (NC₂N, unsaturate) < 81.3˚ (OC₂O) < 83.3˚ (NC₂N, saturate) < 84.2˚ (PC₃P) < 86.5˚ (SCPS) < 89.3˚ (SC₂S) < 93.4˚ (SS₂S) < 93.6˚ (SSCS); and for six-membered: 86.5˚ (PNPNP) < 88.5˚ (PCHCP) < 89.5˚ (NC₃N) < 91.3˚ (PC₃P) < 93.7˚ (SC₃S) < 94.8˚ (OC₃O). 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(η⁴-[16]-aneSe₄)]²⁺ [7].](image-url)
2.3.2. PtO₃X (X = N, P, Br or I), PtN₃X (X = O, C, Cl, S, Br or I)

There are over one hundred and seventy derivatives of the composition PtA₃B. 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 PtO₃X 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 metalloccyclic 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-OH₂ bond distance is 2.053 Å.

The other three derivatives have the composition Pt(η²-hfac)(η¹-hfac)X (X = Pcy₃, 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 PtN₃X. Fifteen have the PtN₃O chromophore. In two of them cis-[Pt(NH₃)₂(1-MeC)(OH)]⁺ and cis-[Pt(NH₃)₂(1-MeC)(H₂O)]²⁺ a square planar geometry consists of four unidentate ligands. The mean Pt-NH₃ bond distance is 2.027 Å and Pt-N (MeC) is 2.034 Å. The Pt-O(H) and Pt-O(H₂) 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(NH₃)₂(η²-N₂O(L)) have a cis arrangement. The bidentate ligands create a five-membered metalloccyclic 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 PtN₃O 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 (O), and 1.99 and 2.05 Å (N) for the central and satellite N-atoms.

There is only one example with PtN₄C chromophore, build up by bidentate o-phenanthroline-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 PtN₃Cl 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(η²-ethylenediamine)(η¹-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 diethylenetriamine 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(CH₂)₂OH ligand created a distorted square planar environment about each Pt(II) atom (Pt₃S). Structure of [Pt(η³-trpy){S(CH₂)₂OH}][NO₃] 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 (PtN₃Br). 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 PtN₃I 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 derivatives one bidentate ethylenediamine –N,N' ligand and one pyridine plus the iodine atom form an approximate 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 PtN₃I 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 distance is 2.591 Å.

The overall data in this subgroup shows the frequency of types of chromophore increasing in the order: PtN₃C(1) < PtN₃S(2) ~ PtN₃Br(2) < PtO₃N(4) < PtN₃I(8) < PtN₃O(15) < PtN₃Cl(40). The mean Pt-N bond distance elongated in the order: 1.98 Å (η³-trpy) < 2.03 Å (NL, η²-dien) < 2.04 Å (NH₃, η²-NL). The chelate five-membered rings (N-Pt-N open in the order: 80.9˚ (η³-trpy) < 83.8˚ (η²-NL) < 85.3˚ (η³-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(η³-trpy){S(CH₂)₂OH}][NO₃] [9].
2.3.3. PtCl₃X (X = N, S or P), PtS₃X (X = O, N, Cl, P, As or I)

The number of PtCl₃X derivatives decreases in the order: PtCl₃N (30) > PtCl₃S (15) > PtCl₃P (2). Parts from Cl atoms, the most common monodentate ligands are N-donor nucleobases, and dimethylsulphoxide as S-donor. There is a \textit{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 (\textit{trans} to N) < 2.324 Å (\textit{trans} to S) < 2.380 Å (\textit{trans} to P). The mean values of the Pt-Cl distances \textit{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 PtS₃X 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-mercaptopyrydine ligand chelates via the S and O atoms. This ambidentate behavior produced a slightly distorted square planar PtS₃O coordination arrangement, and is the only example with such a chromophore. The mean Pt-S(\eta^1-SL) bond distance is 2.294 Å, and Pt-L(\eta^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 \textit{trans} positions to each other. The fourth coordination site, \textit{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 PtS₃Cl chromophore. One has three monodentate S donor ligands (N-propyl-O-ethylthiocarbamate) plus the Cl atom. A second has one bi-(Et₂NCS₂) and one monodentate (MeS₂CNEt) 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^1-dmtt)X]BF₄ (X = Cl, PPh₃ 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)₂PS₂ and monodentate (EtO)₂PS₂ plus Ph₂AsCH₂CH₂P(S)Ph₂ ligand created about the Pt(II) atom a distorted square planar PtS₃As chromophore. The Pt-S distances \textit{trans} to As is significantly longer (2.373 Å) than the other Pt-S distances (2.335 Å). 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 (\eta^3-SL) < 2.305 Å (\eta^1-SL) < 2.340 Å (\eta^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. PtP₃X (X = H, F, Cl, S, Br or I), PtBrₓ₃X (X = N or S), PtIₓ₃X (X = P or Sb)

Thirty derivatives with PtP₃X chromophores are known. Seven of them have PtP₃H chromophore. In six PtP₃H examples only monodentate PR₃ (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 \textit{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 P₂ ligand with PPh₃ plus H atom create a distorted square planar environment about the Pt(II) atom. The Pt-P bond distances \textit{trans} to H is 2.304 Å (\eta^3-SL) < 2.305 Å (\eta^1-SL) < 2.340 Å (\eta^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).

Colorless [Pt(PEt₃)₂F]BF₄ is the only example with the PtP₃F chromophore. The Pt-P bond distance \textit{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 (\textit{trans} to P).

There are fifteen derivatives with the PtP₃Cl 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 examples) with bite angle of 70.0˚; 5-membered PC₂P (2 examples) with bite angle of 85.8˚, and 6-membered PC₃P (1 example) with bite angle of 92.4˚, respectively. For the monodentate ligands, the mean Pt-P bond distance \textit{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 PtP₃S chromophore. In one derivative three PMe₂Ph ligands plus SO₂ form a distorted square planar arrangement about the Pt(II) atom. In another one two bidentate ligands (Ph₃PCH₂Ph₂ –P,P′, and Ph₃PN(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(CH₂CH₃)PPh₂ –P,P′,P″ ligand with monodentate Et₃NCS₂ -S donor atom created a distorted square planar geometry (PtP₃S). 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 PtP₃S derivative (all four ligands are monodentate) the Pt-P bond distance is shorter than the latter (Pt-P) with mean values of 2.268 and 2.298 Å, respectively.

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 PtP₃Br chromophore. In two of them three monodentate ligands (C₁₃H₁₁P, C₁₅H₁₅P) plus Br atom created a distorted square planar geometry about the Pt(II) atom. In remaining one derivative, one bidentate –P,P′ (Bu₂PP = PBu₂), one PPh₃ plus Br atom form a distorted square planar geometry at the Pt(II) atom (PtP₃Br). 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 bond 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 (PtP₃I). 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 PtP₃X 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 PtBr₃N 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 PtBr₃N group. The Pt-Br bond distance trans to the Br atom at 2.257 Å is about 0.083 Å shorter than the other Pt-Br bond distances (2.328 Å, ave).

There are two derivatives [PtBr₃(Ph₂SO)] and [PtBr₃(Ph₂SO)] which have the chromophore PtBr₃S 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 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 PtA₃B. 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 PtA₃B 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. PtH₂P₂, PtO₂X₂ (X = N, Cl, S, P or As), PtN₂X₂ (X = C, Cl, S, P, Br or I)

There are four hundred and twenty derivatives of the composition PtA₂B₂. 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 (PR₃) form distorted a square planar geometry about the Pt(II) atom. Unfortunately, only for one derivative 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') bond angle is 95°. The mean Pt-P bond distances for remaining two (PMē₃) and (PBu₂) are 2.259 and 2.252 Å, respectively. The trans-Pt-Pt bond angle in both derivatives is exact linear, 180.0°.

There are one hundred and twenty six derivatives of the composition PtO₂X₂. The number of examples increases in the order of X atoms: Cl(2), As(2) < S(7) < P(45) < N(70). In this series the PtO₂N₂ 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 sub-groups are four monodentate ligands (1 example); monodentate O-donor and bidentate N-donor ligands with a five-membered 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 (five-membered ring) and bidentate N-donor (seven-membered ring) (2 examples); heterobidentate O,N-donors with five-membered rings (15 examples); tridentate O,N ligand (five- and six-membered rings) plus a monodentate N-donor ligand (1 example).

Structure of Pt(η²-cbdc)(η²-1,4-dach) is shown in Figure 6 as an example [11]. The Pt(II) atom has a slightly 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 distances elongated in the order: 1.97 Å (η²-N, unsaturated) < 2.04 Å (η¹-OL). The mean values of the Pt-O vs Pt-N bond distances in heterobidentate 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 saturated) < 92.8° (six-membered) < 97.8° (seven-membered). For O-Pt-N the values are: 81.3° (five-membered) < 93.0° (six-membered).

Two examples are only derivatives of the PtO₂Cl₂ 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 (η¹-OL) < 2.035 Å (η²-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 PtO₂S₂ chromophore. 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 NO₃ 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 (η²-OL) < 2.048 Å (η¹-Odmso) < 2.214 Å (η¹-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(η²-cbdc)(η²-1,4-dach) [11].
There are forty five derivatives with the PtO₂P₂ 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 Pt-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 RCO₂ group (four-membered chelate rings) and PPh₃. The mean Pt-L bond distance elongated in the sequence: 2.06 Å (η²-OL) < 2.11 Å (η¹-OL) < 2.21 Å (η²-PL) < 2.24 Å (η¹-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° (OC₂P) and 95.8° (PC₃P).

Two derivatives are found for the PtO₂As₂ square planar chromophore. In both examples only monodentate ligand are involved with mean Pt-O and Pt-As bond distances of 2.05 and 2.23 Å, respectively.

There are three hundred PtN₂X₂ (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 PtN₂C₂ 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 (NH₃), 2.047 Å (NH₂Me) 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°.

There are over one hundred and eighty derivatives with the PtN₂Cl₂ 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 PtN₂Cl₂ 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 O-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 PtN₂S₂ 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 (η¹-NL) and
The mean Pt-S bond distances are 2.245 Å ($\eta^2$-SL, five-) and 2.270 Å ($\eta^2$-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$_3$S$_2$ (Pt-N vs Pt-S) are 1.97 vs 2.25 Å. For trans tetradentate (N$_3$S$_2$) 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$_2$SC$_2$S).

There are thirty six derivatives with the PtN$_2$P$_2$ 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($\eta^2$-(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 ($\eta^2$-NL) and 2.255 Å ($\eta^2$-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˚ (N$_2$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˚ (NCCP).

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 than the cis. The mean L-Pt-L bond distances depart 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($\eta^2$-(HN)$_2$SO$_2$(PMePh$_2$)$_2$][12.](image-url)
The mean Pt-N bond distances are 2.04 Å (η¹-NL, trans) < 2.055 Å (η²-NL, five-membered ring) < 2.07 Å (η²-NL, six-membered ring) < 2.075 Å (η¹-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. PtC₂X₂ (X = Cl, S, P or I), PtB₂P₂, PtClₓL₂ (X = S, P, Se or As)

A cis-Pt(CNPh)Cl₂ complex is only example where two PhNC ligands with a pair of Cl atoms create a square planar environment around the Pt(II) atom, PtC₂Cl₂. The mean Pt-L bond distances are 1.89 Å (L = C) and 2.308 Å (Cl). The cis- and trans bond angles depart from the ideal values (90° and 180°) by 1.9° and 2.1° respectively.

There are six examples with the PtC₂P₂ 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 (PtC₂P₂). The mean Pt-C and Pt-P bond distances are 1.98 Å and 2.270 Å, respectively. The five-membered metallocycle has a Pt-P-P bite angle of 70.7°.

In two cis-derivatives two CNR ligands plus two I atoms form a square plane about Pt(II) to give a PtC₂I₂-chromophore. In nine of the derivatives cis-Pt(CNMe)₂Cl₂ complexes only monodentate ligands are involved, PPh₃ and two B-donor ligands (mostly B(catecholate)). In the remaining two examples, one has a bidentate five-membered ring 1,2-bis(diphenylphosphine)ethane-(dppe) P,P' ligand and the other a seven-membered ring, 1,4-bis(diphenylphosphine)butane (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 η²-dppe derivative the Pt-P-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 (η²-dppe) < 2.340 Å (η²-dppb) < 2.360° (PPh₃). The mean Pt-B bond distance is 2.055 Å.

There are almost forty compounds with the PtCl₂S₂ chromophore. More than half have monodentate S-donor ligands and many of these have cis-configuration. Some of the derivatives only monodentate ligands are involved, PPh₃ and two B-donor ligands (mostly B(catecholate)). In the remaining examples, one has a bidentate five-membered ring 1,2-bis(diphenylphosphine)methylamine 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 eleven PtB₂P₂ derivatives with a square planar geometry about the Pt(II) atom. The mean Pt-L bond distances are 1.96 and 2.600 Å (I), respectively.

There are almost forty compounds with the PtCl₂S₂ chromophore. More than half have monodentate S-donor ligands and many of these have cis-configuration. Some of the derivatives only monodentate ligands are involved, PPh₃ and two B-donor ligands (mostly B(catecholate)). In the remaining examples, one has a bidentate five-membered ring 1,2-bis(diphenylphosphine)methylamine 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 almost forty compounds with the PtCl₂S₂ chromophore. For the PtCl₂S₂ 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...
metallocyclic rings are five- and seven-membered. The remaining four examples have tetradentate (S2P2) ligands and six-S-Pt-S with four P-Pt-P membered metallocyclic rings. Forming distorted square planar environments about the Pt(II) atoms. Macrocyclic ligands form five-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 square planar geometry (PtS2I2). A trans-PtCl2(η2-As2L) 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 bond 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. PtS2X2 (X = P, Br, I or As), PtP2X2 (X = Br, Se, Si, I or Te), PtBr2Se2 and PtI2X2 (X = As or Te)

There are over sixty PtS2X2 (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 PPh3) 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 tetradeutate (S2P2) ligands forming distorted square planar environments about the Pt(II) atoms. Macrocyclic ligands form five-membered SPtP and PPtP rings; five SPTP and 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 for S and 2.29 Å for P. In the series of bidentate chelating ligands the mean 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 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 PtCl2Se2 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-PtCl2(q-As2L) 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 bond angle of 177.1˚. The small differences reflect the relevant covalent radii of the donor atoms (As, 1.20; P, 1.06 Å).

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 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˚).
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 PtP2X2 (X = Br (x6), Se (x7), Si (x5), I (x11) or Te (x2)), PtBr2Se2 (x2), PtAs2I2 (x1) and Pt2Te2 (x1). Six derivatives with the PtPBr2 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 P-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 PtP2Se2 chromophore have two trans and five cis examples. Two unidentate P-donor ligands are found in one trans configuration, 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(PPh3)2(η2-Se2CH2) 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.

Seven species with the PtP2Se2 chromophore have two trans and five cis examples. Two unidentate P-donor ligands are found in one trans configuration, 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(PPh3)2(η2-Se2CH2) 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 PtP2Si2. In one derivative two unidentate PPh3 ligands with a bidentate Si-ligands created a 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 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-Si bite angle of 83.3°.

There are eleven derivatives with the PtP2I2 chromophore. In eight of them cis (2 examples) and trans (6 examples), only unidentate ligands are involved. In the remaining three examples a bidentate –P donor ligand is involved, giving five-membered metallocycles with the mean P-Pt-P bond 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(PPh3)2(η2-1,2-Te2C6H4) 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 (PtBr2Se2). 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 geometries.

There is trans-derivative in which pair of iodine atoms with a pair of AsPh3 ligands forming a square planar geometry about the Pt(II) atom (PtAs2I2). 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 (Pt2Te2).

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 = η2-PL) < 2.295 Å (η2-PL) < 2.37 Å (η2-SiL) < 2.47 Å (η2-SeL) < 2.485 Å (Br) < 2.66 Å (I). For the trans-derivatives the order is: 2.313 Å (η2-PL) < 2.325 Å (η2-PL) < 2.405 Å (η2-AsL) < 2.425 Å (η2-SeL) < 2.43 Å (Br) < 2.58 Å (η2-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 metalloccycles. For example, in the four-membered metallocyclics 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° (PC2Si) < 85.5° (PC2P) < 88.4° (TeC2Te) < 88.5° (PC2Te) < 90.4° (PNPSe).

Overall of the data in Chapter 2.5 cover almost eight hundred and twenty Pt(II) derivatives of the composition PtA2B2. 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 (P) < 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 (η²-NL, unsaturated) < 2.045 Å (η²-NL, saturated) < 2.29 Å (η²-PL) < 2.39 Å (η²-SiL) < 2.37 Å (η²-AsL) < 2.58 Å (η²-TeL) < 2.66 Å (η²-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 2.32 Å. 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 metallocyclics 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° (PC2Si) < 85.5° (PC2P) < 88.4° (TeC2Te) < 88.5° (PC2Te) < 90.4° (PNPSe).

Overall of the data in Chapter 2.5 cover almost eight hundred and twenty Pt(II) derivatives of the composition PtA2B2. 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 (P) < 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 (η²-NL, unsaturated) < 2.045 Å (η²-NL, saturated) < 2.29 Å (η²-PL) < 2.39 Å (η²-SiL) < 2.37 Å (η²-AsL) < 2.58 Å (η²-TeL) < 2.66 Å (η²-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 2.32 Å. Some mean Pt-L bond distances are longer for the PtA3B (Chapter 2.4) than in the PtA2B2 (Chapter 2.5) types, especially for H, Cl, \( \eta^1 \) -SL, \( \eta^1 \) -PL and Br, probably because of the steric reasons. Some chelate rings in the PtA3B type are a little more open than in the PtA2B2 type, for example, NC2N, OC2N and NC3N; but the reverse is true for the other examples, such as PCP, CSCS, PC2P, NC2S and PC3P.

**2.3.8. PtA2XY 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 PtO2XY chromophore. In cis-PtO2NCl 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 83.6°. In trans-PtO2NI a heterotridentate ligand forms a five-membered metallocycle like in trans-PtO2NCl. The heterotridentate ligand forms a five-membered metallocycle with the O-Pt-N bite angles of 93.7°. In trans-PtO2NP another heterotridentate 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-PtO2NP another heterotridentate ligand with chlorine atom forms a distorted such geometry. The bidentate ligand forms one five-membered metallocycle with the O-Pt-N bite angles of 82.4° and 94.8°, respectively. In another trans-PtO2NI a heterotridentate ligand with iodine atom created a similar square-planar geometry like in trans-PtO2NCl. The heterotridentate ligand forms a five-membered metallocycle with the O-Pt-N bite angles of 83.2°. In cis-PtO2ClS a bidentate ligand with chlorine atom and dmsd-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 derivatives with PtN2OCl chromophore. In two trans-derivatives a bidentate ligand with chlorine atom and pyridine, or \( \alpha \)-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 (PtN2OCl). In one other examples, 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 PtN₂OS 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 PtN₂ClS chromophore. Two *trans* derivatives have unidentate ligands, two NH₃ 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(η²-mbda)(Cl)(dmso)ClEtOH is shown 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 (N₂S) 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 PtN₂ClP 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 PPh₃ to create a distorted square planar environment about Pt(II) to give the PtN₂SP 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 PPh₃ 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 (PtC₂NS).
The data of PtA₂XY (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 (O₂,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 heterobidentate 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 PtCl₄XY chromophores in which a Pt(II) atom is in a square planar environment with a different degrees of distortion. There are five derivatives, one trans- and four cis with PtCl₂ON chromophore. The trans derivative is the only example in which only unidentate ligands are involved. In cis derivatives (PtCl₂ON) a bidentate O,N ligands form in three derivatives a five-membered metallallocyclic rings (O-Pt-N, 83.6°) and in the fourth one a six-membered metalloclucyce (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-PtCl₂OS. A slightly distorted square planar PtCl₄OP chromophore uses water and a PPh₃ molecule.

There are over thirty derivatives in which two chlorine atoms and N and S donor ligands are found in a PtCl₂NS 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 metallocyclic 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 PtCl₂NP 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 metallallocyclic 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 PtCl₂NSe chromophore and the N-Pt-Se bite angle is 90.3°. In another two derivatives, two chlorine atoms, a unidentate N-donor and AsEt₃ ligand forms PtCl₂NAs chromophore. In cis-PtCl₂NTe 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 PtCl₂SP 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 metallallocyclic 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 PtCl₂STe 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 ON, NS, NP, NSe, NTe, SP and STe. These chelates form metalloccyclic 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) < 91.5° (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 PtS2XY type a trans configuration about Pt(II) is created by a terdeterminate (S,S,N) ligand plus a chloride atom (PtS2NCl) and it is only example with such chromophore. The ligand forms two five-membered metalloccyclics with mean N-Pt-S angle of 87.2°. A similar structure has trans-PtS2NBr derivative, here a terdeterminate (S,S,N) ligand also forms two five-membered metalloccyclics (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 PPh3 molecule (PtS2NP). The chelating ligand forms a four- in one example and five- in another one, membered metalloccycle 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 PtS2XY derivatives in which both X and Y are halogen atoms (Cl + I, Br + I). The chelating (S,S') ligand forms a five-membered metalloccycle 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 PtP2HO 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 PtP2HM 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 PtP2HCl chromophore with P-Pt-P angles ranging from 165.7° to 176.2°, mean value 170.5°. Two trans derivatives also with unidentate ligands have the PtP2HS chromophore. Here the P-Pt-P angles are 161.1° and 162.6°, respectively. A PtP2HBr chromophore with unidentate ligand is found in two examples with P-Pt-P angle of 163.9°.

There are six derivatives with the PtP2HSi 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 remaining have a bidentate (P,P') ligand with an H atom and a S-donor ligand. The chelating ligand forms a seven-membered metalloccycle with cis-P-Pt-P bond angles of 102.3° and 103.5°, respectively. Two PP3 molecules in cis positions, a H atom and a phenyl iodide ligand form a distorted square plane about Pt(II) (PP3H) with a trans P-Pt-P angle of 163.7°.

In the trans derivatives with the PtS2HY chromophore there is a relationship between the trans P-Pt-P angle and the cis-X-Pt-Y angles 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 PtP2OY 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 PPh3 molecules. In seven of these the chelate forms a five-membered metalloccycle with mean O-Pt-N angle of 79.3°. In the other case, there is a six-membered metalloccycle with angle of 87.1°. In the other two derivatives of cis-PtP2ON type there are two chelate ligands, one homo-bidentate (P,P) and the other hetero-bidentate (O,N). Five-membered metalloccyclic 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 PtP2OCI chromophore formed by a hetero-bidentate (O,P) ligand and a P donor ligand. Each chelate ligand forms a five-membered metalloccycle with the mean O-Pt-P angle of 84.8° (OPNP) and 84.2° (OC3P). 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 PtP2OS chromophore created by a hetero-bidentate (O,S) ligand with two PPh3 molecules. In four derivatives there are heterobidentate (O,S) chelating ligands, three with five-membered...
metalloccyclic rings with angles 82.7˚ (OCNS), and 84.2˚ (OC2S). In the fourth case the 1,2-SC6H4COO 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-PtP2OBr chromophore. The O-Pt-P angle of a five-membered metallocycle is 83.11˚. cis-PtP2OSi 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˚ (OC2N) < 81.8˚ (OCNS) < 83.6˚ (ONCS) < 83.8˚ (OC2P) < 84.5˚ (OPNP).

There are three PtP2NSCl derivatives in which hetero-tridentate (P,P’,N) ligand with a Cl atom forms a five-(N-Pt-P) and six-(P-Pt-P) membered rings for which the data are not available. There are twenty two derivatives with the PtP2NS 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 (PtP2NS). Four-membered (3 derivatives), five-membered (13 derivatives), and six-membered (2 derivatives) metallocycles are involved for which the mean N-Pt-P angles are 84.2˚ and 93.3˚. In remaining cis-derivative the PtP2NS chromophore is created by hetero-terdentate (P,N,S) ligand and PPh3 molecule. The terdentate ligand forms two metallocyclic rings four-(N-Pt-P) and five-(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 (PtP2NCl) 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˚ (NC2NP) < 83.5˚ (NC2P); six-membered (2 derivatives) and 85.8˚ (NSNSe) (1 derivative). In the fourth case the 1,2-SC6H4COO 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-PtP2OBr chromophore. The O-Pt-P angle of a five-membered metallocycle is 83.11˚. cis-PtP2OSi chromophore in other derivative is created by a bidentate (P,P’) ligand, a unidentate O-donor ligand and a unidentate Si-ligand.
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 (PtP₂NI). 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 PMe₂Ph molecules and a hetero-bidentate (N,Te) form a distorted square plane (PtP₂NTe). The bidentate ligand forms a five-membered metallocycle with N-Pt-Te angle of 84.9°.

In the PtP₂NY 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° (NC₂P) < 83.8° (NCNSe) < 84.9° (NSNTe) < 85.5° (NSNSe) < 87.2° (NC₂Se) < 89.2° (NC₂P) < 93.9° (NC₂NSe).

Two derivatives trans- and cis, contain the PtP₂BCI 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 (PtBPh) with P-Pt-B angle of 73.6°.

Four species have an inner coordination sphere PtP₂CIS. One cis- and one trans-derivative contain only unidentate ligands. In another two trans-derivatives a hetero-terdentate (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 PtP₂ClSi 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(PEt₃)₂(Br)(SiMe₃) has an inner coordination sphere of PtP₂BrSi another trans-derivative PtP₂SiTe.

The data for the derivatives with PtP₂BCI, PtP₂CISi, PtP₂ClSi, PtP₂BrSi and Pt₂SiTe 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 PtBr₂(MeCN)(dmso) an unidentate ligands created a slightly distorted square planar arrangement about the Pt(II) atom (PtBr₂NS). In trans-PtBr₂Cl(PPh₃) also unidentate ligands created a somewhat distorted square plane about the Pt(II) atom (PtBr₂CIP). Another trans-derivative has the PtSe₂NP chromophore made up from a hetero-bidentate (N,Se) ligand, a unidentate Se-ligand and a PPh₃ molecule. The N-Pt-Se angle of the four-membered metallocycle is 78.2°. Another trans-derivative has a hetero-terdentate (As₂S) ligand and a chlorine atom giving the PtAs₂CIS chromophore. The hetero-terdentate ligand forms two six-membered metallocycles with mean S-Pt-As angle of 93.0°.

Trans-PtI₂(3,5-Me₂py)(dmso) has only unidentate ligands giving a slightly distorted square planar environment (PtI₂NS). There are two derivatives with PtI₂NP 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 PtI₂SP 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) vs 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 (H); 2.08 vs 2.233 Å (S); and 2.168 vs 2.232 Å (P). The PtCl (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 PtP₂XY derivatives with bidentate or terdentate ligands the L-Pt-L angles open in the order: 78.1° (NPSe) < 86.9° (SC₂P) < 88.3° (NC₂P) < 88.5° (mean) (NC₂Te) < 93.0° (SC₂As).

There are thirteen derivatives with the chromophore PtABXY in a distorted square planar geometry. Five species have the inner coordination sphere of PtONCIS. 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 PtONCIP chromophore. Three of these contain a hetero-bidentate (O,N) ligand, a chlorine atom and PR₃ 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 (PtONCIP). 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 PtNCISP chromophore. The terdentate ligand forms five- (NNCS) and six (NC3P) 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 PMe2Ph 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-P₄ 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-Pₐx bond distance of 2.315 Å is somewhat longer than the mean Pt-Pₐx bond (2.210 Å). The Pt-Hₐx bond distances are not available. The tetradentate P₄ ligand forms three five-membered metallovalues with the mean P-Pt-P angles of 85.6°. In another derivative, a tetradentate P₄ ligand with a unidentate P-donor ligand created a trigonal-bipyramidal arrangement about the Pt(II) atom (PtP₅). 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-Pₐx bond distances of 2.372 Å are longer than remaining two Pt-Pₐx 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 (P₃N) ligand with an unidentate PHEt₂ ligand build up a trigonal-bipyramidal environment about the Pt(II) atom. An equatorial plane is occupied by three P atoms of the respective tetradentate ligand and an N atom of the respective ligand with PHEt₂ ligand occupied an axial positions. The mean P-Pt-N “bite” angles are 84.2°. The Pt-P bond distance elongated in the order: 2.196 Å (Pt-Nₐx) < 2.256 Å (Pt-Pₐx) < 2.695 Å (Pt-Pₑx). In other derivative a tetradentate (P₃N) ligand with an unidentate AsPh₂ 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-P bond distance elongated in the order: 2.276 Å (Pt-Nₐx) < 2.350 Å (Pt-Pₑx) < 2.457 Å (Pt-Asₐx). The mean N-Pt-P “bite” angle is 84.0°. Finally, there is a derivative in which a tetradentate-As₄ 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 PtN₄ 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 (PtS₄). 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 (PtSe₂). 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 PtCl₃(η²-en) complex the Pt(III) atom has a square-pyramidal geometry (PtCl₃N₂). 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$_{ap}$) < 2.376 Å (Pt-Cl$_{eq}$). 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(n$^2$-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(n$^2$-ox)$_2$(OH)(H$_2$O)]. 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 metallogycles with a mean O-Pt-O bond distance 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 metallogycles with the N-Pt-N bite angles of 63.9°. In another one a pair of 2,4-pentanedimidinate ligands form a six-membered metallogycles 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$_3^-$ anions and a pyridine to give somewhat elongated tetragonal bipyramidal geometry. The NO$_3^-$ anions occupy axial positions, and the terdentate divalent anion forms two five-membered metallogycles 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 metallogycles with mean N-Pt-N bond 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$_2$N) < 94° (NC$_3$N).

There are forty examples with the PtCl$_6$ chromophore. The geometry in each case is octahedral with varying degrees of distortion. The Pt-Cl$_{eq}$ (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$_{ap}$ (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(n$^2$-S$_5$)$_3$]$^2-$ anion. The S$_3^{2-}$ 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$_3^{2-}$ ligands, which form three seven-membered metallogycles 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(n$^2$-S)$_3$]$^2-$.

Structure of [Pt(n$^2$-P$_3$)(n$^3$-triphos)]$^3-$ 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$_1$) and 2.339 Å (triphos). There are two type of metallogycle, one three-(P$_1$) and one six-(triphos) membered with P-Pt-P bite angles of 52.6° and 90.0°, respectively.
Six bromine atoms form an octahedral geometry about the Pt(IV) in another derivative (PtBr₆) with the mean Pt-Br bond length of 2.456 Å. Three derivatives contain a \( \text{[Pt}(\eta^2-\text{Se}_4)\text{]}^{2-} \) complex anion. The \( \text{S}_2^2 \) 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. Pt₅X₅, Pt₄X₄, Pt₃X₃, Pt₄XY

There are seventeen examples of Pt₅X₅ type. In one derivative the five fluorine atoms and one chlorine atom form an unsymmetrical tetragonal bipyramid about the Pt(IV) atom (PtF₅Cl). 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 an 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 \( \text{[Pt(NH}_3)_2(\eta^2-\text{mec})(\eta^3-\text{mec})(\text{OH})]^{2-} } \) and \( \text{[Pt(}\eta^2\text{-bpy})(\eta^3\text{-tachH}_2)\text{. (H}_2\text{O})]^{2-} \), 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 (PtN₅O). 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 (PtN₅O).

There are four derivatives in which inner coordination sphere about the Pt(IV) centre consists of five N atoms and one chlorine atom (PtN₅Cl). 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 bond 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 2.08 Å (ave. 2.07 Å).

There are three derivatives which have five chlorine atoms and one N atom in the inner coordination sphere (PtCl₅N). 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 (PtCl₅S).
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 [PtCl₄(PEt₃)²⁻] 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 [PtBr₅(PPh₃)²⁻] 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 Pt₅X₆ 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 Pt₅X₂ type. Two derivatives contain [PtF₄Cl₂]⁻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 PtO₄N₂. In two of these four unidentate OH⁻ or CH₃COO⁻ 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 bond 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 bond angle of 84.5°. Two more derivatives have a pairs of OH⁻ and NH₃ ligands with a bidentate-O,O' ligand, or a pairs of CH₃COO⁻ and NH₃ ligands with a bidentate-O,O' ligand. Each chelating ligand forms a six-membered metallocycle with O-Pt-O bond angles of 94.3° and 91.3°, respectively.

The remaining six examples use a pair of OH⁻ groups or CH₃COO⁻ groups plus two bidentate ligand one O,O' and the other N,N' donor, to give PtO₄N₂ chromophore. The chelating-O,O' ligands created a six-membered metallocycle with the mean O-Pt-O bond angle of 92.3° and chelating N,N' ligands a five-membered with the mean N-Pt-N bond 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 acetylacetone groups form a plane about the Pt(IV) with two chlorine atoms (in axial) positions to give tetragonal bipyramidal environment (PtO₄Cl₂). The chelating ligands form five-membered metallocycles in the former with the mean O-Pt-O bond angle of 83.2° and in the latter a six-membered (O-Pt-O) 95.9°. A similar structure is found with two bidentate acetylacetone ligands forming a PtO₄ plane with two CNS groups in axial positions (PtO₄S₂) with equivalent O-Pt-O bond angles of 96.3°.

Two derivatives Pt(η⁷-ox)₂Br₂ and Pt(η⁷-acac)Br₂ 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(η⁷-ox)₂I₂ and Pt(η⁷-acac)I₂ 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)₂F₂ 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 PtN₄O₂ inner coordination sphere. Six of these have a trans-configuration of which five have only unidentate ligands. The other one has a tetradenate (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 PtN₄Cl₂ 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 bond angle of 83°. In another two derivatives a bidentate-N,N' ligand forms a six-membered metallocycle or two bidentate-N,N' ligand each forming a six-membered metallocycle. In the remaining six derivatives, tetradebate N-donor ligands are involved. The mean Pt-Br bond distances in the PtN₄Cl₂ derivatives elongated in the order: 2.05 Å (tetra-NL) < 2.06 Å (uni-NL) < 2.065 Å (bi-NL) < 2.305 Å (CI). 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 bond 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 (PtN₂Br₂). Six derivatives have a similar geometry with iodine atoms in axial positions (PtN₂I₂). Tetragonal bipyramidal geometry is also formed by four in-plane CN⁻ groups with two NH₃ ligands in axial positions (PtC₅N₂). In another derivative four Cl atoms and two O donor
ligands form a pseudo-octahedron (PtCl₄O₂). Sixteen derivatives have four Cl atoms and two N-donor ligands (PtCl₄N₂). 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 PtCl₄S₂ 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-PtCl₄(PEt₃)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 (PtCl₄Se₂). 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(q₃-As₂S₅)₂]²⁻ anion the Pt(IV) atom has PtS₄As₂ 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 (PtS₄I₂). 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(q₃-As₂S₅)₂]²⁻ [15].
Two cis-derivatives PtBr₄(μ²-en) and PtBr₄(μ²-1,3-pn) are isostructural, having a plane containing two bromine atoms and two N atoms from bidentate ethylenediamine in the former and 1,3-propandiamine 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 (PtBr₂N₂). 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 Me₂S ligands in axial positions (PtBr₂S₂). The mean Pt-Br length is 2.471 Å and the mean Pt-S value is 2.363 Å. In another trans-derivative a compressed tetragonal bipyramidal environment about Pt(IV) consisting of a tetradentate (Se₄) 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 BuNC ligands in axial positions (PtSi₄C₂). 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 PEt₃ 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 (PtAs₄Cl₂; PtAs₄I₂). In four cis-PtI₄(μ²-NL) complexes one bidentate-N,N'-ligand with four iodine atoms form a pseudo-octahedral geometry about the Pt(IV) atom (PtI₄N₂). 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 PtA₄X₂ type derivatives showed several types of chromophore: PtF₂Cl₂; PtO₂X₂ (X = N, Cl, Br or I); PtN₂X₂ (X = F, O, Cl, Br or I); PtCl₂X₂ (X = O, N, S, P or S); PtS₂X₂ (X = As or I); PtBr₂X₂ (X = N or S); PtSe₂Cl₂; PtSi₂C₂; PtAs₂X₂ (X = Cl or I) and PtI₄N₂. The ligands are uni-, bi-, ter- and tetradeinate. 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˚ (OC₃O) ~ (NC₂N) ~ (SeC₃Se) < 84.5˚ (OC₃N) < 87.6˚ (SeC₃Se) < 99.5˚ (AsSAs). For six-membered rings the order is: 88.5˚ (SeC₃Se) < 91.5˚ (AsSAsS) < 94.3˚ (NC₂N) < 95˚ (OC₃O).

There are ten derivatives with PtA₃X₃ chromophores. Two derivatives fac- and mer-[PtF₂Cl₃]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 PtN₃Cl 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 diethylentriamine 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 (PtI₃). 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 PtCl₃S₃ 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 \([\text{Pt}(\eta^2\text{-en})(\text{CN})X]^2\) cations \((X = \text{Br or I})\) in which pair of ethylenediamine ligands with two five-membered metalloycles form a plane. The CN and X ligands are in axial positions completing an asymmetrical tetragonal bipyramid about the Pt(IV) atom \((\text{PtN}_4\text{ClBr}, \text{PtN}_4\text{Cl}).\)

There are three derivatives in which the Pt(IV) atom has a PtCl\(_4\text{ON}\) inner coordination sphere. In addition to four Cl atoms the distorted octahedron is completed by heterobidentate \((\text{O,N})\) ligand. Each derivative has three types of Pt-Cl location with bond distances 2.306 Å \((\text{trans to O})\), 2.308 Å \((\text{trans to N})\) and 2.316 Å \((\text{trans to Cl})\). 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\(_4\text{NS}\) chromophore. In one only unidentite ligands are involved and in the other one a heterobidentate-N,S ligand forming a five-membered metalloycle \((\text{N-Pt-S}, 86.9°)\). There are also three types of Pt-Cl bond distances 2.307 Å \((\text{trans to N})\), 2.356 Å \((\text{trans to S})\) and 2.312 Å \((\text{trans to Cl})\). In another derivative four bromine atoms with hetero-bidentate \((\text{O,N})\) ligand forms a PtBr\(_4\text{ON}\) chromophore. The heterobidentate ligand forms a five-membered metalloycle \((\text{O-Pt-N}, 85.6°)\). Three different Pt-Br bond lengths elongated in the order: 2.405 Å \((\text{trans to O}) < 2.439 Å \((\text{trans to N}) < 2.462 Å \((\text{trans to Br})\).

4.3. \(\text{PtA}_3\text{X}_2\text{Y}, \text{PtA}_2\text{X}_2\text{Y}_2, \text{PtCl}_3\text{ONS, PtA}_2\text{X}_2\text{YZ}\)

A derivative with inner coordination sphere of PtO\(_3\text{N}_2\text{Cl}\) contains three unidentate O-donor ligands, a bidentate \((\text{N,N'})\) ligand and a Cl atom. The bidentate ligand forms a six-membered metalloycle with N-Pt-N angle of 91.6°. Two chelating ligands, one bidentate \((\text{N,N'})\) and the other terdentate \((\text{N,O,O'})\) plus a Cl atom give a pseudo-octahedron about the Pt(IV) \((\text{PtN}_3\text{O}_2\text{Cl}).\) There are three five-membered metalloycles 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) \((\text{PtN}_3\text{Cl}_2\text{S}).\) There are two equal five-membered metalloycle \((\text{N-Pt-N}, 83.4°)\). In another derivative a heteroterdentate \((\text{N,N',S})\) ligand forms two five-membered metalloycles \((\text{N-Pt-N} \text{N-Pt-S})\) and with three Br atoms create a distorted octahedron about Pt(IV) \((\text{PtBr}_3\text{N}_2\text{S}).\) There are two Pt-Br locations with the bond distances of 2.456 Å \((\text{average trans to N})\) and 2.477 Å \((\text{trans to S})\), indicating a greater trans influence of S over N as might be anticipated.

In \([\text{PtBr}_3(\eta^2\text{-S}_2\text{N}_4)]^-\) anion the Pt(IV) atom is facially coordinated by three Br atoms together with two S atoms and one N atom from \(\text{S}_2\text{N}_4^2\) ligand \((\text{Figure 11})\) \([16]\). The five-membered ring \((\text{NSNS})\) is essentially planar with N-Pt-S bite angle of 89.9°, whereas the six-membered rings \((\text{SNSNS})\) 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 \((\text{trans to N})\) and 2.495 Å \((\text{trans to S})\).

![Figure 11. Structure of \([\text{PtBr}_3(\eta^2\text{-S}_2\text{N}_4)]^-\) \([16]\).](image)
Another derivative has three unidentate Si donor ligands, a bidentate (P,P') ligand and a hydrogen atom about the Pt(IV) atom (PtSi3P2H). 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 PtO2N2Cl2 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° (OC2N) < 84.7° (NC2N) < 97.0° (OC3N) ~ (NC3N) < 98.7° (NC2N).

A chelating ethylenediamine (N,N'), two unidentate acetate (O) units and two iodine atoms form a distorted octahedron about the Pt(IV) atom (PtO2N2I2). 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 (PtN2Cl2S2) for which only unit cell dimensions are available. A similar arrangement is found in PtCl4(PtCl2)Br2, with three homo-trans axes.

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 (PtCl2ONS). 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 PtCl4[η2-S2N2(NC3PPh)](PMe2Ph), the terdentate meridional S2N4 divalent anion coordinated via two S atoms and one N atom. The anion forms two metalloligocycles, five- and six-membered, with N-Pt-S and S-Pt-S bite 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(PMe2Ph)2Br2[η2-N(H)SNS]1+] 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(PPh3)3 and Pt(η2-dppp)2 complexes are only examples of Pt(0) distortion isomers. In the former three Ph3 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(η2-dppp)2 isomers a pair of bis(diphenylphosphino)propane ligands create a square-planar geometry (PtP4) 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 \textit{trans}-
PtCl₂\{P(But)₂Ph\}₂ exists in three isomeric forms, two monoclinic and one orthorhombic. There are over thirty
examples exist 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 ex-
amples). 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 (NH₄)[Pt(η²-exxp)₂]H₂O 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 crystallo-
graphically 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 in-
dependent molecules within the same crystal. One examples, PtCl₄(η²-dach), contains three such molecules. The
\textit{trans}-Pt(η²-bcd)₂ exists in two isomeric forms, one of which contain two crystallographically independent mo-
lecules 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 \textit{cis} rather than \textit{trans}.

5.2. \textit{Cis-Trans} Isomerism

There are almost thirty examples of Pt(II) complexes which exist in two isomeric forms, \textit{cis} and \textit{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 \textit{cis} isomers and tric-
linic \textit{trans} isomers. Two examples have monomonic \textit{cis} and orthorhombic \textit{trans}, three have orthorhombic \textit{cis} and
monoclinic \textit{trans}, and two have triclinic \textit{cis} and monoclinic \textit{trans}.

5.3. Mixes Isomerism (\textit{Cis-Trans} and Distortion)

Two Pt(II) complexes belong to this unusual combination of isomerism. The PtCl₂(py)(dms) complex exists as
monoclinic \textit{cis} and triclinic \textit{trans} isomers. In addition, the \textit{trans} isomer contains two crystallographically inde-
pendent molecules. Each Pt(II) atom has a square-planar geometry (PtCl₂NS) with different degree of distortion.
The mean Pt-Cl (mean), Pt-N and Pt-S bond distances in the \textit{cis} isomer are 2.313, 2.027 and 2.209 Å, respec-
tively. In the \textit{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(MeNH₂)₂Cl₂ exists in three different \textit{cis} isomeric forms and in a \textit{trans} form. Two of the \textit{cis} forms are
monoclinic and one is orthorhombic. The \textit{cis} isomers are differ from each other. One of the monoclinic forms
contains a single molecule while the other contains three crystallographically independent molecules. The or-
thorhombic \textit{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(η²-4,4'-Me₂bpy)(NCO)₂; and Pt(η²-5,5'-
Me₂bpy)(NCO)₂; Pt(η²-3,3'-Me₂bpy)Cl₂ and Pt(η²-5,5'-Me₂bpy)Cl₂; Pt(η²-3,3'-Bu₂bpy)(PMe₂Ph) and Pt(η²-5,5-Bu₂bpy)Cl₂;
\textit{trans}-PtCl₂(2,3-Me₂pyr). (PMe₂Ph) and PtCl₂(2,5-Me₂pyr)(PMe₂Ph). Each Pt(II) atom has a square-planar geo-
metry with differing degrees of distortion. The mean Pt-N (R₂bpy) bond distance reflects the position of the
R₂bpy 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
(Me₂pyr) bond distance also reflects the position of the Me₂R 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 with 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 crystallize 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 prevail.

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

The Pt(0) atoms are two-(PtP2), linear or almost linear; three-(PtP2S), Y-shape; and four-(PtP4, PtP4S, PtO2S2, PtN2P2, PtN2O, PtN2S and PtP2CS; mostly tetrahedral), coordinated.

The Pt(I) atoms are four-(PtN4 and PtP4, square-planar), coordinated.

The Pt(II) atoms are four-PtA4 (A = O, N, C, Cl, S, P, Br, Se or As); PtO2X (X = N, P, Br or I); PtN3S (X = O, C, Cl, S, Br or I); PtCl2X (X = N, S or P); PtSe2X (X = O, S, Se or Po); PtO2S2, PtCl2S2, PtN2S2, PtSe2S2, PtN2Se2—trigonal-bipyramidal coordinated.

The Pt (III) atoms are four-PtA4 (A = N, S or Se) and PtCl2N—square-planar coordinated.

The Pt (IV) atoms are four-PtA4 (A = N or S)—square-planar coordinated; and six-PtA6 (A = O, N, C, Cl, S, P, Br, Se or I); PtF3Cl; PtN2X (X = O or Cl); PtCl2X (X = O, N, S or P); PtBr2Cl; PtF2Cl; PtO2X (X = N, C, Cl, S, Br or I); PtN2X2 (X = F, O, Cl, Br or I); PtCl2N2, PtCl2X2 (X = O, N, S, Se or As); PtS2Br2; PtBr2X2 (X = N or S); PtSe2Cl, PtSe2X (X = Cl or I); PtCl2S2, PtN2S2, PtSe2S2, PtN2Se2—square-planar 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 seen 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 order: 65.0˚ (OCO, SCSi) < 70.0˚ (NCS) < 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˚ (NCNSe) < 78.2˚ (PSP) < 80.0˚ (NONP) < 82.7˚ (PC2P) < 85.2˚ (PC3P) < 85.8˚ (SeC2P) < 86.5˚ (SeC2P).

The mean L-Pt(II)-L bite angles open in the orders: 40.0˚ (ON) < 42.0˚ (OO) < 43.0˚ (ON) < 45.5˚ (CS) < 52.8˚ (SP) < 53.0˚ (PP); 79.2˚ (NC2N, unsaturated) < 82.7˚ (PC2P) < 96.8˚ (PC3P) < 115.3˚ (PC5P).

The mean L-Pt(III)-L bite angles open in the order: 79.6˚ (PCNCN) < 86.5˚ (NC2NP, NCS2P, PNPNP) < 88.3˚ (NSNSN) < 88.5˚ (NC2NS, PCHCP) < 89.0˚ (SC2P, NCPCN) < 89.4˚ (NC2NP) < 89.7˚ (PC2Si, NCNPN) < 90.0˚ (OC2S) < 90.7˚ (NC2N, NNC2P) < 91.5˚ (PC2P).
M. Melník, P. Mikuš

The range of oxidation state of platinum (zero, +2, +3 and +4), than isomers (+2 only) and ligand isomerism (+2 only). 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. This parallels an increase in the Pt(II) - L 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 borderline 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).

References


(OC₂N) < 91.8˚ (OC₂O, NC₂P) < 92.3˚ (OC₂N, PC₂P) < 93.0˚ (SC₂As) < 93.3˚ (NCNCS) < 93.5˚ (SC₂S) < 94.0˚ (NC₂Se) < 96.3˚ (SPNPS);

87.3˚ (NC₂N, unsaturated) < 89.7˚ (OC₂O) < 92.2˚ (SC₂S) < 98.8˚ (NC₂N, saturated) < 99.0˚ (PC₂P); 89.5˚ (NC₂N) < 90.3˚ (PC₂P) < 102.4˚ (SC₂SC₂S); 87.0˚ (SC₂S) < 95.0˚ (PC₂P) < 99.0˚ (PC₂P, PC₁₃P) < 104.9˚ (PC₂P) < 174.2˚ (AsC₂As) < 175.8˚ (PC₂P) < 176.2˚ (PC₂P).

The mean L-Pt(III)-L bite angle opens in the order: 77.0˚ (NC₂N, unsaturated) < 84.6˚ (NC₂N, saturated) < 89.5˚ (SC₂S) < 90.2˚ (SeC₂Se). The mean L-Pt(IV)-L bite angle opens in the orders: 52.6˚ (PP) < 64.8˚ (CN) < 68.6˚ (SiCSCSi) < 73.5˚ (SCS); 80.8˚ (NC₂N, unsaturated) < 83.2˚ (OC₂O, SiC₂Si) < 83.8˚ (NC₂N, saturated, OC₂N) < 84.8˚ (NC₂S) < 85.0˚ (PC₂P) < 87.7˚ (SC₂S, SeC₂Se) < 91.4˚ (SAsSAs) < 94.9˚ (SeSeSe) < 99.0˚ (NSNS); 90.0˚ (PC₂P) < 90.8˚ (OC₂N) < 91.2˚ (SC₂S) < 92.8˚ (NC₂N) < 93.7˚ (OC₂O) < 99.0˚ (NSNS, SAsSAs).

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, NC₂N, OC₂N, NC₂S, SC₂S, OC₂N, SC₂S, PC₂P and PC₂P, the respective L-Pt-L bite angle classes with an increasing oxidation state of platinum, however in the series: PP, OC₂P, PC₂P, NSNS, SeC₂Se, OC₁₃O and NC₂N, 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 increases. 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).

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).
547


Scientific Research Publishing (SCIRP) is one of the largest Open Access journal publishers. It is currently publishing more than 200 open access, online, peer-reviewed journals covering a wide range of academic disciplines. SCIRP serves the worldwide academic communities and contributes to the progress and application of science with its publication.

Other selected journals from SCIRP are listed as below. Submit your manuscript to us via either submit@scirp.org or Online Submission Portal.