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Review

Stereochemistry of platinum coordination compounds

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Contents

Abstract

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. About 10% of these complexes exist as isomers and are summarised in this review. Included are distortion (65%), *cis–trans* (30%), mixed isomers and ligand isomerism. These 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.

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 wider range of oxidation states 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).

Keywords: Stereochemistry; Platinum; *Cis–trans* isomers

1. Introduction

Systematic studies in the field of stereoselectivity of coordination compounds over the last 50 years have become of increasing interest. Stereoselectivity in coordination compounds is very often related to important stereospecificity of biological systems, catalysis and stereochemical effects in technical processes. Isomers can be broadly classed into two major categories, structural and stereoisomers. The former can be divided into ionization, hydrate, coordination, linkage and polymerisation sub-categories, and the latter can be divided into geometric (*cis–trans*, *fac–mer*), optical and distortion isomerism.

Platinum exists in a wide range of oxidation states from zero to +6, including non-integral Pt(2.25), Pt(2.5) Pt(2.87), Pt(3.25) and Pt(3.5). Of these, particularly in six-coordinate examples, +2 and +4 oxidation states are the most common. The huge area of platinum coordination chemistry has recently been surveyed [1] with over 200 isomeric examples noted. In this review we analyse and classify these examples to show that stereoisomers are more common than structural isomers, and, surprisingly, that

Abbreviations: bcd, 1,2-benzoquinonedioxinate; Bu_2bpy, dibutylbipyridine; cbdc, 1,1-cyclobutanedicarboxylate; cha, cyclobutylamine; cpdta, {4-(4-chlorophenyl)-1,2-dithia-3,5-diazolium}chloride; dach, 1,2-diaminocyclohexane; dmit, 4,5-dimercapto-1,3-dithio-2-thionate; dmso, dimethylsulphoxide; dppp, bis(diphenylphosphine)propane; en, ethylenediamine; Me_2bpy, dimethylbipyridine; mnt, maleonitrildithiolate; PEt_3, triethylphosphine; oxp, oxo-5-prolinate; PMe_2Ph, dimethylphenylphosphine; PPh_3, triphenylphosphine; py, pyridine; pyr, pyrimidine

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distortion isomerism is more common than the better known *cis–trans* isomerism.

Platinum(II) has a strong preference for square-planar coordination geometry. The kinetic inertness of these compounds has allowed their extensive use in the characterisation of geometrical isomerism and reaction mechanistics. The aim of this presentation is to discuss the factors which could lead to a better understanding of stereochemical interactions within the coordination sphere of monomeric platinum coordination compounds, and to examine some cooperative effects between isomeric types.

2. 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 [2]. There are over one hundred and sixty such examples in the chemistry of monomeric platinum coordination compounds. The platinum oxidation states in these isomers are found in the oxidation states of zero, +2 (the most common), +3 and +4.

Pale orange $Pt(PPh_3)_3$ [3] and orange $Pt(\eta^2\text{-dppp})_2$ [4] are the only examples of Pt(0) distortion isomers. In the former, the isomers consist of bulky unidentate PPh_3 ligands in an approximately trigonal geometry about the Pt(0) atom, to give triclinic [3a] and monoclinic [3b] forms. The Pt–P bond distances range from 225 to 228 pm [3a] and from 226.1(2) to 227.1(2) pm [3b], and the P–Pt–P bond angles range from 115° to 122°, and from 117.20(6)° to 128.80(0)°, respectively. In the two monoclinic $Pt(\eta^2\text{-dppp})_2$ isomers a pair of bis(diphenylphosphino)propane ligands create a square-planar geometry (PtP_4) about the Pt(0) atom. The mean Pt–P bond distances and the mean P–Pt–P bond angles within the six-membered rings are 229.2 pm and 97.9° [4a] and 228.6 pm and 97.76(4)° [4b].

There are over 125 Pt(II) distortion isomers which can be divided into several subgroups. One example, *trans*-$PtCl_2\{P(Bu^t)_2Ph\}_2$, exists in three isomeric forms, two monoclinic [5a] and one orthorhombic [5b]. 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 [6–15], orthorhombic [16–21] and triclinic [22–24] classes. 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 [25–30]. In three examples one is monoclinic and the other orthorhombic [31–33]. Of the remainder the mixture is monoclinic and tetragonal [34], triclinic and orthorhombic [35], orthorhombic and trigonal [36].

There are 75 derivatives which contain two crystallographically independent molecules within the same crystal [37–109]. Six derivatives contain three such molecules [110–115] and three derivatives have four such molecules [116–118]. The colourless derivative $(NH_4)[Pt(\eta^2\text{-oxp})_2]H_2O$ [119] contains five such molecules within the same crystal, and the crystal structure of one of the anions is shown in Fig. 1. The pair of heterodentate oxp ligands (O, N–donors) with two five-membered rings create a square-planar geometry about the Pt(II) atom (PtO_2N_2) with differing degrees of distortion. The mean Pt–O and Pt–N bond distances are 202.5 and 199.5 pm (molecule 1); 202.5 and 200.5 pm (molecule 2); 202.0 and 200.0 pm (molecule 3); 200.5 and 195.5 pm (molecule 4) and 201.5 and 200.0 pm (molecule 5). The mean values of O–Pt–N bond angles within the five membered rings are 81.6°, 80.5°, 82.1°, 79.9° and 81.2°, respectively.

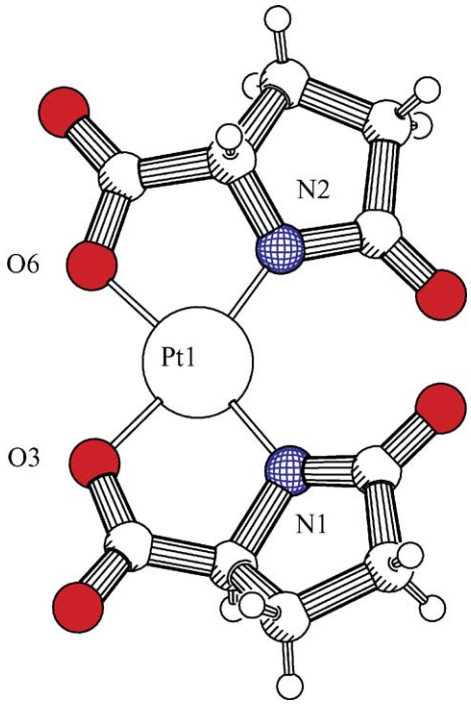

Fig. 1. One independent anion structure of $[Pt(\eta^2\text{-oxp})_2]^-$ [119].

There are several examples in Pt(II) chemistry which exist in two isomeric forms where one form contains two crystallographically independent molecules [78,85,101,120–123], three such molecules [112] and four such molecules [116,124].

Two black Pt(III) derivatives $(cpdta)\{Pt(\eta^2\text{-mnt})_2]$ [125] and $(NHMe_3)[Pt(\eta^2\text{-dmit})_2]_3\cdot MeCN$ [126] contain three such isomers within the same crystal. A pair of mnt [125] and dmit [126] ligands create a square-planar geometry about the Pt(III) atom (PtS_4) with different degrees of distortion. The mean S–Pt–S bond angles within the five-membered metallocycles are 89.7°, 89.8° and 89.6° in the former and 89.7°, 89.5° and 89.1° in the latter. The mean Pt–S bond distances are 226.0, 226.3 and 226.2 pm [125], and 228.9, 229.5 and 228.6 pm [126], respectively.

In the chemistry of Pt(IV) there are twenty derivatives belonging to this class of isomerism. Nine exist in two isomeric forms, orthorhombic [127–130], triclinic [131–133] and monoclinic [134,135]. Ten Pt(IV) derivatives contain two crystallographically independent molecules within the same crystal [132,135–142]. Colourless $PtCl_4(\eta^2\text{-dach})$ [143] contains three such molecules with octahedral coordination ($PtCl_4N_2$) and differing degrees of distortion. The mean Pt–N and Pt–Cl bond distances are 205.8 and 230.9 pm (molecule 1), 205.2 and 231.3 pm (molecule 2) and 206.1 and 230.5 pm (molecule 3). The N–Pt–N bond angles within the five-membered metallocyclic rings is 84.6(9)°, 81.4(9)° and 82.7(8)°, respectively.

Black *trans*-$Pt(\eta^2\text{-bcd})_2I_2$ [132] exists in two isomeric forms, one of which contains two crystallographically independent

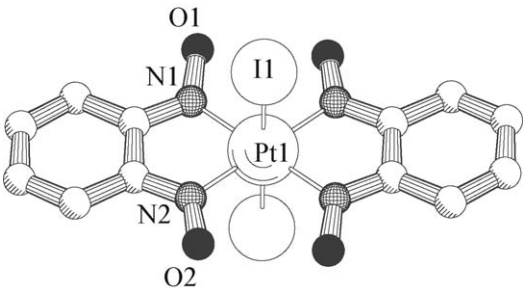

Fig. 2. One independent molecule structure of Pt(η^2-bcd)$_2$I$_2$ [132].

molecules within the same crystal. The isomeric forms as well as the respective molecules differ from each other by degree of distortion. Each Pt(IV) atom is octahedrally coordinated (PtN_4I_2), as shown in Fig. 2, with Pt–N bond distances of 200(1) pm (twice) and 201(1) pm (twice), and Pt–I bond distances of 266.6(1) pm (twice) in one isomeric form. In the other form the values are: 198.7(6) pm (twice), 201.1(6) pm (twice) and 265.4(1) pm (twice), respectively (molecule 1) and 198.0(6) pm twice, 202.4(6) pm (twice) and 264.7(1) pm (twice), respectively (molecule 2). The mean N–Pt–N bond angles within the five-membered metallocycles are 80.0° (form 1), 79.4° (molecule 1) and 78.9° (molecule 2).

In this series of distortion isomers the predominant square-planar configuration about the platinum atom is *cis* rather than *trans*.

3. *Cis–trans* isomerism

Much of the work in this field comes from the Russian School such as the contributions of Chernyaev [144]. In the 1920s he noticed that when there are alternative positions at which incoming ligands could effect a substitution, the choice depended not so much on the two ligands directly involved but rather on the nature of the inactive ligand *trans* to that position. This became known as the "*trans*-effect" and has had considerable influence in the development of the chemistry of platinum(II).

There are two main hypotheses used to account for this effect. That of the Russian School [144] considers it to be mostly electrostatic in origin, depending largely on the polarisability of the ligand. The more polarisable the ligand, the greater its *trans*-effect. The second is that of the English School [145] which is based on the degree of π-back-bonding between the metal and the ligand, the greater π-acceptor ability of the ligand the greater its *trans*-effect.

Pearson [146] proposed the nomenclature of "hard" for poor polarisability and "soft" for high polarisability of ligand atoms. Then "hard–hard" or "soft–soft" bonding interactions are more stable than "hard–soft" ones. The Pt–L bond distances derived from X-ray crystallographically are generally consistent with this general picture, and the qualitative observations of the dependence of the reactivity of a ligand on the ligand *trans* to it.

There are almost thirty examples of Pt(II) complexes which exist in two isomeric forms, *cis* and *trans*. Some pairs of isomers belong to the monoclinic class [147–154], orthorhombic [155,156] or the triclinic class [157–159]. The remaining isomeric derivatives differ in crystal class. Six examples have monoclinic *cis* isomers and triclinic *trans* isomers [160–165]. Two examples have monoclinic *cis* and orthorhombic *trans* [166,167], three have orthorhombic *cis* and monoclinic *trans* [31,69,102], and two have triclinic *cis* and monoclinic *trans* [39,168,169].

4. Mixed isomerism (*cis–trans* and distortion)

Two Pt(II) complexes belong to this unusual combination of isomerism. The X-ray analysis of $PtCl_2$(py)(dmso) shows monoclinic *cis* [170] and triclinic *trans* [102] isomers. In addition, the *trans* isomer contains two crystallographically independent molecules. Each Pt(II) atom has a square-planar geometry ($PtCl_2NS$) with differing degrees of distortion. The Pt–Cl(mean), Pt–N and Pt–S bond distances in the *cis* isomer are 231.3, 202.7 and 220.9 pm, respectively. In the *trans* isomer the values are 228.8, 205.2 and 222.4 pm (molecule 1) and 230.0, 206.1 and 222.5 pm (molecule 2), respectively.

Yellow Pt(MeNH$_2$)$_2$Cl$_2$ exists in three different *cis* isomeric forms [69,112] and in a *trans* form [69]. Two of the *cis* forms are monoclinic [112] and one is orthorhombic [69]. The *cis* isomers differ from each other. One of the monoclinic forms contains a single molecule while the other contains three crystallographically independent molecules, one of which is shown in Fig. 3. The structure of *trans*-Pt(MeNH$_2$)$_2$Cl$_2$ is shown in Fig. 4.

The orthorhombic form contains two such molecules. The differences are found in the degrees of distortion. The mean Pt–N and Pt–Cl bond distances of the first monoclinic form are 203.4 and 230.7 pm. The second has values of 205.8 and 231.5 pm (molecule 1) and 207.1 and 231.2 pm (molecule 2), respectively. In the orthorhombic form the values are 205.5 and 230.6 pm (molecule 1), 206.0 and 230.0 pm (molecule 2), respectively. In the *trans* isomer the values are 203.0 and 228.7 pm, respectively. The mean Pt–N and Pt–Cl bond distances in the *cis* species

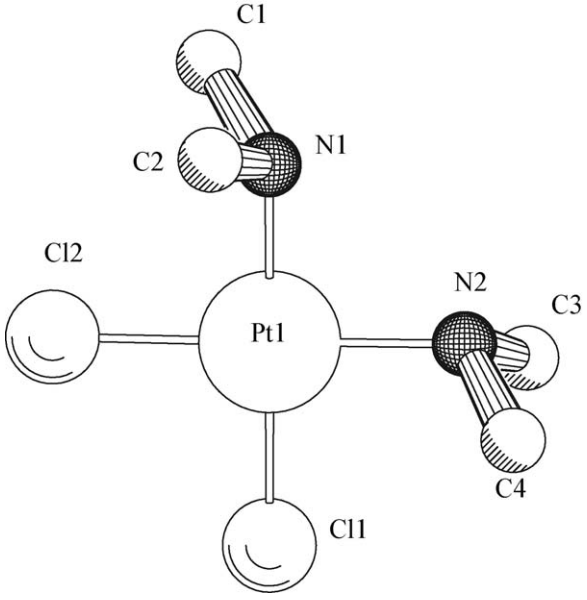

Fig. 3. One independent molecule structure of *cis*-Pt(MeNH$_2$)$_2$Cl$_2$ [112].

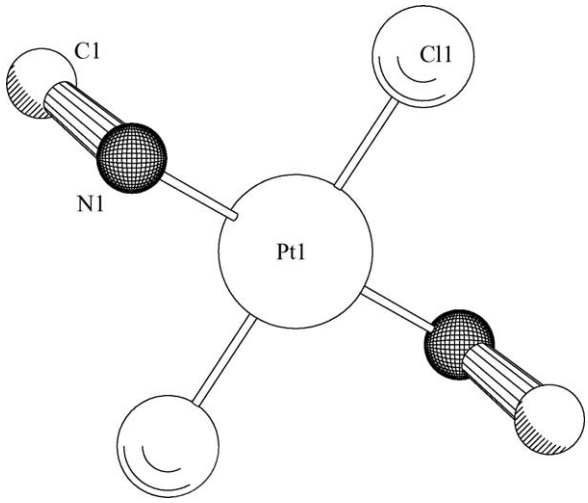

Fig. 4. Structure of *trans*-Pt($MeNH_2$)$_2Cl_2$ [69].

(2.4.9 and 230.7 pm) are somewhat longer than the values in the *trans* isomer. This reflects how distortion isomerism can alter the perception of the *trans*-effect.

5. Ligand isomerism

There are five Pt(II) complexes which exhibit this type of isomerism: orange Pt(η^2-4,4′-Me_2bpy)$(NCO)_2$ [171] and yellow Pt(η^2-5,5′-Me_2bpy)$(NCO)_2$ [172]; pale yellow Pt(η^2-3,3′-Me_2bpy)Cl_2 [76] and yellow Pt(η^2-5,5′-Me_2bpy)Cl_2 [173]; yellow Pt(η^2-3,3′ Bu_2bpy)Cl_2 [174] and Pt(η^2-5,5′-Bu_2bpy)Cl_2 [175]; pale yellow *trans*-$PtCl_2$(2,3-Me_2pyr)(PEt_3) and $PtCl_2$(2,4-Me_2pyr)(PEt_3) [176]; pale yellow $PtCl_2$(η^2-2,3-Mepyr)(PMe_2Ph) [177] and $PtCl_2$(2,5-Me_2pyr)(PMe_2Ph) [178]. Each Pt(II) atom has a square-planar geometry with differing degrees of distortion. The mean (R_2bpy)Pt–N bond distance reflects the position of the R_2bpy group and increases in the order: 198.5 pm (5,5′-) < 201.1 pm (3,3′-) < 203.0 pm (4,4′-). The mean (Me_2pyr)Pt–N bond distance also reflects the position of the Me_2R group, increasing in the order: 212.0 pm (2,5-) < 213.3 pm (2,4-) < 215.3 pm (2,3-).

6. Conclusions

An analysis of almost 2000 monomeric platinum coordination complexes shows that some 10% of them exist in isomeric forms [1]. In general the isomers can be subdivided into two major classes, structural and stereochemical. For platinum chemistry, the latter is more prevalent. The steroisomers can be subdivided into distortion, *cis–trans*, mixed and ligand isomers. Despite the importance of *cis–trans* geometry in the chemistry of Pt(II) compared to other transition metal systems, within platinum chemistry distortion isomersisation is far more common. Such a dominance of this form of isomerism is also seen in the chemistry of copper [2].

In the chemistry of "soft" platinum is found a wide variety of uni-, bi-, ter- and tetradentate ligands forming a square-planar geometry about Pt(II) and an octahedral geometry about Pt(IV), with varying degrees of distortion. Although platinum should preferentially bond to "soft" donor ligands such as PR_3 and S–donor groups, it can also be found bonded to both "borderline" (e.g. bromide) and "hard" donor atoms (commonly N–donor ligands and chloride).

Table 1
Summary of the mean Pt(II)–L bond distances (pm)

X[a] *trans* to (Y)[b]	<X *trans* to X	<X[a] *trans* to (Y)[b]
199.5(N,Cl)	<O 205.8	<207.8(S) < 219.2(P) < 226.5(H)
202.0(Br) < 202.5(Cl) < 205.5(I)	<N 206.3 C 196.5	<209.0(P) < 211.0(H) <199.5(P)
229.2(O) < 229.4(S)	<Cl 230.0	<230.7(N) < 230.8(C) < 236.0(P) < 240.0(H)
223.0(Br) < 225.0(Cl)	<S 225.0	<227.2(I) < 234.5(P) < 238.5(H)
224.1(I) < 224.0(Br) < 223.9(F) < 226.3(N) < 227.2(Se) < 227.6(S)	<P 230.0	<233.5(H)
239.2(N)	<Br 242.5	<243.2(S) < 249.0(P) < 257.2(H)
255.2(N)	<I 260.0	

[a] Ligand affected defined in central column.
[b] *Trans*-effect ligand shown in parentheses.

A summary of the mean Pt(II)–L bond distances are given in Table 1. The mean value of Pt(II)–L bond distances (mutually *trans*) can be seen to increase in the order: 196.5 pm (L = C) < 205.8 pm (O) < 206.3 pm (N) < 225.0 pm (S) < 230.0 pm (Cl or P) < 242.5 pm (Br) < 260.0 pm (I). The *trans* effect on Pt(II)–L distances (*trans* to Y) can be divided into two categories. The first, left side of Table 1, in which a hetero-donor atom Y shortens the *trans* Pt(II)–L bond. The second, right side of Table 1, in which the Y donor atom increases the length of or weakens, the *trans* bond. These results suggest that in the former case there is less transfer of donor electrons from Y to Pt(II) than in the latter case. The "soft" atoms or ligands show a larger *trans* effect than borderline or "hard" ones.

A summary of the Pt(IV)–L bond distances are given in Table 2, where it is seen that the mean value of the Pt(IV)–L bond distance (mutually *trans*) increases in the order: 194 pm (L = F) < 197.0(0) pm (O) < 198.0 pm (CN) < 206.0 pm (N) < 231.0 pm (Cl) < 235.5 pm (S) < 240.0 pm (Si) < 246.0 pm (Br). As before there is a wide variety of "soft" (H, C, S, P, As, I) ligands, borderline (Br) and hard (F, O, N, Cl) donor atoms. The soft atoms have a larger *trans* effect than the borderline or

Table 2
Summary of the mean Pt(IV)–L bond distances (pm)

X[a] *trans* to (Y)[b]	<X *trans* to X	<X[a] *trans* to (Y)[b]
	<F 194	<197(Cl)
	<O 197	<202.5(N) < 204(Cl) < 209.5(Br)
204.5(Cl) < 205.5(Br)	<N 206	<210.0(I)
229.0(Br)	<Cl 231	<234.0(Se) < 236.0(S) < 239.5(P)
238.0(P)	<Si 240	<240.5(H)

[a] Ligand affected defined in central column.
[b] *Trans*-effect ligand shown in parentheses.

Table 3
Summary of the mean L–Pt(II)–L bond angles (°) of chelate rings for homobidentate ligands

Four	
OCO	65.0
PNP	70.0
OPO	71.5
PCP	72.8
OSeO	74.3
SCS	74.5
PBP	74.7
SeCSe	77.0
PPP	78.2
SSS	81.0
SPS	82.2
SePSe	85.3
Five	
NN_2N	76.4
ON_2O	78.0
NCPN	80.2[a], 84.2[b]
OCNO	80.6
NCON	81.7
OC_2O	82.2
SeC_2Se	82.2
NCSN	82.5
PC_2P	85.7
SCPS	86.5
SC_2S	89.0
SSNS	89.8
SS_2S	93.2
SCCS	93.6
Six	
PNCNP	79.6
PNPNP	86.5
PCHCP	88.5
NSNSN	88.7
NCPCN	89.0
NCNPN	89.0
NCNPN	89.5
OC_3O	91.0
NC_3N	91.4
PC_3P	93.3
SC_3S	93.5
Seven	
NC_4N	87.3[a], 98.8[b]
OC_4O	89.7
SC_4S	92.2
PC_4P	99.0
Eight	
NC_5N	89.5
PC_5P	90.3
Nine	
PC_6P	95.0
Eleven	
SC_8S	87.0
Twelve	
PC_9P	104.9
AsC_9As	174.2
Fourteen	
$PC_{11}P$	175.8
Sixteen	
$PC_{15}P$	99.0
Twenty	
$PC_{17}P$	99.0

[a] Unsaturated ligands.
[b] Saturated ligands.

hard atoms. 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.

The *trans* effect on Pt–L bond distances also affects the L–Pt–L′ angles, as the former increases the latter opens. For example the Pt(II)–Cl bond distance increases in the order of the *trans* donor atom: 230.2 pm (*trans* to N) < 232.4 pm (*trans* to S) < 238.0 pm (*trans* to P). The mean value of the Pt(II)–Cl bond distances *trans* to each other is 230.0 pm. The Cl–Pt–Cl angles follow a similar trend, opening in the order: 89.4° (X = N) < 91.0° (S) < 91.5° (P).

The mean Pt–L bond lengths for the homobidentate ligands, which include O–, N–, S–, P–, Se– and As–donors, are somewhat shorter than those of the corresponding monodentate ligands except for the P–donor ligands in which the opposite is seen. There are a variety of hetero-bidentate ligands; O/N, O/S, O/P, N/S, N/P, N/Se, S/P, S/Si, P/Se and P/Si donor atoms. All of these have mean Pt–L bond distances that follow the same trend as the homobidentate ligands. Correspondingly there is a wide variety of metallocyclic rings, and the effects of both steric and electronic factors can be seen from the values of the L–Pt(II)–L bond angles listed in Tables 3 and 4.

As can be seen, homo- as well as heterobidentate ligands form metallocyclic rings with varying atoms and numbers of atoms in the ring. The mean homobidentate chelating ligands have mean L–Pt(II)–L bond angles in the sequence: 76.5° (four-) < 84.4° (five-) < 89.0° (six-) < 93.4° (seven-) < 94.0° (eight-) < 95.0° (nine-membered rings). In the heterobidentate chelating ligands the order is: 73.7° (four-) < 86.0° (five-) < 91.0° (six-membered rings).

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

Table 4
Summary of the mean L–Pt^{II}–L′ bond angles (°) of chelate rings for heterobidentate ligands

Four		Five		Six	
SCSi	65.0	NONP	80.1	NC_2Se	86.5
NCS	70.0	OC_2N	81.6	NC_2NS	88.5
NCP	70.2	OCNS	82.6	SC_3P	89.0
PCSi	70.7	PC_2Si	83.3	NCN_2P	89.4
SCP	73.4	OC_2P	83.6	PC_3Si	89.7
PCB	73.6	NC_2P	84.5	OC_3S	90.0
NCSe	78.0	NCNSe	84.6	NNC_2P	91.2
PCTe	88.5	NNCS	84.9	NC_3P	91.9
		NSNS	85.1	OC_3N	92.3
		OC_2S	85.5	SC_3As	93.0
		OPNP	85.6	NCNCS	93.3
		NC_2S	85.7	NC_3Se	94.0
		PCNS	85.7		
		NC_2NP	86.5		
		SC_2P	87.0		
		NSeNSe	87.1		
		SC_2As	87.4		
		PC_2Se	90.4		
		SPNP	90.5		
		SPCP	91.0		

Table 5
Summary of the mean L–Pt^{IV}–L(L′) bond angles (°) of chelate rings for homo- and hetero-bidentate ligands

Three		Four		Five		Six		Seven	
PP	52.5	NCN	64.0	NC_2N	80.2[a], 84.0[b]	SC_3S	91.2	NC_5N	98.4
		SCS	73.5	OC_2O	83.2	OC_3O	93.4		
				OC_2N	84.5	NC_3N	93.7		
				SeC_2Se	88.0	SC_3As	99.0		
				SC_2S	88.5	SeC_3Se	99.5		
				SC_2As	91.5				

[a] Unsaturated ligands.
[b] Saturated ligands.

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 221.8 pm (four-) < 86.7° and 222.0 pm (five-) < 95.6° and 223.0 pm (six-) < 97.0° and 223.5 pm (seven-) < 102.2° and 224.0 pm (eight-membered ring).

A summary of the mean L–Pt(IV)–L(or L′) bond angles are given in Table 5. The mean bond angle opens, as expected, in the order: 52.5° (three-) < 68.7° (four-) < 85.7° (five-) < 95.4° (six-) < 98.4° (seven-membered rings). These angles are smaller than the homobidentate ring angles, except for the four-membered rings.

This review has focused on stereoisomers in platinum coordination compounds. In the series of distortion isomerism platinum exists in oxidation states zero, +2, +3 and +4, of which +2 is by far the most common. There are a variety of inner coordination spheres about the platinum atom. In Pt(0) complexes there is one trigonal (PtP_3) and one square-planar (PtP_4) example. In Pt(II) complexes there is a wide variety of square-planar environments with varying degrees of distortion: PtA_4 (A = N, C, Cl, S or P); PtN_3Y (Y = O, Cl, Br, or I); PtS_3O, PtP_3H; PtO_2Y_2 (Y = N, P or As); PtN_2Y_2 (Y = C, Cl, S, P, P or I); PtC_2P_2; $PtCl_2Y_2$ (Y = S, P, Se or I); $PtCl_2NY$ (Y = S, P or Se); $PtCl_2SP$; PtP_2NY (Y = O or S) and $PtBr_2NS$. A square-planar environment around Pt(III) is formed by two bidentate S–donor ligands (PtS_4). The environments around Pt(IV) are square-planar (PtS_4), and octahedral (PtN_4O_2, PtN_4I_2, $PtCl_4N_2$, PtI_4N_2, $PtBr_4ON$ and $PtO_2N_2Cl_2$).

In the *cis–trans* series of isomers platinum is found in oxidation states of +2 and +4, with the former most common. The variety of square-planar environments about Pt(II) is much smaller than in the case of the distortion isomers, with chromophores being: PtO_2N_2, PtN_2Y_2 (Y = Cl, Br, I or P), $PtCl_2Y_2$ and $PtCl_2NY$ (Y = S or P), PtS_2P_2, PtP_2Br_2, PtN_2ClS and PtP_2OCl. Pseudo-octahedral coordination about the Pt(IV) atom is exhibited by PtF_4Cl_2 and PtN_4Cl_2 chromophores. Square-planar geometry about Pt(II) atoms with ligand isomerism present is found with PtN_4, PtN_2Cl_2 and $PtCl_2NP$ chromophores.

There is no other transition metal with as many investigated examples of square planar geometry as platinum. There are probably two main reasons for this, the great interest in the *cis–trans* effect and the medical importance of species such as cisplatin type derivatives. Explanation for the *trans*-effect abound [179], with σ- and π-bond effects being important parameters. Ligands exerting the *trans*-effect in the Pt(II) coordination compounds have strongest effect in the order: $H_2O < OH^- < F^- <$ py, $NH_3 < Cl^- < Br^- < I^-$, $SCN^- < SC(NH_2)_2 <$ SL < SeL < TeL < AsR_3, $PR_3 < H^-$. The ligands with the strongest *trans*-effect are those whose bonding to a metal is believed to have the highest degree of π-acceptor character. This reduces overall electron density on the metal atom, particularly *trans* to the ligand concerned, which is then more susceptible to nucleophilic attack. By contrast, a strong σ-donor ligand is expected to produce an axial polarisation of the metal such that a concentration of negative charge occurs on the far side, thus weakening the bond to a *trans* ligand. It should be noted, however, that distortion effects can sometimes partially obscure the *trans*-effect in cases where mixed *cis–trans* and distortion isomerism is observed.

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