Review Article

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Structural aspects of Pt(η^3-$X^1N^1X^2$)(PL) ($X^{1,2}$ = O, C, or Se) and Pt(η^3-$N^1N^2X^1$)(PL) (X^1 = C, S, or Se) derivatives

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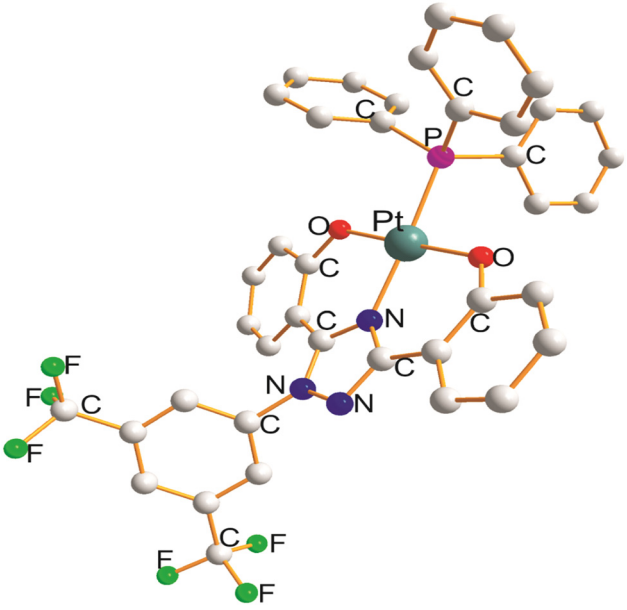
Abstract: This article covers 26 Pt(II) complexes of compositions Pt(η^3-$X^1N^1X^2$)(PL) ($X^{1,2}$ = O, C, or Se) and Pt(η^3-$N^1N^2X^1$)(PL) (X^1 = C, S, or Se). These complexes crystallized in two crystal classes: monoclinic (14 examples) and triclinic (12 examples). The heterotridentate ligand with monodentate PL builds up a distorted square-planar geometry around each Pt(II) atom. Each heterotridentate ligand Pt(η^3-$X^1N^1X^2$)(PL) creates two metallocyclic rings with a common N^1 atom of the $O^1C_2N^1C_3O^2$, $O^1C_3N^1C_3O^2$, $O^1C_2NN^1C_3O^2$, $C^1C_2N^1C_2C^2$, and $Se^1C_2N^1NC_2Se^2$ types. In Pt(η^3-$N^1N^2X^1$)(PL) complexes, the tridentate ligand with a common N^2 atom forms the following types of metallocyclic rings: $N^1C_2N^2C_2C^1$, $N^1C_2N^2NCS^1$, and $N^1CNN^2NCSe^1$. The total mean values of τ_4 for respective complexes as it grows in the sequence: 0.056 (Pt(η^3-$O^1N^1O^2$)(PL)) < 0.091 (Pt(η^3-$Se^1N^1Se^2$)(PL)) < 0.161 (Pt(η^3-$N^1N^2S^1$)(PL)) < 0.174 (Pt(η^3-$N^1N^2Se^1$)(PL)) < 0.188 (Pt(η^3-$C^1N^1C^2$)(PL)) < 0.211 (Pt(η^3-$N^1N^2C^1$)(PL)). The distortion of the square-planar geometry increases in the given sequences. The structural data (Pt–L, L–Pt–L) are analyzed and discussed with attention to the distortion of a square-planar geometry about the Pt(II) atoms as well as of *trans*-influence.

Keywords: structure, heterotridentate, monodentate PL, Pt(II), distortion, *trans*-influence



Graphical abstract

Structure of [Pt(η^3-$C_{22}H_{11}F_6N_3O_2$)(PPh_3)]

List of abbreviations

$C_{10}H_{10}N_5S$	(*N*-(1-(1*H*-benzimidazol-2-yl)ethylidene) carbamohydrazonothiolato)
$C_{12}H_{11}F_6N_3O_2$	(2,2′-(3,5-bis(trifluoromethyl)phenyl)-1*H*-1,2,4-triazole-3,5-diyl)
$C_{12}H_{16}N_2O_4Se_2$	diethyl-3,3′-(diazone-1,2-diyl-*N*)bis(2-(hydroseleno)but-2-enoatato)
$C_{13}H_{11}ClN_6OS$	(*N*-(1-(3-acetyl-1*H*-1,2,4-triazol-5-yl)ethylidene)-*N*-(4-chlorphenyl) carbamohydrazonothiolato)
$C_{13}H_{12}N_6OS$	(*N*-(1-(3-acetyl-1*H*-1,2,4-triazol-5-yl)ethylidene)-*N*-phenylcarbamohydrazonothiolato)
$C_{13}H_9NO_2$	*N*(α,α′-dioxobenzylidene) anilinate
$C_{14}H_{10}N_2O_3$	2-2′-carboxylatophenylazo-4-methylphenolate
$C_{14}H_{10}N_3$	(2-(6-(1*H*-imidazol-5-yl)pyridine-2-yl) phenyl)

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$C_{14}H_{10}N_3$	(2-(6-(3-1*H*-pyrazolyl)-2-pyridyl)phenyl)
$C_{17}H_{11}N$	2,2′-(pyridine-2,6-diyl)diphenyl
$C_{17}H_{14}F_2N_4$	(2-(6-(5-*t*-butyl-1,2,4-triazol-2id-3-yl)pyridine-2-yl)-3,5-difluorophenyl)
$C_{17}H_9F_2N$	(2,2′-(pyridine-2,6-diyl)bis(5-fluorophenyl))
$C_{17}H_9F_2N$	(2,2′-pyridine-2,6-diyl)bis(5-fluorobenzenide)
$C_{18}H_{11}F_2N$	(2-(4-fluoro-2-methylphenyl)-6-(4-fluorophenyl)pyridine)
$C_{18}H_{11}F_2N$	(5-fluoro-2-{6-(fluorobenzene-2-diyl)pyridine-2-yl}-methylbenzenide)
$C_{20}H_{15}NO_2$	(2,6-bis(*O*-phenylene)-4-ethoxycarbonylpyridine)
$C_{24}H_{20}N_3$	(2-(4-(4-dimethylaminophenyl)-2,2′-bipyridin-6-yl)phenyl)
$C_{28}H_{23}N_2$	(3-(4-*t*-butyl-8-(isoquinolin-3-yl)pyridine-2-yl)-2-naphtyl)
$C_{28}H_{24}N_4S_2$	$PhSNC(MeC_6H_4)N\text{-}NC(MeC_6H_4)NSPh$
$C_{30}H_{19}N_2$	(3-(4-phenyl-6-(isoquinolin-3-yl)pyridine-2-yl)-2-naphtyl)
CL	ligand coordinated via the C atom
m	monoclinic
NL	ligand coordinated via the N atom
OL	ligand coordinated via the O atom
$P(C_{14}H_{19}O_5)(Ph_2)$	benzo-15-crown[5] diphenylphosphine
$P(CH_2Et)_3$	tri-*n*-propylphosphine
$P(CH_2Ph)_3$	tribenzylphosphine
$P(tolyl)_3$	tris(2-methylphenyl)phosphine
Pcy_3	tricyclohexylphosphine
PL	ligand coordinated via the P atom
PMe_3	trimethylphosphine
PPh_3	triphenylphosphine
tfh	tetrahydrofuran
tr	triclinic

1 Introduction

Organophosphines as soft P donor ligands are very useful for building a wide variety of platinum complexes. Research activity in this field is always very active. Much attention is paid to heterotridentate organomonophosphines as ligands. Recently, we analyzed and classified structural data of monomeric Pt(II) complexes in which a distorted square-planar geometry about each Pt(II) atom is built up by heterotridentate organomonophosphine with monodentate Y ligands: Pt(η^3-$P^1N^1N^2$)(Y), Pt(η^3-$P^1N^1X^1$)(Y) (X^1 = O^1, C^1, S^1, or Se^2); Pt(η^3-$N^1P^1N^2$)(Cl); Pt(η^3-$S^1P^1S^2$)(Cl); Pt(η^3-$P^1S^1Cl^1$)(Y); and Pt(η^3-$P^1Si^1N^1$)(OL) [1].

Structural data of monomeric Pt(II) complexes of the compositions: Pt(η^3-$P^1C^1C^2$)(Y) (Y = NL or I) and Pt(η^3-$P^1C^1N^1$)(Y) (Y = OL, NL, CL, Cl, or Br) were also analyzed and classified [2]. There are several monomeric Pt(II) complexes where the inner coordination sphere is built up by the homotridentate ligand with monodentate organomonophosphine of the composition: Pt(η^3-$X^1X^2X^3$)(PL) (X = N, S, or Te). Their structural data were also analyzed and classified [3].

The chemistry of platinum complexes is important in the fields of biochemistry, catalysis, and theory. The complexes presented in the article were used predominantly in catalytic processes or theoretical studies. This study aims to analyze and classify the structural data of Pt(η^3-$X^1N^1X^2$)(PL) ($X^{1,2}$ = O, C, or Se) and Pt(η^3-$N^1N^2X^1$)(PL) (X^1 = C, S, or Se).

2 Structural aspects of Pt(η^3-$X^1N^1X^2$)(PL) and Pt(η^3-$N^1N^2X^1$)(PL) derivatives

There are 26 complexes that are based on heterotridentate ligands, and they can be divided into two groups, one of the compositions Pt(η^3-$X^1N^1X^2$)(PL), where (X^1, X^2 = O^1, O^2; C^1, C^2; or Se^1, Se^2), and the other Pt(η^3-$N^1N^2X^1$)(PL) (X^1 = C^1, S^1, or Se^1). Their structural data are given in Tables 1 and 2, respectively. Structural data used in this study for discussion and calculations were obtained from the Cambridge Crystallographic Database (CCDB).

In the first step, Pt–L bond distances as well as L–Pt–L angles (*cis*, *trans*) were identified from the structures registered in the CCDB via program Diamond. In the second step, the sum of covalent radii was calculated from known values of covalent radii of particular atoms in the complexes. In the third step, distortion of the square-planar geometry by parameter τ_4 was calculated according to the formula $\tau_4 = \frac{360 - (\alpha + \beta)}{141}$, where α and β are *trans* angles in the complexes. Finally, these published and calculated data were compared and discussed for particular complexes within the two above-mentioned groups and their subgroups to find relevant structural trends.

2.1 Pt(η^3-$X^1N^1X^2$)(PL) derivatives

There are 12 examples of such a type, and the structural data are given in Table 1. In three complexes, one monoclinic [Pt(η^3-$C_{13}H_9NO_2$)(PPh_3)] [4] and two triclinic [Pt(η^3-$C_{22}H_{11}F_6N_3O_2$)(PPh_3)] (at 173 K) [5] and [Pt(η^3-$C_{14}H_{10}N_2O_3$)

Table 1: Structural data for Pt(η^3-$X^1N^1X^2$)(PL) derivatives (X^1, X^2 = O^1, O^2; C^1, C^2; or Se^1, Se^2)[a]

Complex Pt(η^3-$X^1N^1X^2$)(PL)	Crystal cl. Space gr. *z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	Chromophore (chelate rings) τ4[b]	Pt–L[c] (Å)	L–Pt–L[c] (°)	Ref.
[Pt{η^3-$C_{13}H_9NO_2$-$O^1N^1O^2$}· (PPh_3)]	*m* $P2_1/n$ 4	15.721(4) 9.106(2) 18.500(5)	106.05(2)	PtO_2NP ($O^1C_2N^1C_3O^2$) 0.081	O^1 1.975(9) N^1 2.064(12) O^2 1.996(9) P 2.248	O^1, N^1 82.4(4)[d] N^1, O^2 94.8(4)[e] O^1, O^2 176.1(4) O^1, P 91.5(3) O^2, P 91.5(3) N^1, P 172.4	[4]
[Pt{η^3-$C_{22}H_{11}F_6N_3O_2$-$O^1N^1O^2$}·(PPh_3)] (at 173 K)	*tr* $P\bar{1}$ 2	9.418(0) 13.069(0) 14.123(0)	81.75(0) 88.58(0) 80.29(0)	PtO_2NP ($O^1C_3N^1C_3O^2$) 0.028	O^1 1.994 N^1 2.021 O^2 2.004 P 2.256	O^1, N^1 90.6[e] N^1, O^2 90.2[e] O^1, O^2 179.0 O^1, P 90.6 O^2, P 87.5 N^1, P 177.0	[5]
[Pt{η^3-$C_{14}H_{10}N_2O_3$-$O^1N^1O^2$}·(PPh_3)] (at 150 K)	*tr* $P\bar{1}$ 2	8.928(0) 12.223(0) 14.145(0)	73.64(0) 83.72(0) 69.36(0)	PtO_2NP ($O^1C_2NN^1C_3O^2$) 0.06	O^1 1.995 N^1 2.000 O^2 1.988 P 2.251	O^1, N^1 88.2[e] N^1, O^2 92.0[e] O^1, O^2 176.5 O^1, P 89.0 O^2, P 90.7 N^1, P 175.0	[6]
[Pt{η^3-$C_{17}H_9F_2N$-$C^1N^1C^2$}·{P(*o*-tolyl)$_3$}]·$CHCl_3$ (at 150 K)	*m* $C2_1/c$ 8	36.465(0) 8.393(0) 23.214(0)	104.09(0)	PtC_2NP ($C^1C_2N^1C_2C^2$) 0.168	C^1 2.085 N^1 2.024 C^2 2.094 P 2.255	C^1, N^1 79.8[d] C^2, N^1 79.5[d] C^1, C^2 158.9 C^1, P 103.1 C^2, P 97.5 N^1, P 177.3	[7]
[Pt{η^3-$C_{18}H_{11}F_2N$-$C^1N^1C^2$}·{P(CH_2Ph)$_3$}]·1.4$CHCl_3$ (at 150 K)	*m* $P2_1/a$ 4	14.619(0) 17.398(0) 28.629(0)	98.64(0)	PtC_2NP ($C^1C_2N^1C_2C^2$) 0.282	C^1 2.062 N^1 2.029 C^2 2.071 P 2.241	C^1, N^1 79.9[d] C^2, N^1 80.2[d] C^1, C^2 158.8 C^1, P 102.2 C^2, P 98.7 N^1, P 169.8	[8]
[Pt{η^3-$C_{17}H_9F_2N$-$C^1N^1C^2$}·{P(CH_2Ph)$_3$}] (at 150 K)	*tr* $P\bar{1}$ 2	12.121(0) 12.191(0) 12.273(0)	68.82(0) 69.92(0) 64.64(0)	PtC_2NP ($C^1C_2N^1C_2C^2$) 0.242	C^1 2.075 N^1 2.033 C^2 2.085 P 2.228	C^1, N^1 79.8[d] C^2, N^1 80.0[d] C^1, C^2 159.2 C^1, P 103.8 C^2, P 96.9 N^1, P 168.7	[7]
[Pt{η^3-$C_{18}H_{11}F_2N$-$C^1N^1C^2$}·{P(CH_2Et)$_3$}] (at 150 K)	*m* $P2_1/c$ 4	9.962(0) 9.222(0) 27.300(0)	100.22(0)	PtC_2NP ($C^1C_2N^1C_2C^2$) 0.186	C^1 2.056 N^1 2.027 C^2 2.074 P 2.299	C^1, N^1 79.9[d] C^2, N^1 80.5[d] C^1, C^2 159.8 C^1, P 102.1 C^2, P 97.7 N^1, P 174.2	[9]
[Pt{η^3-$C_{17}H_9F_2N$-$C^1N^1C^2$}·(PMe_3)] (at 150 K)	*m* $C2_1/c$ 4	23.994(0) 12.511(0) 12.169(0)	107.33(0)	PtC_2NP ($C^1C_2N^1C_2C^2$) 0.223	C^1 2.070 N^1 2.005 C^2 2.065 P 2.243	C^1, N^1 79.5[d] C^2, N^1 80.2[d] C^1, C^2 158.5 C^1, P 92.0 C^2, P 102.5 N^1, P 170.0	[10]

(Continued)

Table 1: *Continued*

Complex Pt(η^3-$X^1N^1X^2$)(PL)	Crystal cl. Space gr. *z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	Chromophore (chelate rings) τ4[b]	Pt–L[c] (Å)	L–Pt–L[c] (°)	Ref.
[Pt{η^3-$C_{17}H_{11}N$-$C^1N^1C^2$}·(PPh_3)] (at 100 K)	*m* $P2_1/c$ 4	13.958(0) 9.423(0) 20.659(0)	95.68(0)	PtC_2NP ($C^1C_2N^1C_2C^2$) 0.222	C^1 2.073 N^1 2.049 C^2 2.074 P 2.241	C^1, N^1 79.7[d] C^2, N^1 80.2[d] C^1, C^2 158.8 C^1, P 103.0 C^2, P 98.7 N^1, P 169.8	[11]
[Pt{η^3-$C_{20}H_{15}NO_2$-$C^1N^1C^2$}·(PPh_3)] (at 150 K)	*m* $P2_1/c$ 4	17.866(0) 17.138(0) 9.758(0)	101.97(0)	PtC_2NP ($C^1C_2N^1C_2C^2$) 0.213	C^1 2.075 N^1 2.007 C^2 2.073 P 2.252	C^1, N^1 79.8[d] C^2, N^1 80.4[d] C^1, C^2 159.0 C^1, P 93.2 C^2, P 103.2 N^1, P 171.0	[12]
[Pt{η^3-$C_{17}H_{11}N$-$C^1N^1C^2$}·{P(η^1-$C_{14}H_{19}O_5$)($Ph)_2$}]CH_2Cl_2 (at 100 K)	*tr* $P\bar{1}$ 4	9.114(1) 20.627(2) 22.024(2)	83.56(1) 82.70(1) 88.67(1)	PtC_2NP ($C^1C_2N^1C_2C^2$) 0.219	C^1 2.082 N^1 2.033 C^2 2.083 P 2.227	C^1, N^1 79.4[d] C^2, N^1 80.1[d] C^1, C^2 157.3 C^1, P 100.6 C^2, P 101.0 N^1, P 171.8	[13]
[Pt{η^3-$C_{12}H_{16}N_2O_4Se_2$-$Se^1N^1Se^2$}·(PPh_3)]	*m* $P2_1/c$ 4	9.259(0) 15.525(0) 23.892(0)	110.61(0)	$PtSe_2NP$ ($Se^1C_2N^1NC_2Se^2$) 0.091	Se^1 2.394 N^1 2.078 Se^2 2.349 P 2.259	Se^1, N^1 83.3[d] N^1, Se^2 98.3[e] Se^1, Se^2 176.3 Se^1, P 87.2 Se^2, P 90.7 N^1, P 170.9	[14]

[a]The mean value is tabulated when more than one chemically equivalent distance or angle is present. The first number in parentheses is the e.s.d. and the second is the maximum deviation from the mean value. [b]Parameter τ_4 – degree of distortion of square-planar geometry. [c]The chemical identity of the coordinated atom or ligand is specified in these columns. [d]Five-membered metallocyclic ring, [e]Six-membered metallocyclic ring.

(PPh_3)] (at 150 K) [6], heterotridentate ligands via $O^1N^1O^2$ donor atoms and monodentate PPh_3 ligands build up a distorted square-planar geometry about each Pt(II) atom. The structure of [Pt(η^3-$C_{22}H_{11}F_6N_3O_2$)(PPh_3)] [5] is shown in Figure 1 as an example. Each chelate ligand forms two metallocyclic rings with the common N^1 atom of the $O^1C_2N^1C_3O^2$ (monoclinic), $O^1C_3N^1C_3O^2$ (triclinic), and $O^1C_2NN^1C_3O^2$ (triclinic) types. The values of the respective chelate O^1–Pt–N^1/N^1–Pt–O^2 angles are 82.4/94.8° (monoclinic), 90.6/90.2° (triclinic), and 88.2/92.0° (triclinic).

The remaining L–Pt–L bond angles open in the order (mean values): 89.9 (±2.4)° (O^2–Pt–P) < 90.4 (±1.4)° (O^1–Pt–P) < 174.8 (±2.2)° (N^1–Pt–P) < 177.2 (±1.8)° (O^1–Pt–O^2). The Pt–L bond distance elongates in the sequence (mean values): 1.988 (±0.004) Å (Pt–O^1, *trans* to O^2) < 1.996 (±0.008) Å (Pt–O^2) < 2.028 (±0.036) Å (Pt–N^1, *trans* to P) < 2.251 (±0.005) Å (Pt–P).

In the following eight complexes: monoclinic [Pt(η^3-$C_{17}H_9F_2N$)({P(*o*-tolyl)$_3$}]·$CHCl_3$ (at 150 K) [7], monoclinic [Pt(η^3-$C_{18}H_{11}F_2N$) {P($CH_2Ph)_3$}]·$14CHCl_3$ (at 150 K) [8], triclinic [Pt(η^3-$C_{17}H_9F_2N$){P($CH_2Ph)_3$}] (at 150 K) [8], monoclinic [Pt(η^3-$C_{18}H_{11}F_2N$) {P($CH_2Et)_3$}] (at 150 K) [9], monoclinic [Pt(η^3-$C_{17}H_9F_2N$)(PMe_3)] (at 150 K) [10], monoclinic [Pt(η^3-$C_{17}H_{11}N$)(PPh_3)] (at 100 K) [11], monoclinic [Pt(η^3-$C_{20}H_{15}NO_2$)(PPh_3)] (at 150 K) [12], and triclinic [Pt(η^3-$C_{17}H_{11}N$){P(η^1-$C_{14}H_{19}O_5$)($Ph)_2$}]·CH_2Cl_2 (at 150 K) [13]; each heterotridentate ligand via $C^1N^1C^2$ donor atoms with monodentate PL donor ligand creates a distorted square-planar geometry about each Pt(II) atom. Each chelate ligand forms a pair of five-membered metallocycles with a common N^1 atom of the $C^1C_2N^1C_2C^2$ type with the mean values of C^1–Pt–N^1 and N^1–Pt–C^2 angles 79.7(±0.3)° and 80.1(±0.4)°, respectively. The mean values of the remaining values of L–Pt–L bond angles open in the order: 98.4(±2.6)° (C^2–Pt–P) < 102.3(±1.7)° (C^1–Pt–P) <

Table 2: Structural data for Pt(η^3-$N^1N^2X^1$)(PL) derivatives[a] (X^1 = C^1, S^1, Se^1)[a]

Complex Pt(η^3-$N^1N^2X^1$)(PL)	Crystal cl. space gr. *z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	Chromophore (chelate rings) τ_4[b]	Pt–L[c] (Å)	L–Pt–L[c] (°)	Ref.
[Pt{η^3-$C_{14}H_{10}N_3$-$N^1N^2C^1$}·(PPh_3)]ClO_4 (at 173 K)	*trP*$\bar{1}$2	9.406(0) 12.549(0) 13.139(0)	70.95(0) 73.13(0) 79.99(0)	PtN_2CP ($N^1C_2N^2C_2C^1$) 0.168	N^1 2.124 N^2 2.022 C^1 2.018 P 2.243	N^1, N^2 78.2[d] N^2, C^1 80.6[d] N^1, C^1 158.8 N^1, P 103.2 C^1, P 97.1 N^2, P 177.5	[15]
[Pt{η^3-$C_{14}H_{10}N_3$-$N^1N^2C^1$}·(PPh_3)]ClO_4 (at 193 K)	*trP*$\bar{1}$2	9.198(0) 9.511(0) 16.467(0)	91.57(0) 92.52(0) 92.95(0)	PtN_2CP ($N^1C_2N^2C_2C^1$) 0.178	N^1 2.101 N^2 2.025 C^1 2.005 P 2.227	N^1, N^2 78.5[d] N^2, C^1 81.1[d] N^1, C^1 159.1 N^1, P 103.0 C^1, P 97.6 N^2, P 175.8	[15]
[Pt{η^3-$C_{28}H_{23}N_2$-$N^1N^2C^1$}·(Pcy_3)] ClO_4·$2CH_3CN$ (at 253 K)	*mP*2_1/*n*4	16.423(3) 17.976(4) 17.270(4)	110.42(3)	PtN_2CP ($N^1C_2N^2C_2C^1$) 0.307	N^1 2.103 N^2 2.023 C^1 2.054 P 2.283	N^1, N^2 78.5[d] N^2, C^1 79.7[d] N^1, C^1 156.4 N^1, P 101.6 C^1, P 102.4 N^2, P 160.3	[16]
[Pt{η^3-$C_{30}H_{19}N_2$-$N^1N^2C^1$}·(Pcy_3)] ClO_4·0.5 CH_3CN (at 253 K)	*mC*2_1/*c*4	26.188(5) 14.708(3) 24.052(5)	99.88(3)	PtN_2CP ($N^1C_2N^2C_2C^1$) 0.266	N^1 2.154 N^2 2.029 C^1 2.042 P 2.297	N^1, N^2 77.8[d] N^2, C^1 80.5[d] N^1, C^1 156.6 N^1, P 103.3 C^1, P 99.8 N^2, P 165.9	[16]
[Pt{η^3-$C_{30}H_{19}N_2$-$N^1N^2C^1$}·(PPh_3)] ClO_4·MeOH (at 253 K)	*trP*$\bar{1}$2	10.713(2) 13.300(3) 16.081(3)	71.77(3) 75.45(3) 77.53(3)	PtN_2CP ($N^1C_2N^2C_2C^1$) 0.203	N^1 2.133 N^2 1.975 C^1 2.000 P 2.243	N^1, N^2 77.6[d] N^2, C^1 81.1[d] N^1, C^1 158.4 N^1, P 105.1 C^1, P 96.3 N^2, P 173.0	[16]
[Pt{η^3-$C_{17}H_{14}F_2N_4$-$N^1N^2C^1$}·(PPh_3)]thf (at 223 K)	*trP*$\bar{1}$2	10.215(0) 10.881(0) 15.715(0)	96.11(0) 104.36(0) 104.29(0)	PtN_2CP ($N^1C_2N^2C_2C^1$) 0.179	N^1 2.076 N^2 2.033 C^1 2.027 P 2.241	N^1, N^2 78.3[d] N^2, C^1 80.7[d] N^1, C^1 158.8 N^1, P 104.2 C^1, P 96.8 N^2, P 176.0	[17]
[Pt{η^3-$C_{24}H_{20}N_3$-$N^1N^2C^1$}·(PPh_3)]ClO_4 (at 113 K)	*trP*$\bar{1}$2	8.526(2) 10.015(3) 21.052(6)	101.27(0) 101.72(0) 90.23(0)	PtN_2CP ($N^1C_2N^2C_2C^1$) 0.184	N^1 2.147 N^2 2.022 C^1 2.022 P 2.246	N^1, N^2 77.8[d] N^2, C^1 80.9[d] N^1, C^1 158.2 N^1, P 106.1 C^1, P 95.3 N^2, P 175.8	[18]
[Pt{η^3-$C_{14}H_{10}N_3$-$N^1N^2C^1$}·(PPh_3)]ClO_4	*mP*2_1/*n*4	15.135(1) 10.811(0) 17.558(1)	93.06(0)	PtN_2CP ($N^1C_2N^2C_2C^1$) 0.202	N^1 2.130 N^2 2.029 C^1 2.005 P 2.242	N^1, N^2 79.0[d] N^2, C^1 81.0[d] N^1, C^1 157.4 N^1, P 101.8 C^1, P 100.6 N^2, P 174.1	[19]
[Pt{η^3-$C_{10}H_{10}N_3S$-$N^1N^2S^1$}·(PPh_3)] Cl·CH_3CN·H_2O	*mP*2_1/*n*4	10.505(5) 21.722(5)	95.11(0)	PtN_2SP ($N^1C_2N^2NCS^1$) 0.145	N^1 2.092 N^2 2.057	N^1, N^2 78.8[d] N^2, S^1 83.5[d]	[20]

(Continued)

Table 2: *Continued*

Complex Pt(η^3-$N^1N^2X^1$)(PL)	Crystal cl. space gr. *z*	*a* (Å) *b* (Å) *c* (Å)	*α* (°) *β* (°) *γ* (°)	Chromophore (chelate rings) τ_4[b]	Pt–L[c] (Å)	L–Pt–L[c] (°)	Ref.
		14.104(5)			S^1 2.249 P 2.257	N^1, S^1 162.3 N^1, P 103.5 S^1, P 94.2 N^2, P 177.2	
[Pt{η^3-$C_{13}H_{11}ClN_6OS$-$N^1N^2S^1$}·(PPh_3)]·Me_2SO	*trP*$\bar{1}$2	9.037(0) 14.343(0) 15.183(0)	103.87(0) 101.62(0) 105.96(0)	PtN_2SP ($N^1C_2N^2NCS^1$) 0.148	N^1 2.029 N^2 2.039 S^1 2.261 P 2.251	N^1, N^2 79.0[d] N^2, S^1 82.9[d] N^1, S^1 161.9 N^1, P 99.7 S^1, P 90.4 N^2, P 177.3	[21]
[Pt{η^3-$C_{13}H_{12}N_6OS$-$N^1N^2S^1$}·(PPh_3)]·Me_2SO	*trP*$\bar{1}$2	9.195(0) 13.929(0) 14.943(0)	70.20(0) 76.73(0) 73.55(0)	PtN_2SP ($N^1C_2N^2NCS^1$) 0.15	N^1 2.022 N^2 2.031 S^1 2.258 P 2.250	N^1, N^2 79.0[d] N^2, S^1 83.1[d] N^1, S^1 162.1 N^1, P 97.9 S^1, P 100.1 N^2, P 176.7	[22]
[Pt{η^3-$C_{20}H_{31}N_9S_2$-$N^1N^2S^1$}·(PPh_3)]EtOH (at 100 K)	*trP*$\bar{1}$2	10.769(5) 12.054(5) 17.499(5)	81.09(2) 89.09(6) 70.97(1)	PtN_2SP ($N^1C_2N^2NCS^1$) 0.184	N^1 2.042 N^2 2.000 S^1 2.270 P 2.268	N^1, N^2 79.0[d] N^2, S^1 82.0[d] N^1, S^1 161.0 N^1, P 100.0 S^1, P 96.0 N^2, P 173.0	[23]
[Pt{η^3-$C_{28}H_{24}N_4S_2$-$N^1N^2S^1$}·(PPh_3)].0.5thf	*mP*$2_1/c$4	14.234(5) 18.922(3) 16.032(3)	105.19(2)	PtN_2SP ($N^1CNN^2NCS^1$) 0.179	N^1 2.031(8) N^2 1.987(7) S^1 2.266(3) P 2.279(3)	N^1, N^2 78.5(4)[d] N^2, S^1 81.6(2)[d] N^1, S^1 162.2(2) N^1, P 99.9(2) S^1, P 99.7(1) N^2, P 172.5(2)	[24]
[Pt{η^3-$C_{28}H_{24}N_4Se_2$-$N^1N^2Se^1$}·(PPh_3)]·Et_2O	*mP*$2_1/c$4	14.410(1) 19.003(3) 16.169(2	105.72(1)	PtN_2SeP ($N^1CNN^2NCSe^1$) 0.174	N^1 2.020(1) N^2 1.980(1) Se^1 2.368(2) P 2.272(4)	N^1, N^2 78.7(4)[d] N^2, Se^1 82.3(3)[d] N^1, Se^1 162.0 N^1, P 100.0(3) Se^1, P 98.6(1) N^2, P 173.4(1)	[25]

[a]The mean value is tabulated when more than one chemically equivalent distance or angle is present. The first number in parentheses is the e.s.d. and the second is the maximum deviation from the mean value, [b]Parameter τ_4 – degree of distortion of square-planar geometry, [c]The chemical identity of the coordinated atom or ligand is specified in these columns, [d]Five-membered metallocyclic ring.

158.8(±1.5)° (C^1–Pt–C^2) < 171.8(±3.1)° (N^1–Pt–P). The Pt–L bond distance (mean value) elongates in the sequence 2.036(±0.013) Å (Pt–N^1, *trans* to P) < 2.072(±0.013) Å (Pt–C^1, *trans* to C^2) < 2.080(±0.014) Å (Pt–C^2) < 2.248(±0.046) Å (Pt–P, *trans* to N^1).

The structure of monoclinic [Pt(η^3-$C_{12}H_{16}N_2O_4Se_2$)(PPh_3)] [14] is shown in Figure 2. The heterotridentate $Se^1N^1Se^2$ donor ligand with monodentate PPh_3 ligand builds up a distorted square-planar geometry about the Pt(II) atom. The chelate ligand creates five- and six-membered metallocycles with a common N^1 atom of the $Se^1C_2N^1NC_2Se^2$ type. The values of Se^1–Pt–N^1 and N^1–Pt–Se^1 angles are 83.3° and 98.3°. The remaining L–Pt–L bond angles open in the order: 87.2° (Se^1–Pt–P) < 90.7° (Se^2–Pt–P) < 170.9° (N^1–Pt–P) < 176.3° (Se^1–Pt–Se^2). The Pt–L bond distance elongates in the sequence: 2.078 Å (Pt–N^1, *trans* to P) < 2.259 Å (Pt–P) < 2.349 Å (Pt–Se^2, *trans* to Se^1) < 2.394 Å (Pt–Se^1) (Table 1).

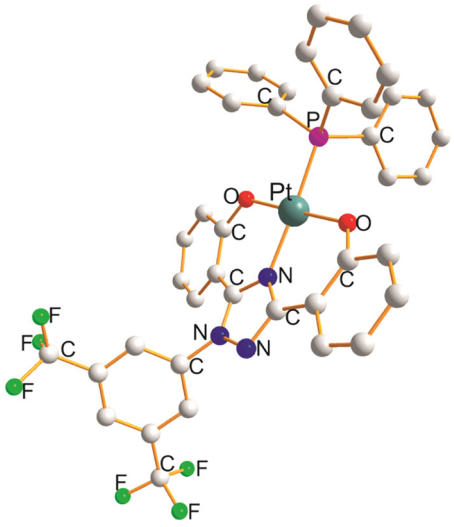

Figure 1: Structure of $[Pt(\eta^3\text{-}C_{22}H_{11}F_6N_3O_2)(PPh_3)]$ [5].

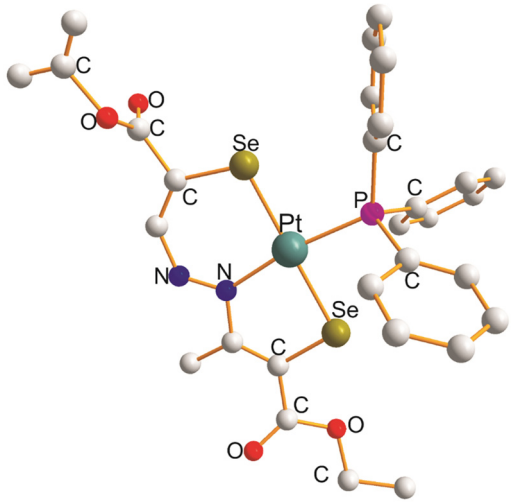

Figure 2: Structure of $[Pt(\eta^3\text{-}C_{12}H_{16}N_2O_4Se_2)(PPh_3)]$ [14].

2.2 $Pt(\eta^3\text{-}N^1N^2X^1)(PL)$ (X^1 = C^1, S^1, or Se^1) derivatives

Structural data for these complexes are displayed in Table 2. In eight complexes, triclinic $[Pt(\eta^3\text{-}C_{14}H_{10}N_3)(PPh_3)]ClO_4$ (at 173 K) [15], triclinic $[Pt(\eta^3\text{-}C_{14}H_{10}N_3)(PPh_3)]ClO_4$ (at 273 K) [15], monoclinic $[Pt(\eta^3\text{-}C_{28}H_{23}N_2)(Pcy_3)]ClO_4{\cdot}2CH_3CN$ (at 253 K) [16], monoclinic $[Pt(\eta^3\text{-}C_{30}H_{19}N_2)(Pcy_3)]ClO_4{\cdot}0.5CH_3CN$ [16], triclinic $[Pt(\eta^3\text{-}C_{30}H_{19}N_2)(PPh_3)]ClO_4{\cdot}MeOH$ (at 253 K) [16], triclinic $[Pt(\eta^3\text{-}C_{17}H_{14}F_2N_4)(PPh_3)]$thf (at 223 K) [17], triclinic $[Pt(\eta^3\text{-}C_{24}H_{20}N_3)(PPh_3)]ClO_4$ (at 113 K) [18], and monoclinic $[Pt(\eta^3\text{-}C_{14}H_{10}N_3)(PPh_3)]ClO_4$ [19], each heterotridentate ligand via $N^1N^2C^1$ donor atoms with monodentate PL ligand builds up a distorted square-planar geometry about the Pt(II) atom. Each heterotridentate ligand creates a pair of five-membered metallocycles with a common N^2 atom of the $N^1C_2N^2C_2C^1$ type. The N^1–Pt–N^2 and N^2–Pt–C^1 bond angles (mean values) are 78.2(±0.5)° and 80.7(±1.0)°. The remaining L–Pt–L bond angles (mean values) open in the order 98.3(±4.1)° (C^1–Pt–P) < 103.5(±2.6)° (N^1–Pt–P) < 157.9(±1.5)° (N^1–Pt–C^1) < 172.3(±7.5)° (N^2–Pt–P). The Pt–L bond distance elongates (mean values) in the sequences: 2.020(±0.045) Å (Pt–N^2, *trans* to P) < 2.022(±0.032) Å (Pt–C^1, *trans* to N^1) < 2.124(±0.048) Å (Pt–N^1, *trans* to C^1) < 2.252(±0.045) Å (Pt–P, *trans* to N^2).

The heterotridentate ligands coordinated via $N^1N^2S^1$ donor atoms with monodentate PPh_3 build up a distorted square-planar geometry about each Pt(II) atom. There are five such complexes: monoclinic $[Pt(\eta^3\text{-}C_{10}H_{10}N_5S)(PPh_3)]Cl{\cdot}MeCN{\cdot}H_2O$ [20], triclinic $[Pt(\eta^3\text{-}C_{13}H_{11}ClN_6OS)(PPh_3)]Me_2SO$ [21], triclinic $[Pt(\eta^3\text{-}C_{13}H_{12}N_6OS)(PPh_3)]Me_2SO$ [22], triclinic $[Pt(\eta^3\text{-}C_{20}H_{31}N_9S_2)(PPh_3)]$EtOH (at 100 K) [23], and monoclinic $[Pt(\eta^3\text{-}C_{28}H_{24}N_4S_2)(PPh_3)]{\cdot}0.5$thf [24]. The structure of $[Pt(\eta^3\text{-}C_{10}H_{10}N_5S)(PPh_3)]^+$ [20] is shown in Figure 3 as an example. Each heterotridentate ligand in these complexes creates two five-membered metallocycles with a common N^2 atom of the $N^1C_2N^2C_2S^1$ [20–22], $N^1C_2N^2NCS^1$ [23], and $N^1CNN^2NCS^1$ [24] types. The mean values of N^1–Pt–N^2 and N^2–Pt–S^1 bond angles are 78.8(±0.3)° and 82.6(±1.4)°. The remaining L–Pt–L bond angles (mean values) open in the sequence: 69.0(±3.8)° (S^1–Pt–P) < 99.8(±3.6)° (N^1–Pt–P) < 161.5(±1.8)° (N^1–Pt–S^1) < 175.3(±2.8)° (N^2–Pt–P). The Pt–L bond distance (mean values) elongates in the order: 2.022(±0.035) Å (Pt–N^2, *trans* to P) < 2.049(±0.043) Å (Pt–N^1, *trans* to S^1) < 2.260(±0.010) Å (Pt–S^1) < 2.262(±0.018) Å (Pt–P) (Table 2).

The structure of $[Pt(\eta^3\text{-}C_{28}H_{24}N_4Se_2)(PPh_3)]{\cdot}Et_2O$ [25] is shown in Figure 4. This is the only example with heterotridentate ligand coordinated via $N^1N^2Se^1$ donor atoms.

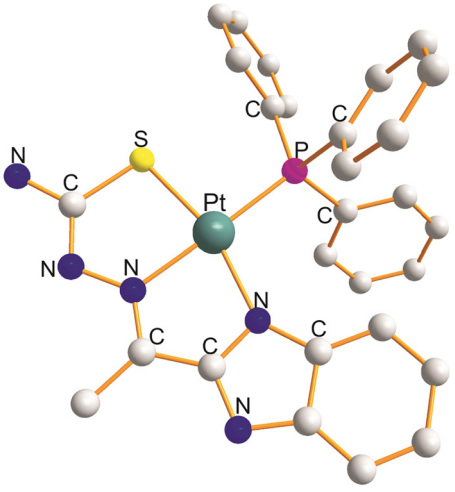

Figure 3: Structure of $[Pt(\eta^3\text{-}C_{10}H_{10}N_5S)(PPh_3)]^+$ [20].

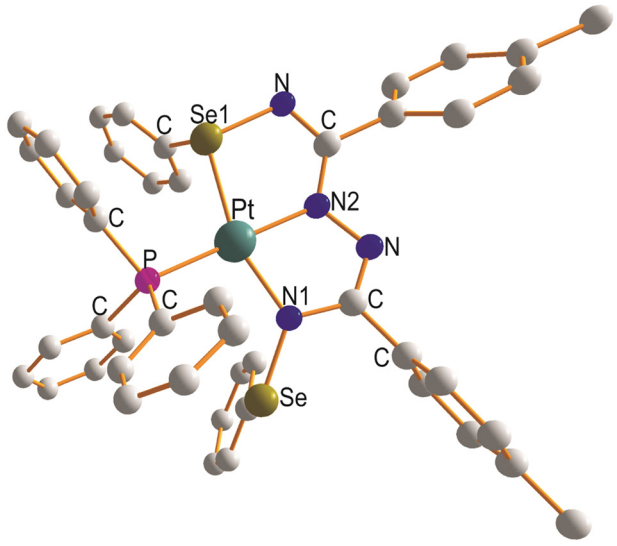

Figure 4: Structure of [Pt(η^3-$C_{28}H_{24}N_4Se_2$)(PPh_3)] [25].

Monodentate PPh_3 completed a distorted square-planar geometry about the Pt(II) atom. The heterotridentate ligand forms two five-membered metallocyclic rings of the $N^1CNN^2NCSe^1$ type. The values of N^1–Pt–N^2 and N^2–Pt–Se^1 bond angles are 78.7(4)° and 82.3(3)°, respectively. The remaining L–Pt–L bond angles open in the order: 98.6(1)° (N^1–Pt–P) < 100.0(3)° (Se^1–Pt–P) < 162.0° (N^1–Pt–Se^1) < 173.4(1)° (N^2–Pt–P). The Pt–L bond distance elongates in the order: 1.980(1) Å (Pt–N^2, *trans* to P) < 2.020(1) Å (Pt–N^1, *trans* to Se^1) < 2.272(4) Å (Pt–P) < 2.368(2) Å (Pt–Se^1) (Table 2).

3 Conclusions

This structural study includes 26 monomeric Pt(II) coordination complexes with compositions of Pt(η^3-$X^1N^1X^2$) (PL) ($X^{1,2}$ = O^1,O^2; C^1,C^2; or Se^1, Se^2) and Pt(η^3-$N^1N^2X^1$) (PL) (X^1 = C^1,S^1, or Se^1). These complexes crystallized in two crystal classes: monoclinic (14 examples) and triclinic (12 examples). The variable combination of donor atoms of heterotridentates which with PL build up Pt(η^3-$X^1N^1X^2$)(PL) and Pt (η^3-$N^1N^2X^1$)(PL) can be divided into two sub-groups. In each sub-group, the Pt–L bond distances (mean values) with sums of Pt–L(x4) bond distances are

3.1 Pt(η^3-$X^1N^1X^2$)(PL)

Pt(η^3-$O^1N^1O^2$)(PL): 1.986 Å (Pt–O^1); 2.043 Å (Pt–N^1); 1.996 Å (Pt–O^2); 2.252 Å (Pt–P); Σ 8.28 Å [4–6]; Σ 3.27 Å, covalent radius.

Pt(η^3-$C^1N^1C^2$)(PL): 2.072 Å (Pt–C^1); 2.036 Å (Pt–N^1); 2.080 Å (Pt–C^2); 2.248 Å (Pt–P); Σ 8.436 Å [7–13]; Σ 3.35 Å, covalent radius

Pt(η^3-$Se^1N^1Se^2$)(PL): 2.394 Å (Pt–Se^1); 2.078 Å (Pt–N^1); 2.349 Å (Pt–Se^2); 2.259 Å (Pt–P); Σ 8.98 Å [14]; Σ 4.13 Å, covalent radius.

3.2 Pt(η^3-$N^1N^2X^1$)(PL)

Pt(η^3-$N^1N^2C^1$)(PL): 2.124 Å (Pt–N^1); 2.020 Å (Pt–N^2); 2.022 Å (Pt–C^1); 2.25 Å (Pt–P); Σ 8.418 Å [15–19]; Σ 3.33 Å, covalent radius;

Pt(η^3-$N^1N^2S^1$)(PL): 2.043 Å (Pt–N^1); 2.028 Å (Pt–N^2); 2.258 Å (Pt–S^1); 2.259 Å (Pt–P); Σ 8.588 Å [20–24]; Σ 3.58 Å, covalent radius;

Pt(η^3-$N^1N^2Se^1$)(PL): 2.020 Å (Pt–N^1); 1.98 Å (Pt–N^2); 2.363 Å (Pt–Se^1); 2.272 Å (Pt–P); Σ 8.640 Å [25]; Σ 3.72 Å, covalent radius.

As expected, the sums of respective Pt–L (×4) bond distances grow with a covalent radius of coordinated donor atoms. The Pt–L bond distance in Pt(η^3-$X^1N^1X^2$) (PL) derivatives elongates in the orders (mean values):

Pt–X^1(*trans* to X^2): 1.985 Å ($X^{1,2}$ = O) < 2.072 Å ($X^{1,2}$ = C) < 2.394 Å ($X^{1,2}$ = Se);

Pt–X^2(*trans* to X^1): 2.000 Å ($X^{1,2}$ = O) < 2.080 Å ($X^{1,2}$ = C) < 2.349 Å ($X^{1,2}$ = Se);

Pt–N^1(*trans* to P, when $X^{1,2}$ are): 2.036 Å (C) < 2.043 Å (O) < 2.078 Å (Se);

Pt–P (*trans* to N^1, when $X^{1,2}$ are): 2.248 Å (C) < 2.252 Å (O) < 2.259 Å (Se).

In Pt(η^3-$N^1N^2X^1$) (PL) derivatives, the Pt–L bond distance elongates in the orders (mean value):

Pt–N^1(*trans* to X^1, when X^1 is): 2.020 Å (X^1 = Se) < 2.043 Å (S) < 2.124 Å (C);

Table 3: Mean values of *trans*-α-L–Pt–L and *trans*-β-N'–Pt–P as well as τ_4

Metallocyclic rings	α-L–Pt–L (°)	β–N'–Pt–P (°)	τ_4
5 + 5 membered			
$N^1C_2N^2C_2C^1$	157.5	177.3	0.179
$C^1C_2N1C_2C^2$	158.8	171.6	0.210
$N^1CNN^2NCS^1$	151.6	171.8	0.259
$N^1CNN^2NCSe^1$	162.0	176.2	0.154
$N^1C_2N^2NCS^1$	162.2	177.1	0.147
5 + 6 membered			
$Se^1C_2N^1NC_2Se^2$	176.2	170.9	0.091
$O^1C_2N^1C_3O^2$	176.4	172.2	0.081
6 + 6 membered			
$O^1C_2NN^1C_3O^2$	170.5	175.0	0.103
$O^1C_3N^1C_3O^2$	176.0	177.0	0.048

Pt–N^2(*trans* to P, when X^1 is): 1.982 Å (X^1 = Se) < 2.020 Å (C) < 2.028 Å (S);

Pt–X^1(*trans* to N^1, when X^1 is): 2.022 Å (C) < 2.258 Å (S) < 2.368 Å (Se);

Pt–P (*trans* to N^2, when X^1 is): 2.252 Å (X^1 = C) < 2.259 Å (S) < 2.272 Å (Se).

These orders correspond quite well with the *trans*-influence of the respective donor atoms.

The heterotridentate ligands create variates of the metallocyclic rings. Each of these ligands forms two metallocyclic rings with a common N^1 atom in Pt(η^3-$X^1N^1X^2$) (PL) derivatives and an N^2 atom in Pt(η^3-$N^1N^2X^1$) (PL). In Pt(η^3-$X^1N^1X^2$) (PL) derivatives, the respective chelate L–Pt–L angles are of the types

5 + 5-membered: $C^1C_2N^1C_2C^2$ 79.7° (C^1–Pt–N^1) and 80.1° (N^1–Pt–C^2);
5 + 6-membered: $O^1C_2N^1C_3O^2$ 82.4° (O^1–Pt–N^1) and 94.8° (N^1–Pt–O^2);
5 + 6-membered: $Se^1C_2N^1NC_2Se^2$ 83.3° (Se^1–Pt–N^1) and 98.3° (N^1–Pt–Se^2);
6 + 6-membered: $O^1C_3N^1C_3O^2$ 90.6° (O^1–Pt–N^1) and 90.2° (N^1–Pt–O^2);
6 + 6′-membered: $O^1C_2NN^1C_3O^2$ 88.2° (O^1–Pt–N^1) and 92.0° (N^1–Pt–O^2).
In Pt($\eta^3N^1N^2X^1$) (PL) derivatives are
5 + 5-membered: $N^1C_2N^2C_2C^1$ 78.2° (N^1–Pt–N^2) and 80.7° (N^2–Pt–C^1);
5 + 5′-membered: $N^1C_2N^2NCS^1$ 78.8° (N^1–Pt–N^2) and 82.8° (N^2–Pt–S^1);
5 + 5-membered: $N^1CNN^2NCSe^1$ 78.7° (N^1–Pt–N^2) and 82.3° (N^2–Pt–Se^1).

There are at least two contributing factors to the size of chelate bond angles, both ligands based. One is steric constraints imposed on the ligand, and the other is the need to accommodate denticity appropriately.

In transition metal complexes, the oxidation state plays a leading role in the geometry formed, and platinum is no exception. In four coordinates, Pt(II) prefers a square-planar geometry. The utility of a simple metric to assess molecule shape and degree of distortion as well as exemplified best the τ_4 parameter for a square-planar geometry by an equation introduced by Yang et al. [26]:

$$\tau_4 = \frac{360 - (\alpha + \beta)}{141} F.$$

The values of τ_4 range from 0.00 for a perfect square-planar geometry to 1.00 for a perfect tetrahedral geometry since 360 − 2(109.5) = 141.

It is well known that the *trans* L–Pt–L bond angles and the number and type of atoms involved in respective rings are responsible for a distortion of the square-planar geometry about the Pt(II) atom. The total mean values of *trans*-α-L–Pt–L (L are terminal atoms of the respective η^3-ligand) bond angles, and *trans*-β-N′–Pt–P (N′ central atom N^1 or N^2 of the rings) bond angles and τ_4 are given in Table 3.

There is a cooperative effect between a degree of distortion of square-planar geometry about Pt(II) atom and the *trans*-L–Pt–L angles. The degree of distortion grows (τ_4) when *trans*-L–Pt–L angles diminish. There is also a cooperative effect between a degree of distortion and *trans*-influence of X atom/ligand when *trans*-influence of the respective X weakness degree of distortion increases.

The covalent radii of the donor atoms and their sums in evaluated structures are responsible for the main structural characteristics (L–Pt–L angles, bond lengths of donor and acceptor atoms) and, by that, distortion (τ_4) of the complexes. These structural characteristics and distortion, evaluated and calculated in our study, as well as resulting structural trends, discussed therein, will be reflected in the physical–chemical properties of the complexes (e.g., catalytic activity being relevant for the synthesis and catalysis studies).

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