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Chirality in mononuclear square planar complexes

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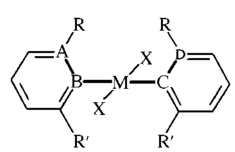
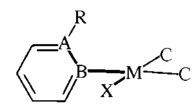
The aim of this paper is to draw chemists' attention to the chirality of square planar complexes and to ensure that authors of publications take this chemical aspect into consideration. Some simple prochiral or chiral complexes of Pd(II) or Pt(II) with 2-methyl or 2-ethylpyridine were prepared and structurally characterized by X-ray diffraction methods in order to prove that the chirality in square planar complexes is a rather common event. The situation regarding the stereodescriptors for axial chirality, planar chirality and helicity is both confused and confusing and in our opinion it would be better to adopt only the *P* and *M* terms that are related to the sign of the appropriate torsion angles.

Most textbooks on General and Inorganic Chemistry or Inorganic Chemistry rarely approach the inorganic stereochemistry of square planar complexes and when it is taken into account only *cis-trans* isomerism is considered. What is more, the likelihood of obtaining enantiomers is pointed out as a rare event, limited to specially chosen bidentate ligands or through the use of a chiral ligand. One of the first articles in the chemical literature, which presents stereoisomerism with different optical properties in square planar complexes, dates back to 1935.[1] The chirality in square planar complexes is also important from a biological point of view, in fact many chiral complexes of Pt(II) with potential antitumor activity have been synthesized. Generally, it was observed that the two isomers present different activity on tumors. These studies are important because they allow the investigation of the interaction mechanism of Pt(II) complexes with chiral transport agents or with DNA.[2,3,4]

A square planar complex may be dissymmetric even if it does not bind ligands with chiral centres or special bidentate ligands. Using the terms so carefully developed by organic chemists, for the square planar complexes, it is possible to distinguish two other types of chirality: (a) axial chirality (term used to refer to stereoisomerism resulting from the non-planar arrangement of four groups in pairs about a chirality axis).[5] Axial chirality can be created when two monodentate planar rings are *trans*-coordinated and their *ortho*-substituents are bulky enough to determine a rotation of the two rings about the axial B–C axis (see below). The torsion angle that defines the chirality is τ[A–



B–C–D] if R presents a CIP (Cahn–Ingold–Prelog) priority greater than R′. If τ is positive (right-handed helix) the chirality term is *P*, otherwise the term is *M*. (b) Planar chirality (term used to refer to stereoisomerism resulting from the arrangement of out-of-plane groups with respect to a chirality plane).[5] Planar chirality can arise when a monodentate planar ring with only C_s local symmetry is orthogonally bound to a metal centre and two other different ligands are *cis*-coordinated with respect to the ring (see below).

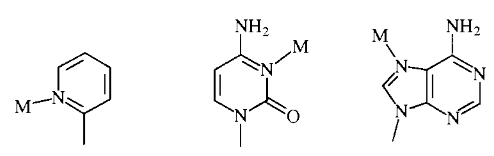


The torsion angle that defines the chirality is τ[A–B–M–X] if X presents a CIP priority greater than C. If τ is positive (right-handed helix) the chirality term is *P* or otherwise the term is *M*.

Results and discussion

In order to determine all the possible chiral square planar complexes, the *cis-trans* stereoisomers obtained with four different monodentate ligands (A, B, C, D) with spherical symmetry are first examined (MA_4, MB_4, MC_4 and MD_4 are considered symmetrically equivalent as are MA_3B, MA_3C, MA_3D and so on) (see Scheme 1).

Now every stereoisomer drawn is considered and the ligand A is substituted with Z, where Z is any planar monodentate ligand that presents the C_s local symmetry when coordinated as shown in below.

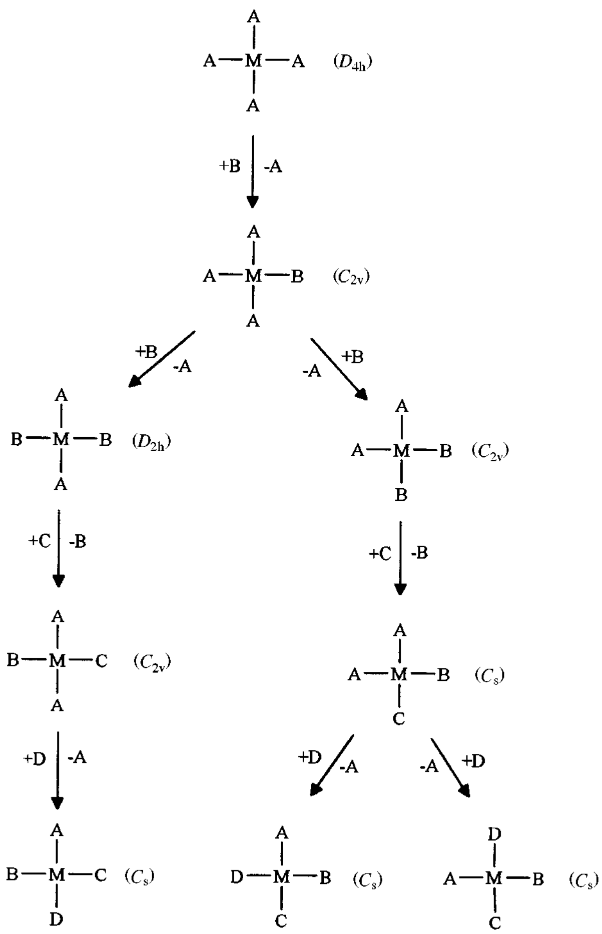


2-methylpyridine 1-methylcytosine 9-methyladenine

The two possible orientations of the ligand with respect to the square planar coordination are indicated as Z^+ and Z^-, assuming that it is coordinated orthogonally. For clarity Z = 2-methylpyridine is considered in the perspective diagrams. When a chiral complex is shown in the diagrams only one of the two enantiomers is depicted.

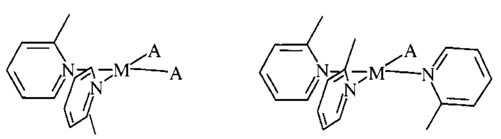
MA_4

The substitution of A with Z generates twelve diastereoisomers



Scheme 1

(see Scheme 2), two of which, *cis*-$MA_2Z^+Z^-$ (C_2) and *cis*-$MAZ^+Z^+Z^-$ (C_1), have enantiomers and present planar chirality (see below).



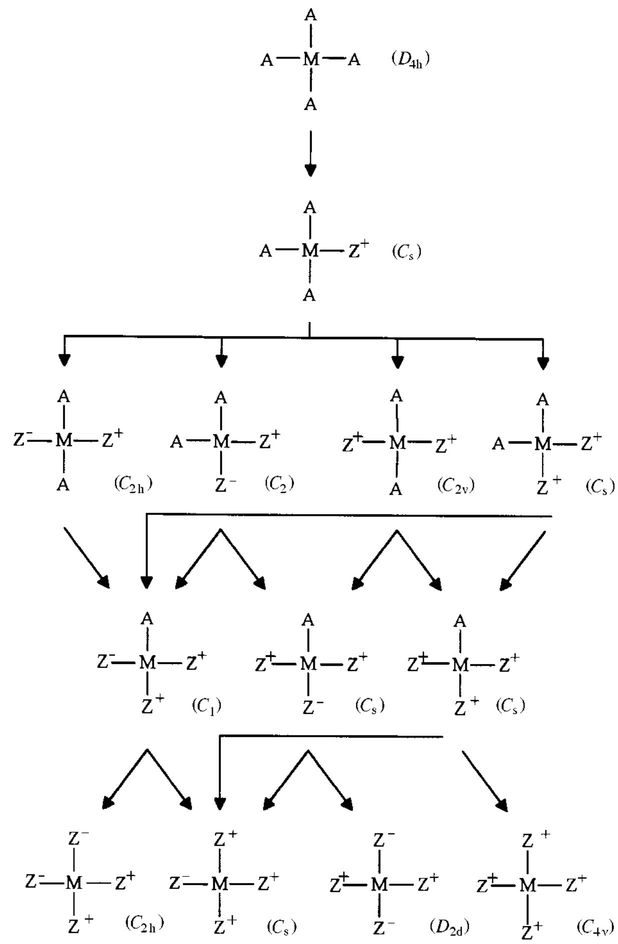
When the steric hindrance of Z is relevant (bulky substituent in the *ortho* position of the pyridine) the complexes *trans*-$MA_2Z^+Z^+$ (C_{2v}), *trans*-$MAZ^+Z^-Z^+$ (C_s), $MAZ^+Z^+Z^+$ (C_s), $MZ^-Z^+Z^+Z^+$ (C_s), $MZ^+Z^-Z^+Z^-$ (D_{2d}) and $MZ^+Z^+Z^+Z^+$ (C_{4v}) can also present chirality (atropisomerism) and the symmetry groups become C_2, C_1, C_1, C_1, D_2 and C_4, respectively.

MA_3B

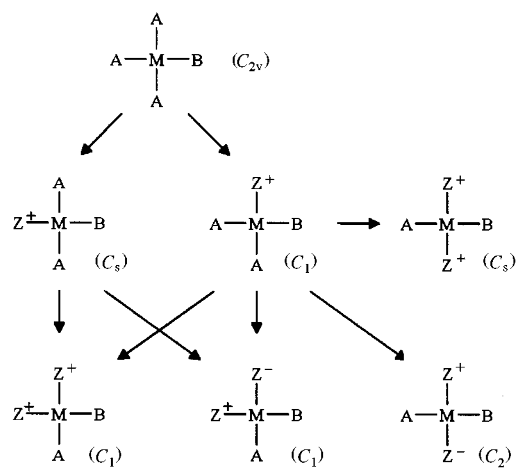
The substitution of A with Z is now reduced to only two possibilities because the species MBZ_3 is symmetrically equivalent to MAZ_3, already examined. In Scheme 3 four planar chiral complexes are envisaged: *cis*-MA_2BZ^+ (C_1), *cis*-$MABZ^+Z^+$ (C_1), *cis*-$MABZ^+Z^-$ (C_1) and *trans*-MAZ^-BZ^+ (C_2). Moreover, where the steric hindrance of Z is relevant, the complex *trans*-MAZ^+BZ^+ (C_s) can present atropisomerism and the symmetry drops to C_1.

trans- and *cis*-MA_2B_2

The substitution of A with Z generates the species *trans*- and *cis*-MAB_2Z, *trans*- and *cis*-MB_2Z_2 that are symmetrically equivalent to *trans*- and *cis*-MA_2BZ and *trans*- and *cis*-MA_2Z_2, already examined.



Scheme 2



Scheme 3

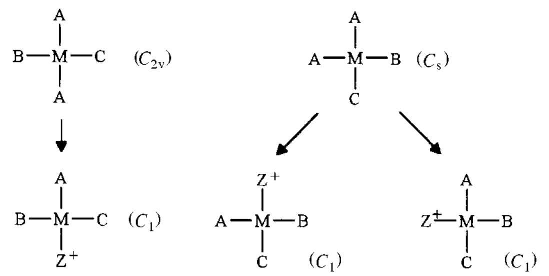
trans- and *cis*-MA_2BC

Only one substitution of A with Z is considered because the double substitution leads to cases which have already been examined (*trans*-MBZ^+CZ^+ = *trans*-MAZ^+BZ^+ and so on). The planar chiral complexes in this case are: MZ^+BAC (C_1), MZ^+BCA (C_1), MZ^+ABC (C_1) (see Scheme 4).

MACDB, MABCD, MADBC

The substitution of A with Z leads to species symmetrically equivalent to the ones considered in the former case.

Summarizing, the cases in which a square planar complex can present chirality, without using special bidentate or chiral ligands, are numerous. Examples of the two kinds of chirality are found: planar: *cis*-$MA_2Z^+Z^+$ (C_2), *cis*-$MAZ^+Z^+Z^-$ (C_1),



Scheme 4

cis-MA_2BZ^+ (C_1), *cis*-$MABZ^+Z^+$ (C_1), *cis*-$MABZ^+Z^-$ (C_1), *trans*-MAZ^-BZ^+ (C_2), MZ^+BAC (C_1), MZ^+BCA (C_1), MZ^+-ABC (C_1). Axial: *trans*-$MA_2Z^+Z^+$ (C_{2v}), *trans*-$MAZ^+Z^-Z^+$ (C_s), $MAZ^+Z^+Z^+$ (C_s), $MZ^-Z^+Z^+Z^+$ (C_s), $MZ^+Z^-Z^+Z^-$ (D_{2d}), $MZ^+Z^+Z^+Z^+$ (C_{4v}) and *trans*-MAZ^+BZ^+ (C_s), which can present chirality (atropisomerism) and the symmetry groups become C_2, C_1, C_1, C_1, D_2, C_4 and C_1, respectively.

Axial chirality, planar chirality and helicity in square planar complexes, here treated, are not different kinds of chirality since each of them can be characterized by a torsion angle, nevertheless some complexes are best described as presenting helical dissymmetry of the hexahelicene type; as in the case of *cis*-bis(2,6-diphenylpyridinato-$N,C^{2'}$)platinum(II).[6]

In this paper only monodentate ligands have been considered, but the case can easily be extended to bidentate chelating ligands. In fact, when the chelating donor atoms are equivalent we fall into the category of *cis*-MA_2ZY, and when they are different to that in MABZY (A and B in *cis* position), where Y is Z or a monodentate spherical ligand. Cases of chiral dimeric or polymeric square planar complexes are more complicated and will be examined at a later date. To prove our assertions we have synthesized some complexes of Pd(II) and Pt(II) with the simplest ligands of Z type *i.e.* 2-methyl- and 2-ethylpyridine (2mepy and 2etpy), some of them being prochiral and others chiral.

Single-crystal structures of [H2etpy][$PtCl_3$(2etpy)] 1, *trans*-[$PdCl_2(2etpy)_2$] 2, *trans*-[$PdCl_2(2mepy)_2$] 3 and *cis*-[$PtI_2(2etpy)_2$] 4

The structure of **1** consists of anionic square planar complexes of Pt(II) where three chlorine atoms and a 2-ethylpyridine molecule are coordinated to the metal centre (Fig. 1). The counter ion is a protonated 2-ethylpyridine molecule. The complex shows a pseudo C_s symmetry with the pyridine ring nearly orthogonal to the coordination plane [the dihedral angle between the two planes is 82.9(3)°]. The complex is prochiral, in fact it is sufficient to substitute one of the two chlorine atoms in *cis* positions with respect to the coordinated pyridine molecule with any other ligand in order to obtain a chiral complex.

The structure of **2** consists of centrosymmetric neutral square planar complexes of Pd(II) in which two chlorine atoms and two 2-ethylpyridine molecules are *trans*-coordinated (Fig. 2). As in **1** the pyridine ring is nearly orthogonal to the coordination plane [86.8(2)°]. This complex is prochiral too and the substitution of one of the two chlorine atoms with any other ligand makes it chiral.

The structure of **3** consists of neutral square planar complexes of Pd(II) in which the two *trans*-coordinated 2-methylpyridine molecules show a *cis* disposition of the methyl groups, the coordination is completed by two chlorine atoms. The steric hindrance of the methyl groups determines a desymmetrization of the complex that belongs to the C_2 symmetry group and not to the C_{2v} one. One pyridine ring is canted at an angle of 18.6(5)° to the other pyridine ring and the angles the rings form with the coordination plane are 74.1(2) and 87.4(2)°, respectively. The complex could be considered an example of atropisomerism even if the two methyl groups are not

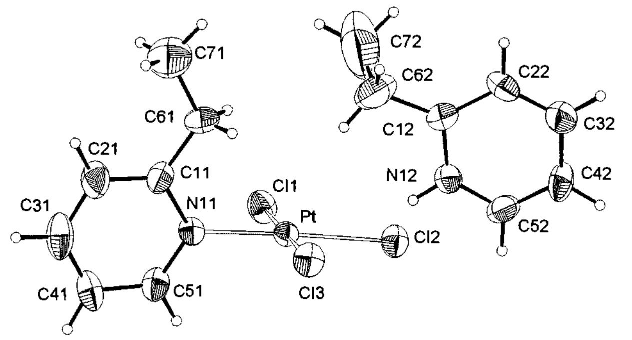


Fig. 1 Perspective view of complex **1**. The thermal ellipsoids are drawn at the 30% probability level.

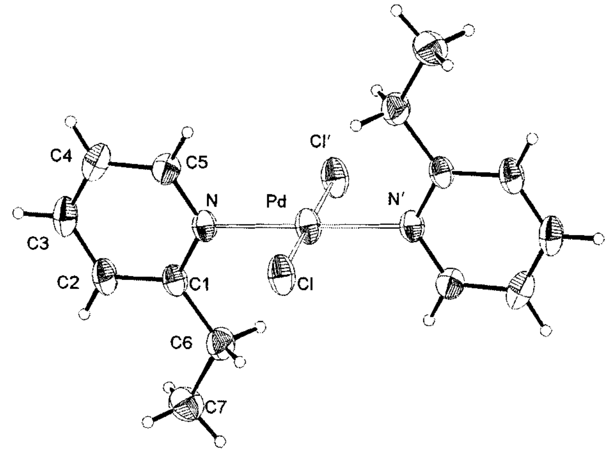


Fig. 2 Perspective view of complex **2**. The thermal ellipsoids are drawn at the 30% probability level.

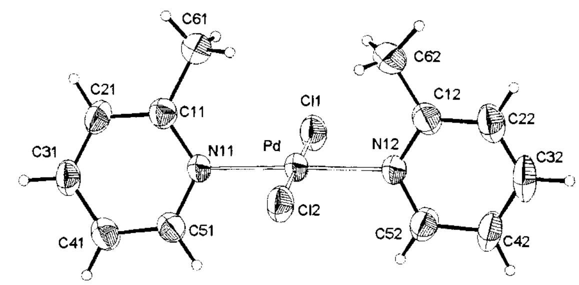


Fig. 3 Perspective view of complex **3**. The thermal ellipsoids are drawn at the 30% probability level.

sufficiently bulky to determine a high barrier of interconversion. The torsion angle that defines the axial chirality is τ[C(11)–N(11)–N(12)–C(12)] = 18(1)°. The isomer represented in Fig. 3 could be defined as R_a or *P*.

The structure of **4** consists of neutral complexes of Pt(II) in which the square planar coordination is achieved by two iodine atoms and two 2-ethylpyridine molecules *N*-coordinated in *cis* positions. The pyridine rings are not completely orthogonal to the coordination plane [76.5(2) and 77.4(2)°] but are tilted in the same direction, with a dihedral angle between them of 89.7(3)°. The complex presents a non-crystallographic C_2 symmetry and thus is chiral. There are two chiral planes and the configuration of the enantiomer represented in Fig. 4 is S_p,S_p or *MM*. The torsion angles defining the chirality are τ[I(1)–Pt–N(11)–C(11)] = −77.2(7)° and τ[I(2)–Pt–N(12)–C(12)] = −75.4(6)°. In the solid-state structure both enantiomers are present. Free rotation of the pyridine ligand about the N–Pt bond is hindered by two energy barriers of 482 and 1054 kJ mol^{-1} involving the I(1)···H(61B), I(1)···C(61) and C(52)···H(61B), C(52)···C(61), N(12)···H(61B) contacts, respectively. These values were calculated using the ROTENER program.[7]

The presence of the ethyl or methyl group in the *ortho*

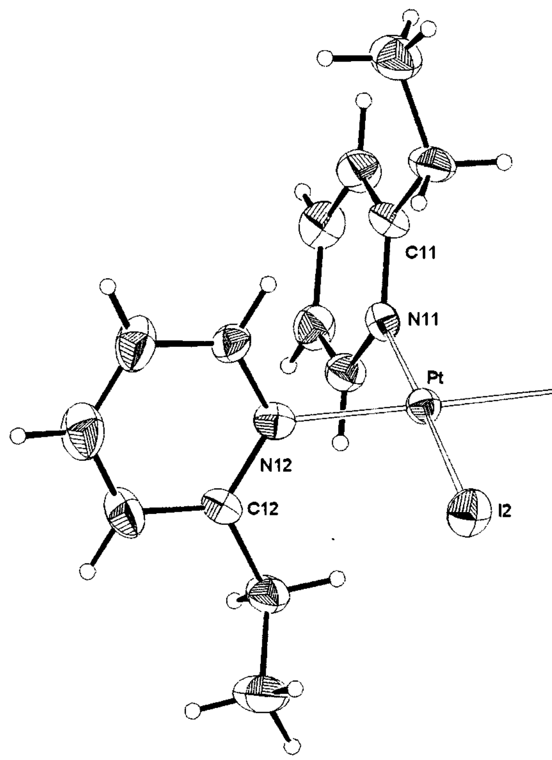


Fig. 4 Perspective view of complex **4**. The thermal ellipsoids are drawn at the 30% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Pt–Cl(1)	2.305(4)	Pt–Cl(3)	2.305(4)
Pt–Cl(2)	2.300(4)	Pt–N(11)	1.992(10)
N(11)–C(51)	1.33(2)	N(12)–C(52)	1.32(2)
N(11)–C(51)	1.37(2)	N(12)–C(12)	1.35(2)
C(11)–C(21)	1.37(2)	C(12)–C(22)	1.41(2)
C(11)–C(61)	1.48(2)	C(12)–C(62)	1.56(2)
C(21)–C(31)	1.39(2)	C(22)–C(32)	1.37(2)
C(31)–C(41)	1.38(2)	C(32)–C(42)	1.39(2)
C(41)–C(51)	1.38(2)	C(42)–C(52)	1.34(2)
C(61)–C(71)	1.49(2)	C(62)–C(72)	1.46(2)
N(11)–Pt–Cl(2)	177.9(3)	Cl(3)–Pt–Cl(1)	178.9(1)
N(11)–Pt–Cl(3)	90.6(3)	N(11)–Pt–Cl(1)	88.7(3)
Cl(2)–Pt–Cl(1)	91.1(1)	Cl(2)–Pt–Cl(3)	89.7(1)
C(51)–N(11)–Pt	119.0(9)	C(11)–N(11)–Pt	124.3(9)
C(51)–N(11)–C(11)	116.7(11)	C(52)–N(12)–C(12)	126.1(15)

Table 2 Selected bond lengths (Å) and angles (°) for complex **2**

Pd–N	2.031(4)	C(2)–C(3)	1.382(8)
Pd–Cl	2.299(2)	C(3)–C(4)	1.365(8)
C(1)–C(2)	1.385(6)	C(4)–C(5)	1.373(7)
C(1)–C(6)	1.498(7)	C(6)–C(7)	1.494(7)
N–Pd–Cl	90.1(1)	C(2)–C(1)–C(6)	122.7(4)
C(1)–N–C(5)	120.4(4)	C(1)–C(2)–C(3)	119.5(5)
C(1)–N–Pd	122.3(3)	C(4)–C(3)–C(2)	119.5(5)
C(5)–N–Pd	117.4(3)	C(5)–C(4)–C(3)	118.4(5)
N–C(1)–C(2)	120.1(4)	N–C(5)–C(4)	122.1(5)
N–C(1)–C(6)	117.2(4)	C(1)–C(6)–C(7)	116.5(4)

Table 3 Selected bond lengths (Å) and angles (°) for complex **3**

Pd–Cl(1)	2.300(3)	Pd–Cl(2)	2.313(3)
Pd–N(11)	2.033(6)	Pd–N(12)	2.043(6)
N(11)–C(51)	1.34(1)	N(12)–C(52)	1.32(1)
N(11)–C(11)	1.35(1)	N(12)–C(12)	1.33(1)
C(11)–C(21)	1.37(1)	C(12)–C(22)	1.35(1)
C(11)–C(61)	1.50(1)	C(12)–C(62)	1.51(1)
C(21)–C(31)	1.38(1)	C(22)–C(32)	1.37(2)
C(31)–C(41)	1.38(1)	C(32)–C(42)	1.39(2)
C(41)–C(51)	1.38(1)	C(42)–C(52)	1.37(1)
Cl(1)–Pd–Cl(2)	178.81(7)	N(11)–Pd–N(12)	177.5(2)
N(11)–Pd–Cl(1)	90.6(2)	N(11)–Pd–Cl(2)	90.0(2)
N(12)–Pd–Cl(1)	88.7(2)	N(12)–Pd–Cl(2)	90.6(2)
C(51)–N(11)–C(11)	119.6(7)	C(52)–N(12)–C(12)	120.8(8)
C(51)–N(11)–Pd	117.2(5)	C(52)–N(12)–Pd	116.9(6)
C(11)–N(11)–Pd	123.2(5)	C(12)–N(12)–Pd	122.3(6)

Table 4 Selected bond lengths (Å) and angles (°) for complex **4**

Pt–I(1)	2.591(1)	Pt–I(2)	2.582(1)
Pt–N(11)	2.059(7)	Pt–N(12)	2.074(8)
N(11)–C(51)	1.34(1)	N(12)–C(52)	1.32(1)
N(11)–C(11)	1.34(1)	N(12)–C(12)	1.35(1)
C(11)–C(21)	1.38(1)	C(12)–C(22)	1.38(1)
C(11)–C(61)	1.49(1)	C(12)–C(62)	1.51(1)
C(21)–C(31)	1.38(1)	C(22)–C(32)	1.37(2)
C(31)–C(41)	1.36(1)	C(32)–C(42)	1.37(2)
C(41)–C(51)	1.36(1)	C(42)–C(52)	1.36(1)
C(61)–C(71)	1.50(1)	C(62)–C(72)	1.51(2)
I(1)–Pt–I(2)	91.73(3)	N(11)–Pt–N(12)	89.5(3)
N(11)–Pt–I(2)	178.3(2)	N(12)–Pt–I(1)	179.2(2)
N(11)–Pt–I(1)	89.9(2)	N(12)–Pt–I(2)	88.9(2)
C(51)–N(11)–C(11)	118.7(8)	C(52)–N(12)–C(12)	118.9(8)
C(51)–N(11)–Pt	116.7(6)	C(52)–N(12)–Pt	117.4(6)
C(11)–N(11)–Pt	124.6(6)	C(12)–N(12)–Pt	123.6(6)

position of the coordinated pyridine causes an asymmetry in the Pt–N–C or Pd–N–C bond angles in all four complexes, the one involving the substituted carbon atom is greater [C(51)–N(11)–Pt = 119.0(9)°, C(11)–N(11)–Pt = 124.3(9)° for **1**, C(5)–N–Pd = 117.4(3)°, C(1)–N–Pd = 122.3(3)° for **2**, C(51)–N(11)–Pd = 117.2(5)°, C(11)–N(11)–Pd = 123.2(5)°, C(52)–N(12)–Pd = 116.9(6)°, C(12)–N(12)–Pd = 122.3(6)° for **3** and C(51)–N(11)–Pt = 116.7(6)°, C(11)–N(11)–Pt = 124.6(6)°, C(52)–N(12)–Pt = 117.4(6)°, C(12)–N(12)–Pt = 123.6(6)° for **4**]. Selected bond distances and angles are provided in Tables 1–4. Bond distances and angles of the anionic complex **1** are comparable to those found in tetraammineplatinum(II) bis[trichloro(2,6-dimethylpyridine)platinate(II)][8] and in potassium trichloro(2,6-dimethylpyridine)platinate(II)[9] although in these compounds the Pt–N–C bond angles of the 2,6-dimethylpyridine molecules are obviously symmetrical [119.6(5)°, 120.2(5)° and 119(1)°, 119(1)°, respectively], in *cis*-dichloro(dimethyl sulfoxide)(2-methyl pyridine)platinum(II)[10] these bond angles are surprisingly symmetric [119.1(9)°, 119.6(9)°] while in *trans*-dichloro(dimethyl sulfoxide)(2-methylpyridine)platinum(II)[11] they are, as expected, [116.0(8)°, 125.7(8)°] comparable with those found in complexes **1**–**4**. In complex **4** the lengthening of the Pt–N bond distances are in accord with the greater *trans* influence of the iodine atoms with respect to the chlorine atoms. Bond distances and angles of the Pd complexes are normal and comparable with those found in *trans*-dichlorobis(2,6-dimethylpyridine)palladium(II)[12] apart from the Pd–N–C bond angles that are symmetric in this last compound [120.12(15)°, 119.87(15)°].

Conclusion

As already stated the object of this paper is to attract chemists' attention to the chirality of square planar complexes. We have undertaken a bibliographic search on the Cambridge Structural Database and despite the limited number of complexes of Pd or Pt halides with *N*-bonded pyridine derivatives we found some square planar complexes that the authors did not recognize as chiral. To demonstrate the facility with which the chirality in square planar complexes can be found we have prepared and characterized some simple complexes of Pd or Pt with 2-methyl- or 2-ethylpyridine that are prochiral or chiral. In the chemical literature some of the most interesting chiral complexes of Pt that show their importance in biochemistry are

Table 5 Crystal data and structure refinement for compounds **1**–**4**

Compound	1	2	3	4
Chemical formula	$C_{14}H_{19}Cl_3N_2Pt$	$C_{14}H_{18}Cl_2N_2Pd$	$C_{12}H_{14}Cl_2N_2Pd$	$C_{14}H_{18}I_2N_2Pt$
M	516.75	391.60	363.55	663.19
T/K	293(2)	293(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	1.54184	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/a$
a/Å	17.029(8)	7.453(5)	8.603(5)	10.693(6)
b/Å	9.523(4)	7.522(5)	10.786(7)	13.656(7)
c/Å	11.261(5)	8.423(6)	8.286(5)	11.749(6)
α/°		97.36(2)	91.17(2)	
β/°	102.42(2)	114.85(2)	116.37(2)	93.41(2)
γ/°		107.97(2)	91.54(2)	
V/Å^3	1783.4(14)	389.0(5)	688.2(7)	1712.6(16)
Z	4	1	2	4
D_c/Mg m^{-3}	1.925	1.672	1.754	2.572
μ/mm^{-1}	8.309	1.524	14.274	11.788
No. observed reflections (unique)	3292 (3134) [*R*(int) = 0.0771]	1373 (1373)	1996 (1996)	5212 (5001) [*R*(int) = 0.0427]
Final *R* indices [$I > 2\sigma(I)$] (*R*1, *wR*2)^a	0.0472, 0.1031	0.0416, 0.1012	0.0579, 0.1577	0.0455, 0.1233
R indices (all data) (*R*1, *wR*2)	0.1102, 0.1242	0.0547, 0.1044	0.0648, 0.1693	0.0725, 0.1315

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

the *cis*-$[(NH_3)_2Pt(9\text{-MeA-}N7)(9\text{-EtGH-}N7)][NO_3]_2\cdot H_2O$ [13] and the *cis*-$[(NH_3)_2Pt(9\text{-MeA-}N7)(9\text{-EtGH-}N7)][PF_6]_2\cdot 1.5H_2O$ [14] (9-MeA = 9-methyladenine; 9-EtGH = 9-ethylguanine). These complexes can be considered as model compounds of the second most abundant DNA adduct of the antitumor agent cisplatin. These complexes present planar chirality and the descriptors of the four isomers in two pairs of enantiomers can be represented by *PM*, *MP* and *PP*, *MM*, where *P* and *M* stand for plus and minus (signs of the torsion angles α and β). In our opinion, for clarity, it would be better not to introduce new stereodescriptors when the source of the chirality is the same. The situation regarding the stereodescriptors for axial chirality, planar chirality and helicity is both confused and confusing and we believe that only the *P* and *M* terms, related to the sign of the appropriate torsion angles, should be adopted.

Experimental

Starting reagents and transition metal salts $PdCl_2$ and K_2PtCl_4 were pure commercial products (Aldrich, Fluka). Elemental analyses (C, H, N) were performed with a Carlo Erba EA 1108 automated analyzer. FT-IR spectra were recorded on a Nicolet 5PC FT spectrometer. The melting points (not corrected) were determined with a Gallenkamp apparatus.

Syntheses

2-Ethylpyridinium trichloro(2-ethylpyridine)platinate(II) 1. 2-Ethylpyridine (0.026 g, 0.24 mmol) was added dropwise to a solution of K_2PtCl_4 (0.050 g, 0.12 mmol) in 20 cm^3 of H_2O. The colour changed immediately from red to orange. The solution was stirred on a ice bath for 5 h and then 0.2 cm^3 of HCl (37%) was added. The solution was left to stand at 4 °C and after 20 days a few yellow crystals of the product formed together with red crystals of K_2PtCl_4. Yield 0.024 g, 39% (Found: C, 33.02; H, 3.15; N, 5.01. Calc. for $C_{14}H_{19}Cl_3N_2Pt$: C, 32.54; H, 3.71; N, 5.42%). Mp (capillary) > 300 °C.

***trans*-Dichlorobis(2-ethylpyridine)palladium(II) 2.** 2-Ethylpyridine (0.230 g, 2.15 mmol) was added to a solution of $PdCl_2$ (0.177 g, 1.00 mmol) and LiCl (0.085 g, 2.00 mmol) in 50 cm^3 of MeOH. The colour changed from red-brown to yellow-orange then a yellow precipitate was formed. The reaction mixture was stirred at room temperature for 30 min. The precipitate was filtered off and washed with MeOH, then dissolved in CH_2Cl_2 and recrystallized by slow evaporation. Yellow crystals of the product were obtained. Yield 0.286 g, 73% (Found: C, 43.02; H, 4.15; N, 7.01. Calc. for $C_{14}H_{18}Cl_2N_2Pd$: C, 42.94; H, 4.63; N, 7.15%). Mp (capillary) 261 °C (decomp.). IR (KBr discs/cm^{-1}): 3069w, 2971w, 1607s, 1482s, 804s, 774s.

***trans*-Dichlorobis(2-methylpyridine)palladium(II) 3.** The title complex was obtained during an attempt to obtain a chiral compound by reacting the prochiral complex $[PdCl_2(Hmeatur)]\cdot H_2O$ **5** [15] (Hmeatur = 4-amino-3-methyl-1,2,4-Δ^2-triazoline-5-thione) with 2-methylpyridine in the molar ratio 1 : 1, in acetone. To a solution of **5** (0.065 g, 0.20 mmol) in acetone (30 cm^3) 2-methylpyridine (0.019 g, 0.20 mmol) was added dropwise. After a few minutes a yellow precipitate formed. The filtered precipitate was treated and extracted repeatedly with small amounts of acetone until the washings were colourless. After a few days of slow evaporation of the solution pale yellow crystals of the product were formed. Yield 0.023 g, 31% (Found: C, 40.02; H, 3.45; N, 7.31. Calc. for $C_{12}H_{14}Cl_2N_2Pd$: C, 39.64; H, 3.88; N, 7.70%). Mp (capillary) 273 °C (decomp.). IR (KBr discs/cm^{-1}): 3085w, 2920w, 1630s, 1424s, 1384s, 766s.

***cis*-Diiodobis(2-ethylpyridine)platinum(II) 4.** To a concentrated aqueous solution of KI (0.160 g, 0.96 mmol) 10 cm^3 of an aqueous solution of K_2PtCl_4 (0.050 g, 0.12 mmol) were added and the resulting solution was stirred for 45 min. The colour changed from yellow to brown and a precipitate was observed. To the filtered brown solution, 2-ethylpyridine (0.032 g, 0.30 mmol) was added and a few minutes later the solution turned from brown to yellow, it was then stirred at room temperature for 5 h. A non-homogeneous yellow-brown precipitate formed which was filtered off and washed first with H_2O, then with EtOH and finally with diethyl ether. The brown impurities were eliminated and the yellow product was dissolved in acetone and yellow crystals of the product were obtained by slow evaporation. Yield 0.029 g, 36% (Found: C, 25.62; H, 2.15; N, 4.01. Calc. for $C_{14}H_{18}I_2N_2Pt$: C, 25.35; H, 2.74; N, 4.22%). Mp (capillary) 157 °C (decomp.). IR (KBr discs/cm^{-1}): 3065w, 2966w, 1603s, 1474vs, 797s, 702vs.

X-Ray crystallography

The crystallographic data for the four compounds are summarized in Table 5. The data collections were performed on a Philips PW 1100 (**1**), an Enraf-Nonius CAD4 (**3**) and a Siemens AED (**2, 4**) diffractometer. The individual profiles were analyzed following the method of Lehmann and Larsen.[16] Intensities were corrected for Lorentz and polarization effects. A correction for absorption was applied for **1**, **3** and **4**.[17] The structures were solved by direct methods (SIR92)[18] and refined first isotropically then anisotropically by full-matrix least-squares using the SHELXL-97 program[19] for all the non-hydrogen atoms. For every compound, the hydrogen atoms were placed at their geometrically default-distance calculated positions and refined riding on their parent atoms. The final difference map for compound **4** revealed a residual electron density of 2.49 e $Å^{-3}$, 0.04 Å away from the Pt atom. All calculations were carried out on the DIGITAL AlphaStation 255 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma. The programs Parst[20] and ORTEP[21] were also used.

CCDC reference number 186/1393.

See http://www.rsc.org/suppdata/dt/1999/1575/ for crystallographic files in .cif format.

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