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Organomonophosphines in Pt(η^3-$X^1X^2X^3$)(PR_3), (X = N^1, N^2, N^3; S^1, S^2, S^3; or Te^1, Te^2, Te^3) Derivatives: Structural Aspects

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Abstract: This paper covers nineteen Pt(II) complexes of the composition Pt(η^3-$X^1X^2X^3$)(PR_3), (X = N^1, N^2, N^3; S^1, S^2, S^3; or Te^1, Te^2, Te^3). These complexes crystallized in three crystal classes: triclinic (eleven examples), monoclinic (six examples), and orthorhombic (two examples). Each tridentate ligand creates two metallocyclic rings with common N^2, S^2, or Te^2 donor ligands of the types $N^1C_2N^2C_2N^3$, $N^1C_2N^2NC_2N^3$, $S^1C_2S^2C_2S^3$, $S^1C_3S^2C_3S^3$, and $Te^1CNTe^2NCTe^3$. The homotridentate ligand with monodentate PR_3 ligand builds up a distorted square planar geometry about Pt(II) atoms. The degree of distortion ranges from 0.029 to 0.092, and the reason for the distortion is discussed. There is an example that contains two crystallographically independent molecules within the same crystal. This is a classic example of distortion isomerism.

Keywords: structure; Pt(η^3-$X^1X^2X^3$) (PR_3); trans-influence; distortion

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1. Introduction

The coordination chemistry of platinum covers a huge number, as shown by a survey covering the crystallographic and structural data of almost two thousand monomeric examples [1–3]. Research activity in this field is always very active, and one of the reasons is the biological activity of platinum complexes [4]. Organophosphines as soft donor ligands are very useful for building a wide variety of platinum complexes. Much attention has been paid to organophosphines ligands in the chemistry of platinum. There have been numerous structural studies published of such complexes that were classified and analyzed [5]. Another review covers structural data of numerous platinum(II) coordination complexes with inner coordination spheres: PtP_4, PtP_3X (X = H, F, O, N, Cl, S, Br or I), and PtP_2X_2 (X – H, F, O, N, CN or B), in which P-donor ligands are monodentate organomonophosphines [6]. There are also numerous structures of Pt(II) complexes with organodiphosphines [7].

The aim of this paper is to analyze structural data of Pt(η^3-$X^1X^2X^3$)(PR_3) (X = N^1, N^2, N^3; S^1, S^2, S^3; or Te^1, Te^2, Te^3) complexes, where PR_3 represents the ligand coordination via the P atom.

2. Pt(η^3-$X^1X^2X^3$)(PR_3) Derivatives

Pt(η^3-$X^1X^2X^3$)(PR_3) derivatives are divided into three groups, classified and discussed in this paper, namely Pt(η^3-$N^1N^2N^3$)(PR_3), Pt(η^3-$S^1S^2S^3$)(PR_3), and Pt(η^3-$Te^1Te^2Te^3$)(PR_3) derivatives; their X-ray data are gathered in Table 1, Table 2 and Table 3, respectively.

Table 1. Structural data for Pt (η^3-$N^1N^2N^3$)(PR_3) derivatives [a].

Pt (η^3-$N^1N^2N^3$)(PR_3)	**Crystal cl. Space gr. z**	**a [Å] b [Å] c [Å]**	**α [°] β [°] γ [°]**	**Chromophore (Chelate Rings) τ_4**	**Pt-L [b] [Å]**	**L-Pt-L [b] [°]**	**Ref.**
[Pt{η^3-$C_{31}H_{30}F_6N_4O_8S_2$}.(PPh_3)]	tr $P\bar{1}$ 2	11.925 14.820 17.550	94.77 103.02 111.67	PtN_3P ($N^1C_2N^2C_2N^3$) 0.080	N^1 2.017 N^2 2.040 N^3 2.038 P 2.266	N^1,N^2 79.8(4) [c] N^2,N^3 79.2(3) [c] N^1,N^3 160.4 N^1,P 104.0 N^3,P 96.9(2) N^2,P 170.8	[8,9]
[Pt{η^3-$C_{17}H_{28}N_3$}(PPh_3)].CH_2Cl	tr $P\bar{1}$ 2	11.135(2) 11.462(2) 13.808(2)	80.18(2) 81.74(2) 88.27(2)	PtN_3P ($N^1C_2N^2C_2N^3$) 0.089	N^1 1.996 N^2 2.035 N^3 2.032 P 2.268	N^1,N^2 78.5 N^2,N^3 78.2 N^1,N^3 156.5 N^1,P 97.3 N^3,P 106.1 N^2,P 172.2	
[Pt{η^3-$C_{13}H_5F_6N_5$}.(PPh_3)]	tr $P\bar{1}$ 2	9.142 10.264 16.507	103.04 103.07 99.68	PtN_3P ($N^1C_2N^2C_2N^3$) 0.075	N^1 2.011 N^2 2.024 N^3 2.015 P 2.257	N^1,N^2 79.0 [c] N^2,N^3 78.9 N^1,N^3 157.8 N^1,P 102.7 N^3,P 99.5 N^2,P 175.1	[10]
[Pt{η^3-$C_{25}H_{19}N_5$}(PPh_3)]. $3CH_2Cl_2$ (at 223 k)	m $P2_1/n$ 4	6.068(0) 8.323(0) 33.868(0)	90.86(0)	PtN_3P ($N^1C_2N^2C_2N^3$) 0.070	N^1 2.015 N^2 2.017 N^3 1.996 P 2.253	N^1,N^2 79.2 [c] N^2,N^3 79.3 [c] N^1,N^3 158.4 N^1,P 96.9 N^3,P 104.6 N^2,P 176.2	[11]
[Pt{η^3-$C_{29}H_{33}N_7$}(PPh_3)]. CH_2Cl_2 (at 223 k)	tr $P\bar{1}$ 2	11.926(0) 13.052(0) 14.258(0)	97.75(0) 102.93(0) 95.73(0)	PtN_3P ($N^1C_2N^2C_2N^3$) 0.070	N^1 2.012 N^2 2.036 N^3 2.009 P 2.244	N^1,N^2 78.9 [c] N^2,N^3 78.9 [c] N^1,N^3 157.7 N^1,P 99.9 N^3,P 102.2 N^2,P 177.1	[11]
[Pt{η^3-$C_{30}H_{35}N_5$}(PPh_3)] (at 223 k)	tr $P\bar{1}$ 2	11.005(0) 12.424(0) 15.305(0)	75.50(0) 82.31(0) 87.08(0)	PtN_3P ($N^1C_2N^2C_2N^3$) 0.067	N^1 2.009 N^2 2.022 N^3 2.010 P 2.243	N^1,N^2 79.1 [c] N^2,N^3 78.8 [c] N^1,N^3 157.5 N^1,P 99.4 N^3,P 102.3 N^2,P 178.4	[11]
[Pt{η^3-$C_{12}H_6F_6N_7O$}(PPh_3)] (at 223 k)	tr $P\bar{1}$ 2	7.952(0) 11.542(0) 16.515(0)	76.83(0) 83.35(0) 89.27(0)	PtN_3P ($N^1C_2N^2C_2N^3$) 0.077	N^1 2.015 N^2 2.031 N^3 2.035 P 2.263	N^1,N^2 78.0 [c] N^2,N^3 78.4 [c] N^1,N^3 156.4 N^1,P 97.6 N^3,P 105.9 N^2,P 175.7	[12]
[Pt{η^3-$C_{18}H_{23}N_7O$}(PPh_3)] (at 223 k)	m $P2_1/n$ 4	13.371(0) 17.428(0) 15.657(0)	114.69(0)	PtN_3P ($N^1C_2N^2C_2N^3$) 0.081	N^1 2.016 N^2 2.026 N^3 2.008 P 2.256	N^1,N^2 78.4 [c] N^2,N^3 78.5 [c] N^1,N^3 156.9 N^1,P 98.4 N^3,P 104.6 N^2,P 173.9	[12]
[Pt{η^3-$C_{22}H_{15}N_7O$}(PPh_3)] (at 223 k)	m C2/6 8	24.786(0) 30.842(0) 10.313(0)	101.98(0)	PtN_3P ($N^1C_2N^2C_2N^3$) 0.072	N^1 2.006 N^2 2.033 N^3 2.012 P 2.269	N^1,N^2 78.0 [c] N^2,N^3 78.3 [c] N^1,N^3 156.3 N^1,P 101.2 N^3,P 102.4 N^2,P 177.8	[12]

Table 1. *Cont.*

Pt (η^3-$N^1N^2N^3$)(PR_3)	Crystal cl. Space gr. z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore (Chelate Rings) τ_4	Pt-L [b] [Å]	L-Pt-L [b] [°]	Ref.
[Pt{η^3-$C_{17}H_{21}N_7$}(PPh_3)] (at 223 k)	tr $P\bar{1}$ 4	15.098(0) 16.025(0) 17.125(0)	114.45(0) 94.20(0) 112.02(0)	PtN_3P ($N^1C_2N^2C_2N^3$) 0.078	N^1 2.022 N^2 2.021 N^3 2.010 P 2.263	N^1,N^2 78.5 [c] N^2,N^3 78.7 [c] N^1,N^3 157.0 N^1,P 101.0 N^3,P 101.9 N^2,P 174.8	[12]
[Pt{η^3-$C_{11}H_3F_6N_7$}(PPh_3)] (at 223 k)	m $P2_1/n$ 4	17.477(0) 7.859(0) 22.016(0)	112.64(0)	PtN_3P ($N^1C_2N^2C_2N^3$) 0.076	N^1 2.027 N^2 2.037 N^3 2.012 P 2.275	N^1,N^2 78.3 [c] N^2,N^3 78.5 [c] N^1,N^3 156.8 N^1,P 105.9 N^3,P 97.7 N^2,P 175.7	[12]
[Pt{η^3-$C_{15}H_{11}N_3$}(PPh_3)]. $2SO_3CF_3$ [e] (at 173 k)	tr $P\bar{1}$ 4	9.054(7) 19.936(14) 22.196(16)	111.04(1) 99.18(1) 99.74(1)	PtN_3P ($N^1C_2N^2C_2N^3$) 0.070 PtN_3P ($N^1C_2N^2C_2N^3$) 0.082	N^1 2.043 N^2 1.978 N^3 2.052 P 2.276 N^1 2.057 N^2 1.975 N^3 2.040 P 2.288	N^1,N^2 79.6 [c] N^2,N^3 80.0 [c] N^1,N^3 159.2 N^1,P 101.8 N^3,P 98.8 N^2,P 175.4 N^1,N^2 79.9 [c] N^1,N^3 79.3 [c] N^1,N^3 158.5 N^1,P 103.2 N^3,P 98.1 N^2,P 172.0	[13]
[Pt{η^3-$C_{11}H_3F_6N_7$}. {P(CH_3)Ph_2}] (at 223 k)	tr $P\bar{1}$ 2	7.892(0) 10.614(0) 16.050(0)	90.75(0) 97.77(0) 108.22(0)	PtN_3P ($N^1C_2N^2C_2N^3$) 0.068	N^1 2.005 N^2 2.032 N^3 2.006 P 2.256	N^1,N^2 78.6 [c] N^2,N^3 79.2 [c] N^1,N^3 157.7 N^1,P 100.0 N^3,P 102.2 N^2,P 177.9	[14]
[Pt{η^3-$C_{15}H_{11}N_3$}{P(η^1-$C_{14}H_{19}O_5$)Ph_2}]. $2SO_3CF_3.2Me_2CO$ (at 223 k)	m C2/c 4	31.541(4) 17.658(4) 24.072(4)	121.50(0)	PtN_3P ($N^1C_2N^2C_2N^3$) 0.068	N^1 1.918(16) N^2 2.000(1) N^3 2.097(10) P 2.287(3)	N^1,N^2 79.8(5) [c] N^2,N^3 79.5(3) [c] N^1,N^3 158.7(5) N^1,P 97.9(3) N^3,P 103.0(3) N^2,P 176.6(3)	[15]
[Pt{η^3-$C_{12}H_{10}N_4$}(PPh_3)] (at 100 k)	or $P2_12_12_1$ 6	10.417(0) 13.328(0) 18.299(0)		PtN_3P ($N^1C_2N^2NC_2N^3$) 0.034	N^1 1.984 N^2 2.025 N^3 1.964 P 2.255	N^1,N^2 81.7 [c] N^2,N^3 89.6 [d] N^1,N^3 170.6 N^1,P 93.0 N^3,P 96.3 N^2,P 177.2	[16]

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is e.s.d., and the second is the maximum deviation from the mean; [b] the chemical identity of a coordinate atom or ligand is specified in these columns; [c] five-membered metallocyclic ring; [d] six-membered metallocyclic ring; [e] there are two crystallographically independent molecules.

2.1. Pt(η^3-$N^1N^2N^3$)(PR_3) Type

There were fifteen complexes of such types which crystallized in three crystal classes: triclinic (nine examples), monoclinic (four examples), and orthorhombic (two examples) (see Table 1). In [Pt(η^3-$C_{12}H_{10}N_4$)(PPh_3)] (at 100 K) (see Figure 1) [16], the tridentate ligand creates two dissimilar rings. Five- and six-membered complexes of the $N^1C_2N^2NC_2N^3$ type had values of respective angles of 81.7° (N^1-Pt-N^2) and 89.6° (N^2-Pt-N^3). The values of the remaining L-Pt-L bind angles opened in the order 93.0° (N^1-Pt-P) < 96.3° (N^3-Pt-P) <

170.6° (N^1-Pt-N^3) < 177.2° (N^2-Pt-P). The Pt-L bond distance elongated in the order 1.964 Å (Pt-N^3, trans to N^1) < 1.984 Å (Pt-N^1) < 2.025 Å (Pt-N^2, trans to P) < 2.255 Å (Pt-P).

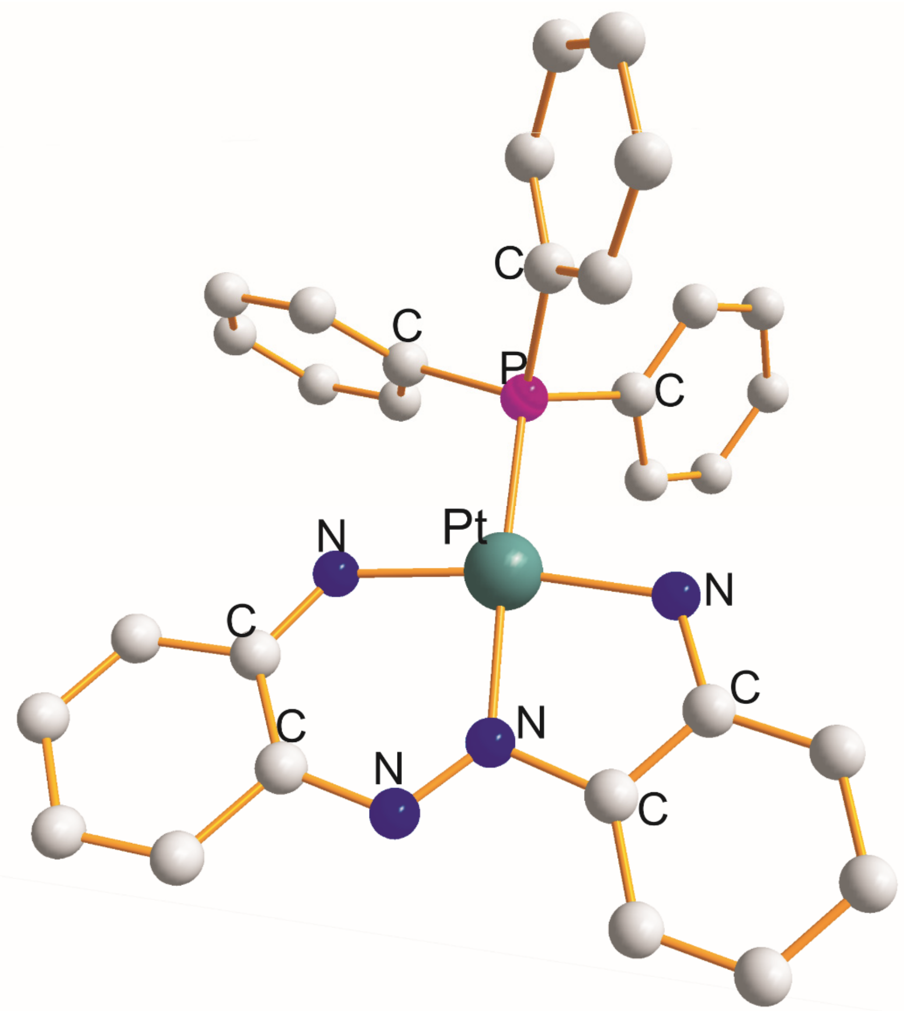

Figure 1. Structure of [Pt(η^3-$C_{12}H_{10}N_4$)(PPh_3)] [16].

Table 2. Structural data for Pt(η^3-$S^1S^2S^3$)(PPh_3) derivatives [a].

Pt(η^3-$S^1S^2S^3$)(PPh_3)	**Crystal cl. Space gr. z**	**a [Å] b [Å] c [Å]**	**α [°] β [°] γ [°]**	**Chromophore (Chelate Rings) τ_4**	**Pt-L [b] [Å]**	**L-Pt-L [b] [°]**	**Ref.**
[Pt{η^3-S(C_6H_4)S(C_6H_4)S}.(PPh_3)]	m $P2_1/n$ 4	8.990(1) 11.393(3) 25.587(3)	9093(1)	PtS_3P ($S^1C_2S^2C_2S^3$) 0.051	S^1 2.312(1) S^2 2.287(1) S^3 2.312(1) P 2.261(1)	S^1,S^2 87.69(4) S^2,S^3 87.08(4) S^1,S^3 163.92(3) S^1,P 94.40(1) S^3,P 90.76(4) S^2,P 177.85(4)	[17]
[Pt{η^3-MeS(CH_2)$_3$S(CH_2)$_3$.SMe}(PPh_3)]BF_4	tr $P\bar{1}$ 2	13.266(3) 11.315(2) 13.970(2)	106.04(2) 84.95(2) 86.56(2)	PtS_3P ($S^1C_3S^2C_3S^3$) 0.035	S^1 2.330(2) S^2 2.339(2) S^3 2.338(2) P 2.332(2)	S^1,S^2 87.1(2) [c] S^2,S^3 89.5(2) [c] S^1,S^3 176.3(2) S^1,P 91.1(2) S^3,P 92.3(2) S^2,P 171.0(2)	[18]

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is e.s.d., and the second is the maximum deviation from the mean; [b] the chemical identity of coordinate atom or ligand is specified in these columns; [c] six-membered metallocyclic ring.

In the remaining fourteen Pt(η^3-N^{1}N^{2}N^3) (Pt) complexes (see Table 1), a distorted square planar geometry around each Pt(II) atom was built up by η^3-N^{1}N^{2}N^3 with monodentate Pt ligands. Each tridentate donor ligand formed a pair of five-membered metallocyclic rings of the N^{1}C$_2$N^{2}C$_2$N^3 type, with total mean values of the respective angles of 78.8° (N^1-Pt-N^2) and 79.9° (N^2-Pt-N^3). The remaining L-Pt-L bond angles opened in the order (total mean values) 100.5° (N^1-Pt-P) < 102.9° (N^3-Pt-P) < 157.2° (N^3-Pt-N^3) < 176.0° (N^2-Pt-P). The Pt-L bond distance elongated in the order (total mean values) 2.013 Å (Pt-N^3, trans to N^1) < 2.017 Å (Pt-N^1) < 2.018 Å (Pt-N^2, trans to P) < 2.265 Å (Pt-P).

2.2. *Pt(η^3-S^{1}S^{2}S^3)(PR$_3$) Type*

Monoclinic [Pt{η^3-S(C$_6$H$_4$)S(C$_6$H$_4$)S}(PPh$_3$)](PPh$_3$)] [17] and triclinic [Pt{η^3-MeS(CH$_2$)$_3$S(CH$_2$)$_3$SMe}(PPh$_3$)].BF$_4$ [18] are the only examples of such a type (Table 2). The structure of the cation is shown in Figure 2 [18]. The tridentate ligand formed a pair of six-membered metallocyclic rings with a common S^2 atom of the monoclinic S^{1}C$_2$S^{2}C$_2$S^3 and triclinic S^{1}C$_3$S^{2}C$_3$S^3 type. The values of the respective angles were 87.69(4)° (S^1-Pt-S^2) and 87.08(4)° (S^2-Pt-S^3) in monoclinic and in triclinic were 87.1(2)° (S^1-Pt-S^2) and 89.5(2)° (S^2-Pt-S^3).

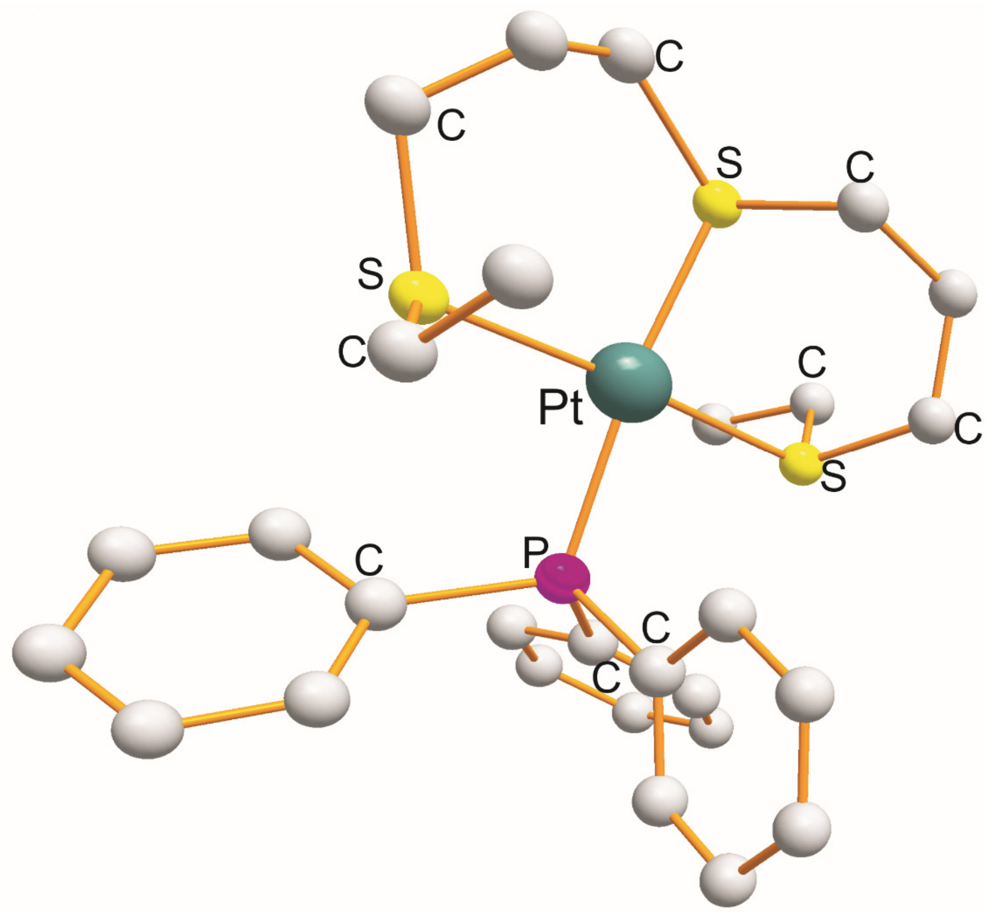

Figure 2. Structure of [Pt{η^3-MeS(CH$_2$)$_3$S(CH$_2$)$_3$SMe}(PPh$_3$)]$^+$ [18].

The remaining L-Pt-L bond angles opened in the order 91.1(2)° (S^1-Pt-P) < 92.3(2)° (S^3-Pt-P) < 171.0(2)° (S^2-Pt-P) < 176.3(2)° (S^1-Pt-S^3). The Pt-L bond distance elongated in the order 2.330(2) Å (Pt-S^1, trans to S^3) < 2.332(2) Å (Pt-P, trans to S^2) < 2.338(2) Å (Pt-S^3) < 2.339(2) Å (Pt-S^2). The monodentate PPh$_3$ ligand completed a distorted squared planar geometry around the Pt(II) atom.

Table 3. Structural data for Pt(η^3-Te^{1}Te^{2}Te^3)(PPh$_3$) derivatives [a].

Pt(η^3-S^{1}S^{2}S^3)(PPh$_3$)	Crystal cl. Space gr. z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore (Chelate Rings) τ_4	Pt-L [b] [Å]	L-Pt-L [b] [°]	Ref.
[Pt{η^3-C$_{10}$H$_8$N$_2$Te$_3$}(PPh$_3$)]	m C2/c 4	39.040(7) 13.261(4) 11.943(1)	93.85(1)	PtTe$_3$P (Te^{1}CNTe^{2}NCTe^3) 0.044	Te^1 2.5940(7) Te^2 2.5752(2) Te^3 2.570(2) P 2.282(2)	Te^1,Te^2 92.83(2) [c] Te^2,Te^3 92.56(2) [c] Te^1,Te^3 172.74(2) Te^1,P 86.10(5) Te^3,P 89.29(6) Te^2,P 171.40(2)	[19]
[Pt{η^3-C$_{12}$H$_{12}$N$_2$Te$_3$}(PPh$_3$)]. C$_6$H$_6$	tr $P\bar{1}$ 2	12.300(12) 15.251(8) 10.029(7)	107.38(3) 99.51(6) 83.25(4)	PtTe$_3$P (Te^{1}CNTe^{2}NCTe^3) 0.029	Te^1 2.588(3) Te^2 2.569(2) Te^3 2.612(3) P 2.283(3)	Te^1,Te^2 91.59(6) [c] Te^2,Te^3 91.40(7) [c] Te^1,Te^3 173.99(11) Te^1,P 90.40(10) Te^3,P 86.99(10) Te^2,P 17.56(9)	[19]

[a] Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is e.s.d., and the second is the maximum deviation from the mean; [b] the chemical identity of coordinate atom or ligand is specified in these columns; [c] five-membered metallocyclic ring.

2.3. Pt(η^3-Te^{1}Te^{2}Te^3)(PR$_3$) Type

There were two complexes of such a type; monoclinic [Pt{η^3-C$_{10}$H$_8$N$_2$Te$_3$}(PPt$_3$)] and triclinic [Pt{η^3-C$_{12}$H$_{12}$N$_2$Te$_3$}(PPh$_3$)]C$_6$H$_6$ [19] (see Table 3). The structure of the former is shown in Figure 3. Each tridentate ligand formed a pair of five-membered metallocyclic rings of the Te^{1}CNTe^{2}NCTe^3 type with the values of the respective angles of 92.8° (Te^1-Pt-Te^2) and 92.5° (Te^2-Pt-Te^3) in monoclinic; in triclinic they were 91.6° and 91.4°. The remaining L-Pt-L bond angles opened in the order 81.1° (Te^1-Pt-P) < 89.3° (Te^3-Pt-P) < 171.4° (Te^2-Pt-P) < 171.172.27° (Te^1-Pt-Te^3) in monoclinic, and in triclinic the order of 87.0° (Te^3-Pt-P) < 90.4° (Te^1-Pt-P) < 174.0° (Te^1-Pt-Te^3) < 175.5° (Te^2-Pt-P).

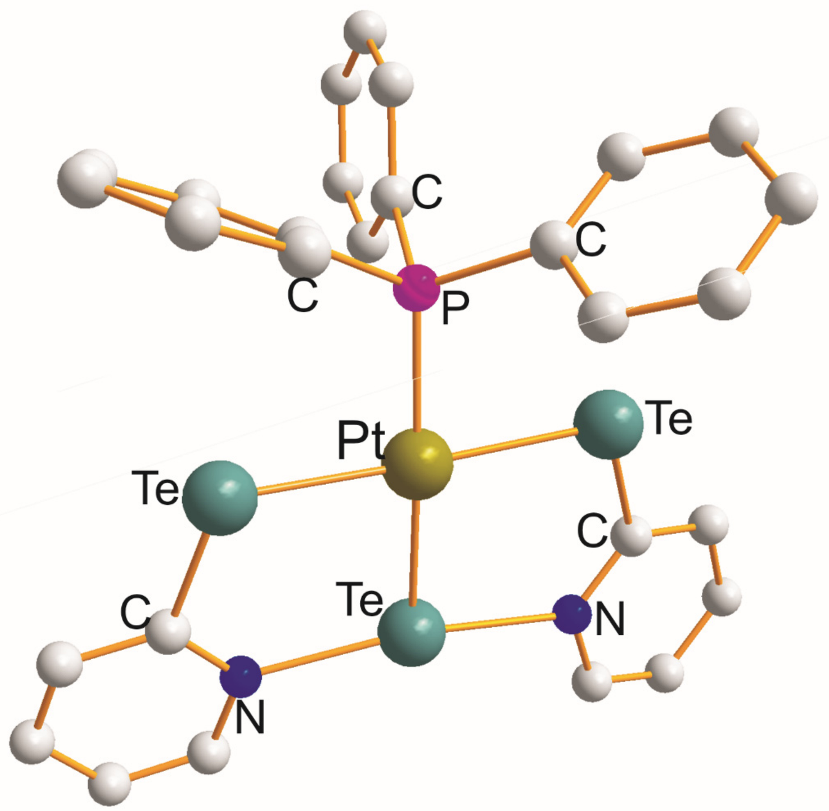

Figure 3. Structure of [Pt{η^3-C$_{12}$H$_{12}$N$_2$Te$_3$}(PPh$_3$)] [19].

The Pt-L bond distance elongated in the order 2.282(2) Å (Pt-P, trans to Te^2) < 2.5720(2) Å (Pt-Te^3, trans to Te^1) < 2.5752(2) Å (Pt-Te^2) < 2.5940(7) Å (Pt-Te^1) (in monoclinic); in triclinic, the order was 2.283(3) Å (Pt-P, trans to Te^2) < 2.569(2) Å (Pt-Te^2) < 2.588(3) Å (Pt-Te^1, trans to Te^3) < 2.612(3) Å (Pt-Te^3). The monodentate PPh_3 completed a distorted square-planar geometry around the Pt(II) atoms.

3. Conclusions

This paper includes nineteen monomeric Pt(II) complexes with the composition of (Pt (η^3-$X^1X^2X^3$)(R_3), (X = N, S or Te)). These complexes crystallized in three classes: triclinic (eleven examples), monoclinic (six examples), and orthorhombic (two examples). Based on tridentate ligands, these complexes could be divided into three sub-groups. In each subgroup, the Pt-L bond distance (mean values) with sums of Pt-L(x4) bond distances were:

Pt(η^3-N^1 N^2 N^3)(PR_3);

PtN_3P: 2.017 Å (Pt-N^1, trans to N^3); 2.018 Å (Pt-N^2, trans to P); 2.013 Å (Pt-N^3); 2.265 Å (Pt-P); Σ 8.313 Å (see Table 1);

Pt(η^3-S^1 S^2 S^3)(PR_3);

PtS_3P: 2.330 Å (Pt-S^1, trans to S^3); 2.339 Å (Pt-S^2, trans to P); 2.338 Å (Pt-S^3); 2.332 Å (Pt-P); Σ 9.339 Å (see Table 2);

Pt(η^3-Te^1 Te^2 Te^3)(PR_3);

$PtTe_3P$: 2.591 Å (Pt-Te^1, trans to Te^3); 2.572 Å (Pt-Te^2, trans to P); 2.592 Å (Pt-Te^3); 2.283 Å (Pt-P); Σ 10.038 Å (see Table 3).

The total mean values of Pt-L(x4) bond distances grew with the value of the covalent radius of coordinated atoms in the sequence 8.313 Å (0.73 Å, N) (PtN_3P) < 9.339 (1.02 Å, S) (PtS_3P) < 10.038 Å (1.36 Å, Te) ($PtTe^3P$).

Each tridentate ligand formed two metallocyclic rings with common N^2, S^2, or Te^2 of the following types, with the mean value of L-Pt-L bond angles:

5 + 5, rings $N^1C_2N^2C_2N^3$ 78.8° (N^1-Pt-N^2) and 78.9° (N^2-Pt-N^3);

5 + 5, rings $S^1C_2S^2C_2S^3$ 87.69(4)° (S^1-Pt-S^2) and 87.08(4)° (S^2-Pt-S^3)

5 + 5, rings $Te^1CNTe^2NCTe^3$ 92.1° (Te^1-Pt-Te^2) and 92.0° (Te^2-Pt-Te^3);

5 + 6, rings $N^1C_2N^2NC_2N^3$ 81.7° (N^1-Pt-N^2) and 89.6° (N^2-Pt-N^3);

6 + 6, rings $S^1C_3S^2C_3S^3$ 87.1° (S^1-Pt-S^2) and 89.5° (S^2-Pt-S^3).

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 the molecule shape and degree of distortion as well as exemplify best the τ_4 parameter for a perfect square-planar geometry is provided by the equation introduced by [20].

$$\tau_4 = \frac{360 - (\alpha + \beta)}{360} \text{ for square planar, and}$$

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

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

There is a cooperative effect between the size of the metallocyclic rings and donor atoms and the distortion of square-planar geometry around the Pt(II) atom. The distortion diminishes when the size of the metallocyclic rings grows, and the covalent radius increases as 0.75 Å (N) < 1.02 Å (S) < 1.31 Å (Te) of donor atoms, as can be seen:

5 + 5, rings 0.068 (τ_4) 78.8° ($N^1C_2N^2C_2N^3$) < 0.053 (τ_4) 81.4° ($S^1C_2S^2C_2S^3$) < 0.036 (τ_4) 92.0° ($Te^1CNTe^2NCTe^3$);

5 + 5, rings 0.068 (τ_4) 78.8° ($N^1C_2N^2C_2N^3$);

5 + 6, rings 0.034 (τ_4) 81.7° and 84.6° ($N^1C_2N^2C_2N^3$);

5 + 5, rings 0.053 (τ_4) 87.4° $S^1C_2S^2C_2S^3$;

6 + 6, rings 0.035 ($\tau_{4)}$) 87.1° and 89.54.6° $S^1C_3S^2C_3S^3$.

Monoclinic [Pt{η^3-$C_{15}H_{11}N_3$}(PPh_3)].SO_3CF_3 (at 173 k) [13] contains two crystallographically independent molecules within the same crystal (Table 1). These two molecules are different from each other by the degree of distortion, with values of τ_4 0.070 and 0.082. They are a classic example of a distortion isomerism [21].

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Abbreviations

m	monoclinic
$C_{25}H_{19}N_5$	(2,6-bis(3-(4-methyl)-1H-pyrazol-5yl)pyridinate)
PPh_3	triphenylphosphine
$C_{29}H_{33}N_7$	(2,6-bis(3-(adamantam-1-yl)-1H-1,2,4-triazol-5-yl) pyridinate)
$C_{31}H_{35}N_5$	(2,6-bis(3-(adamantam-1-yl)-1H-pyrazol-5-yl) pyridinate)
$C_{12}H_6F_6N_7O$	(4-methoxy-2,6-bis(3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl))pyridinate)
$C_{13}H_5F_6N_5$	{2,6-bis[3-(trifluoromethyl)-1H-pyrazol-5-yl]pyridinato}
$C_{18}H_{23}N_7O$	(2,6-bis(3-t-butyl-1H-1,2,4-triazol-5-yl)-4-methoxypyridinate)
$C_{22}H_{15}N_7O$	(4-methoxy-2,6-bis(3-phenyl-1H-1,2,4-triazol-5-yl)pyridinate)
$C_{17}H_{21}N_7$	(2,6-bis(3-t-butyl-1H-1,2,4-triazol-5-yl))pyridinate)
$C_{17}H_{22}N_8$	(2-(3-(adamantan-1-yl)-1H-1,2,4-triazol-5-yl)-6-(1H-tetrazol-5-yl)pyridinato)
$C_{11}H_3F_6N_7$	(2,6-bis(3-(trifluoromethyl)-1H-1,2,4-triazol-5-yl)pyridinate)
$C_{15}H_{11}N_3$	(2,2′.6′2″-terpyridine)
$C_{31}H_{30}F_6N_4O_8S_2$	4′-[4-(4-morpholinobutyloxy)phenyl]-2,2′:6′,2″-terpyridine
$P(CH_3)Ph_2$	methyldiphenylphenylphosphine
$P(\eta^1$-$C_{14}H_{19}$-$O_5)(Ph)_2$	(benzo-5-crown[5])diphenylphosphine)
$C_{12}H_{10}N_4$	(2-(2-amino)phenyl diazenyl)anilinate)
$C_{10}H_8N_2Te_3$	(1,1′-tellanyl)bis(5-pyridine-2-tellurolate)
$C_{12}H_{10}N_2Te_3$	(1,1′-tellanyl)bis(3-methyl-1λ5-pyridine-2-tellurolate)

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