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Platinum(II) phosphine and orotate complexes with aminopyridine co-ligands, and their molecular recognition *via* hydrogen bonding †

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Received 4th February 2000, Accepted 27th March 2000
First published as an Advance Article on the web 20th September 2000

The new complexes $[Pt(dppp)(py)_2][OTf]_2$, **1**, $[Pt(dppp)(2\text{-ap})_2][OTf]_2$, **2**, $[(dppp)Pt(\mu\text{-OH})\{\mu\text{-NH}(C_5H_3N)NH_2\}\text{-}Pt(dppp)][OTf]_2$, **3** (py = pyridine, 2-ap = 2-aminopyridine, $NH(C_5H_3N)NH_2$ = 2,6-diaminopyridine anion, dppp = 1,3-bis(diphenylphosphino)propane, OTf = O_3SCF_3) have been prepared *via* reactions between $[Pt(dppp)(OTf)_2]$ and pyridine, 2-aminopyridine or 2,6-diaminopyridine (2,6-dap) respectively. The amines exhibit a range of co-ordination modes. Pyridine and 2-aminopyridine co-ordinate to platinum through *endo*-nitrogen atoms in complexes **1** and **2**, the latter existing as a pair of rotomers due to the steric hindrance introduced by the 2-substituent. However, 2,6-diaminopyridine co-ordinates to platinum through the *exo*-nitrogen of one amino group, to give the unusual μ-amido complex **3**. Reaction of the known orotate chelate complex $[Pt(PEt_3)_2(N,O\text{-HL})]$ [HL = orotate, the dianion of 2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid (orotic acid)] with 2,6-dap gave $[Pt(PEt_3)_2(2,6\text{-dap})(N\text{-HL})]$ **4**, which contains an unconventional monodentate orotate ligand. In this co-ordination mode the orotate retains an ADA hydrogen bonding site and was found to co-crystallise with 2,6-dap *via* complementary ADA : DAD triple hydrogen bonds to give $[Pt(PEt_3)_2(N\text{-HL})(2,6\text{-dap})]\cdot 2,6\text{-dap}$, **5**. Complex **5** exhibits a helical chain structure of associated [1 + 1] adducts in the solid state.

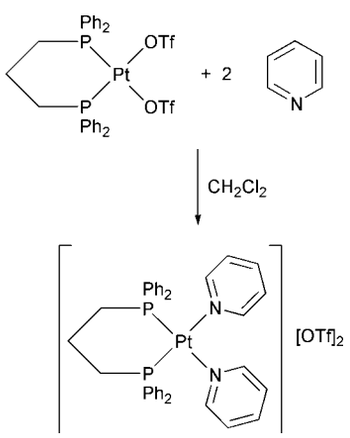
Introduction

The study of the co-ordination of nucleobases and amines to platinum(II) centres is relevant to the development of metallodrugs.[1] We and others have investigated complexes of the uracil derivative orotic acid (2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid) which co-ordinates generally as the dianion, and in particular we have studied its ability to co-ordinate to platinum group metal ions and simultaneously form hydrogen bonds to other molecules.[2,3] This bifunctionality leads to control over the aggregation of metal complexes, and to molecular recognition of complementary organic molecules *via* hydrogen bonding. Dimers, infinite tapes[2,3] and sheets[3] of orotate complexes, as well as co-crystals with 2,6-diaminopyridine, have been generated in the solid state by using different metal ions, co-ligands and solvents. 2,6-Diaminopyridine has been used as a hydrogen bonding partner since it bears the requisite complementary DAD (donor–acceptor–donor) hydrogen bonding motif. Serendipitously, during our studies, we observed that in addition to adduct formation *via* hydrogen bonding, 2,6-diaminopyridine may also act as a ligand toward platinum(II) in orotate complexes. We were aware of only limited previous studies of the co-ordination of aminopyridines to platinum(II),[4] and therefore studied the complexes in more detail. We report here our observations on the diversity of co-ordination behaviour exhibited by pyridine (py), 2-aminopyridine (2-ap) and 2,6-diaminopyridine (2,6-dap) with platinum–phosphine and platinum–orotate complexes.

Results and discussion

Reactions between $[Pt(dppp)(OTf)_2]$ and pyridine, 2-aminopyridine and 2,6-diaminopyridine

The complex $[Pt(dppp)(OTf)_2]$ (dppp = 1,3-bis(diphenylphosphino)propane) was selected as the starting material for reactions with pyridine, 2-aminopyridine and 2,6-diaminopyridine because of the lability of the triflate anions and convenient spectroscopic NMR handles provided by the presence of the chelating diphosphine. The experiments were carried out in CH_2Cl_2 solvent at room temperature using two equivalents of py, 2-ap or 2,6-dap and monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. On addition of pyridine, the signal at δ −9.46 ($J_{Pt\text{-}P}$ = 3712 Hz) for the starting material $[Pt(dppp)(OTf)_2]$ was replaced rapidly and quantitatively by a singlet at δ −14.7 ($J_{Pt\text{-}P}$ = 3034 Hz) indicating that the reaction between $[Pt(dppp)(OTf)_2]$ and pyridine leads, as expected, to a single product, eqn. (1). A white solid separated which analysed correctly for



(1)

† Based on the presentation given at Dalton Discussion No. 3, 9–11th September 2000, University of Bologna, Italy.

Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b000974l

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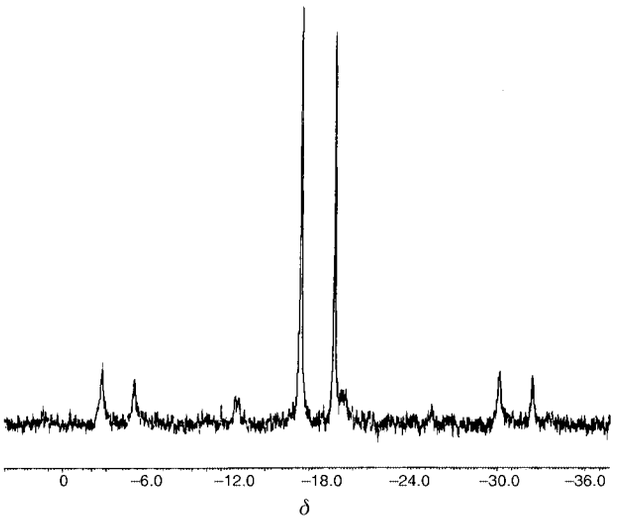


Fig. 1 ^{31}P-{^{1}H} NMR spectrum showing the singlets and associated ^{195}Pt satellites of the 1 : 1 mixture of complexes **2a** and **2b**.

[Pt(dppp)(py)$_2$][OTf]$_2$ **1**. Its IR spectrum shows absorptions at 3072, 2928 cm^{-1} ν(C–H) and strong bands at 1281, 1256 cm^{-1} which are similar to those of *cis*-[Pt(dppp)(pyz)$_2$][OTf]$_2$ (pyz = pyrazine) reported by Stang *et al.*[5] The positive ion FAB mass spectrum shows the cation [Pt(dppp)(py)$_2$(OTf)]$^+$ at *m*/*z* 914 and the negative ion FAB mass spectrum has the anion [OTf]$^-$ at *m*/*z* 149. The ^{1}H NMR spectrum shows the protons of the pyridine ligands at δ 7.03, 8.59 and 8.97, which have distinct downfield shifts compared to free pyridine, in addition to the methylene protons at δ 2.24–2.38 and phenyl protons at δ 7.30–7.67 of dppp. The probable structure of the complex [Pt(dppp)(py)$_2$][OTf]$_2$ **1** is therefore as shown in eqn. (1).

Under similar conditions the reaction of [Pt(dppp)(OTf)$_2$] with 2-aminopyridine was monitored by ^{31}P-{^{1}H} NMR spectroscopy. When a 1 : 2 ratio was achieved the spectrum showed two singlets at δ −15.25 ($^{1}J_{Pt\text{-}P}$ = 2988) and −17.73 ($^{1}J_{Pt\text{-}P}$ = 2986 Hz) in a 1 : 1 ratio, exhibiting very similar Pt–P coupling constants (see Fig. 1). No P–P coupling was observed indicating that the two phosphorus atoms contained in a given dppp ligand remained equivalent. This in turn implies that two different complexes were formed in a 1 : 1 ratio, each with two equivalent phosphorus centres. The similar spectroscopic parameters further suggest that the two complexes have similar structures. On standing, colourless crystals precipitated from the 1 : 2 solution. The IR spectrum of these crystals was similar to that of complex **1** except that two additional broad, medium strength bands at 3334 and 3424 cm^{-1} due to the two NH_2 groups were also present. The negative ion FAB mass spectrum gave the OTf$^-$ peak at *m*/*z* 149, and in the positive ion FAB only a peak at *m*/*z* 850 due to [Pt(dppp)(2-ap)(OTf)]$^+$ was identified. Their ^{1}H NMR spectrum indicated two different chemical shifts for the amino protons of 2-aminopyridine, both of them shifted downfield compared to the "free" ligand. It further confirmed the ratio of dppp to 2-aminopyridine to be 1 : 2.

Slow evaporation of dichloromethane from a 1 : 2 mixture of [Pt(dppp)(OTf)$_2$] and 2-aminopyridine gave two types of colourless crystals simultaneously, rhomboids (**2a**) and plates (**2b**). Compound **2a** was analysed by single crystal X-ray crystallography, which showed it to have a solid state structure (Fig. 2) very similar to that of the closely related pyrazine analogue reported by Stang *et al.*[5] The molecule has non-crystallographic C_s symmetry about a plane passing through platinum and C(14) and bisecting both the N(1)–Pt–N(7) and P(1)–Pt–P(2) angles, and the two 2-aminopyridine ring systems **A** and **C** overlay two of the diphosphine phenyl rings **B** and **D** respectively, at distances consistent with π–π stacking interactions. The co-ordination at platinum is planar to within 0.04 Å and the 2-aminopyridine rings are approximately orthogonal to this plane [86° for ring **A** and 81° for ring **C**]. The Pt–P and Pt–N co-ordination distances (Table 1) do not differ significantly from those in the related pyrazine complex.[5] The two amino groups both lie on the same side of the platinum co-ordination plane and they each have one of their amino hydrogen atoms (those oriented inwardly in Fig. 2) directed towards one of the oxygen atoms of one of the triflate anions at distances consistent with N–H · · · O hydrogen bonds. Both triflate anions exhibit distinct disorder and the above approaches are to one of the oxygen atoms of a major occupancy orientation [the N · · · O distances are 2.91 and 3.00 Å for N(2) and N(8) respectively]. The two outwardly directed amino hydrogen atoms lie within hydrogen bonding distances of a poorly resolved water molecule which has been included into the lattice, and one of the other oxygen atoms of a symmetry related counterpart of the same major occupancy triflate anion as above [the N(8) · · · O(water) and N(2) · · · O(triflate) distances are 2.90 and 3.00 Å respectively].

The complexes pack to form C_i-symmetric "dimer pairs" (Fig. 3) that are stabilised by a combination of face-to-face π

Table 1 Selected bond lengths (Å) and angles (°) for complex **2a**

Pt–N(7)	2.097(8)	Pt–N(1)	2.114(6)
Pt–P(2)	2.267(2)	Pt–P(1)	2.271(2)
N(7)–Pt–N(1)	86.4(3)	N(7)–Pt–P(2)	176.2(2)
N(1)–Pt–P(2)	91.6(2)	N(7)–Pt–P(1)	91.5(2)
N(1)–Pt–P(1)	177.9(2)	P(2)–Pt–P(1)	90.54(8)

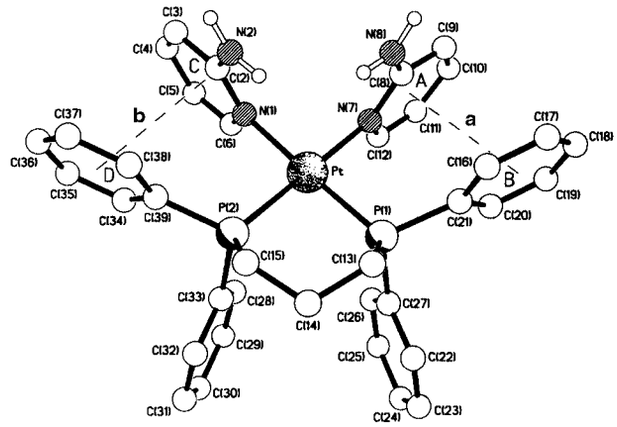


Fig. 2 The molecular structure of complex **2a**. The π–π stacking centroid · · · centroid distances are **a** 3.76 and **b** 3.84 Å.

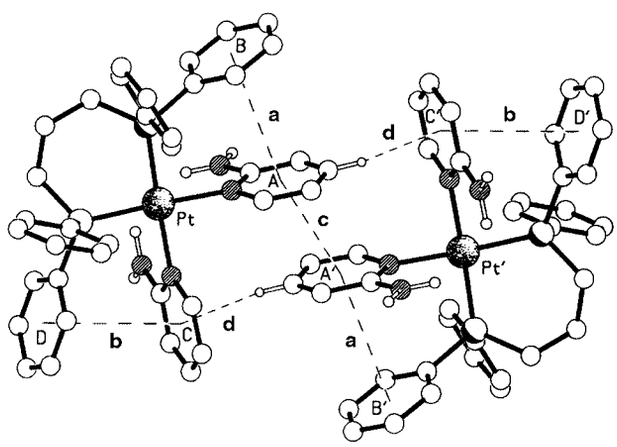


Fig. 3 The "dimer pairs" formed by π–π face-to-face and C–H · · · π edge-to-face contacts in the structure of complex **2a**. The centroid · · · centroid and mean interplanar separations of the face-to-face stacking interaction **c** are 3.79 and 3.42 Å respectively; the H · · · π distance and C–H · · · π angle for the edge-to-face contact **d** are 2.84 Å and 148° respectively.

Table 2 Selected bond lengths (Å) and angles (°) for complex **3a**

Pt(1)–N(2)	2.096(12)	Pt(1)–O(1)	2.103(11)
Pt(1)–P(1)	2.216(4)	Pt(1)–P(2)	2.238(4)
Pt(2)–O(1)	2.097(11)	Pt(2)–N(2)	2.110(12)
Pt(2)–P(4)	2.226(4)	Pt(2)–P(3)	2.244(5)
N(2)–Pt(1)–O(1)	77.4(4)	N(2)–Pt(1)–P(1)	95.3(4)
O(1)–Pt(1)–P(1)	172.6(3)	N(2)–Pt(1)–P(2)	171.2(4)
O(1)–Pt(1)–P(2)	94.2(3)	P(1)–Pt(1)–P(2)	93.2(2)
O(1)–Pt(2)–N(2)	77.2(4)	O(1)–Pt(2)–P(4)	171.2(3)
N(2)–Pt(2)–P(4)	94.3(3)	O(1)–Pt(2)–P(3)	95.3(3)
N(2)–Pt(2)–P(3)	172.5(3)	P(4)–Pt(2)–P(3)	93.2(2)

stacking of the 2-aminopyridine rings of type **A** [centroid · · · centroid and mean interplanar separations of 3.79 and 3.42 Å respectively] and edge-to-face C–H · · · π interactions between the *para*-hydrogen of a type **A** 2-aminopyridine ring in one molecule and the face of a type **C** 2-aminopyridine ring in the other and *vice versa* [H · · · π 2.84 Å, C–H · · · π 148°]. There are no inter-dimer interactions of note.

The crystal structure of the plates **2b** could not be obtained because of their rapid desolvation. Therefore, in order to gain more information on the other compound formed in the reaction, variable temperature ^{31}P-{^{1}H} NMR spectroscopy was carried out on the mixture of **2a** and **2b** in $CHCl_2CHCl_2$. The peaks due to each of the two compounds, which are sharp at room temperature, become broader as the temperature is raised. At 120 °C there is only one singlet, for which the chemical shift and ^{195}Pt coupling are the averages of those of **2a** and **2b**. The 1 : 1 ratio of the starting complexes was again observed when the sample was cooled back to room temperature. This suggests that the two complexes interconvert in solution and that this process is fast on the NMR timescale at 120 °C. It seems most likely that **2b** is a rotamer of **2a**, *i.e.* having one amino substituent on each side of the platinum co-ordination plane. The origin of the hindered rotation about the two Pt–N bonds would result from the steric inhibition resulting from the 2-amino substituents. This is supported by the fact that the reaction of 3-aminopyridine with [Pt(dppp)(OTf)$_2$] in dichloromethane gave a solution exhibiting only one singlet in its ^{31}P-{^{1}H} NMR spectrum, with δ_P −14.0 and $^{1}J_{Pt\text{-}P}$ = 3023 Hz. These data are similar to those of the pyridine complex, **1**, and the 2-aminopyridine complexes **2a** and **2b**. The two amino groups in 3-aminopyridine appear to be sufficiently far from each other that the two pyridine rings can rotate freely in solution.

The reaction of [Pt(dppp)(OTf)$_2$] with 2,6-diaminopyridine in a 1 : 2 ratio gave a yellow solution which again contained a mixture of two compounds, as revealed by ^{31}P-{^{1}H} NMR spectroscopy (see Fig. 4). One species exhibited an AB pattern with δ_{P1} −6.39 and δ_{P2} −10.62, $^{1}J_{Pt\text{-}P1}$ 2910, $^{1}J_{Pt\text{-}P2}$ 3512 and $^{2}J_{PP}$ 27.4 Hz (**3a** in Fig. 4). The other also exhibited an AB pattern with δ_{P1} −12.42, δ_{P2} −17.45, $^{1}J_{Pt\text{-}P1}$ 2829, $^{1}J_{Pt\text{-}P2}$ 3153 and $^{2}J_{PP}$ 26.7 Hz (**3b** in Fig. 4). The relative intensities suggest a ratio of approximately 80% **3a** and 20% **3b** after a reaction time of *ca.* ten minutes. However, after 24 hours the situation was reversed with about 20% of **3a** and 80% of **3b**. Diffusion of diethyl ether into this solution for one week gave a small amount of yellow crystals, which were analysed by single crystal X-ray crystallography. This revealed an unexpected binuclear structure in which a deprotonated amino nitrogen atom of a 2,6-diaminopyridine ligand bridges between two Pt(dppp)$^{2+}$ units, together with a μ-hydroxo ligand, presumably having originated from adventitious water (Fig. 5). Recently there have been two reports of related structurally characterised $M_2(NHR)(OH)$ (M = Pt or Pd) four membered rings, specifically in complexes $[(Ph_3P)_2Pt(NHC_6H_4CH_3\text{-}p)(OH)Pt(PPh_3)_2][BF_4]_2$ and $[Ph(Ph_3P)Pd(NHC_6H_4OCH_3\text{-}p)PdPh(PPh_3)]$.[6] The Pt–N [2.096(12) and 2.110(12) Å] and Pt–O [2.097(11) and 2.103(11) Å] bridges are each symmetric (Table 2) and have lengths very similar to those in the palladium complex.[6] The

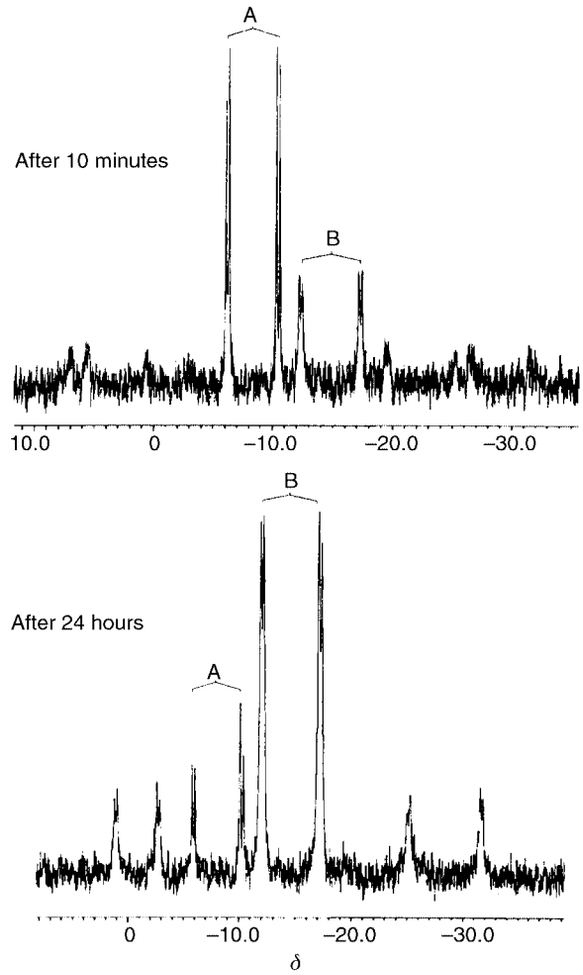


Fig. 4 ^{31}P-{^{1}H} NMR spectrum showing the two AB patterns and associated ^{195}Pt satellites of complexes **3a** and **3b**, after reaction times of 10 minutes (above) and 24 h (below).

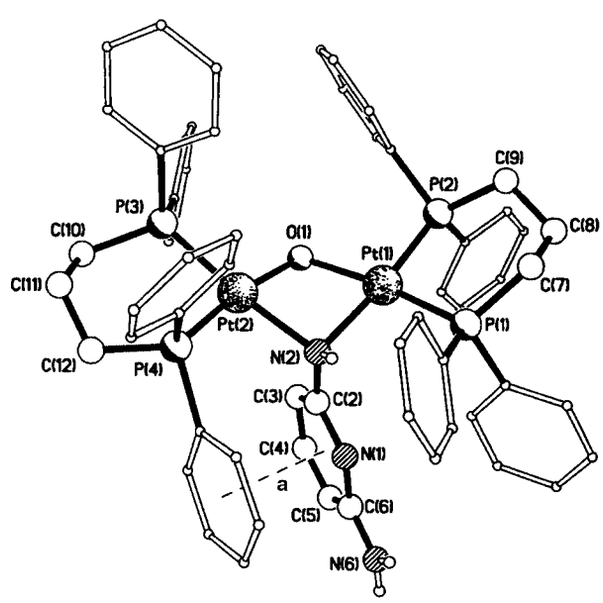
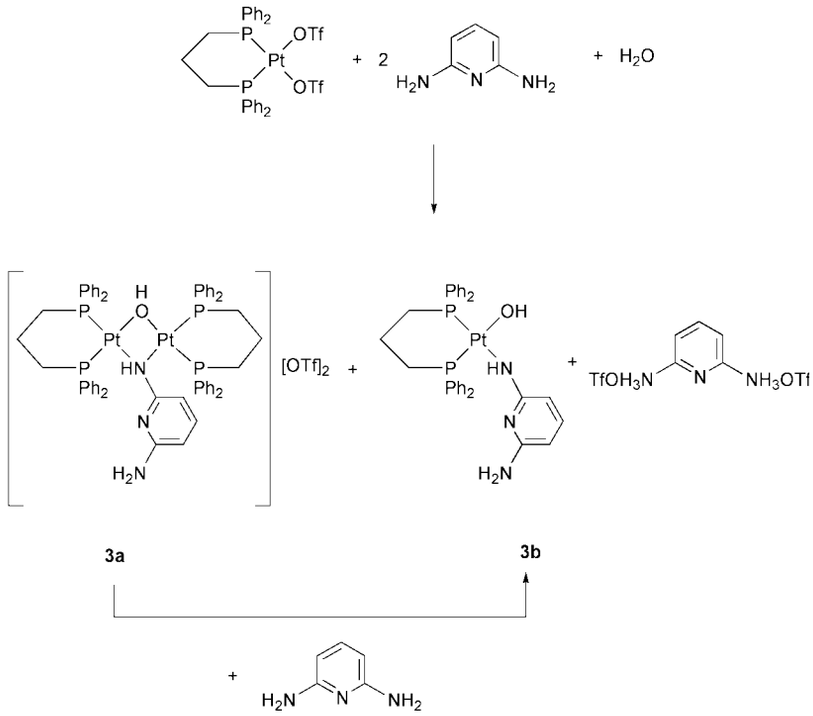


Fig. 5 The molecular structure of complex **3a**. The centroid · · · centroid separation in the π–π stacking interaction **a** is 3.89 Å.

four-membered ring is slightly puckered, being folded by *ca.* 36° about the O(1) · · · N(2) vector; the non-bonded Pt · · · Pt separation is 3.126(1) Å. The unsymmetric nature of the Pt_2ON ring is reflected in the Pt–P distances, with those *trans* to nitrogen [2.238(4) and 2.244(5) Å] being longer than those *trans* to oxygen [2.216(4) and 2.226(4) Å]. This is also consistent with the AB pattern observed in its ^{31}P NMR spectrum. Unlike **2a**,



Scheme 1 Reactions of [Pt(dppp)(OTf)$_2$] with 2,6-dap.

here the molecule does not have approximate C_s symmetry; only one of the diphosphine phenyl rings π-stacks with the pyridine ring. Both six-membered chelate rings have chair conformations very similar to that seen in **2a**.

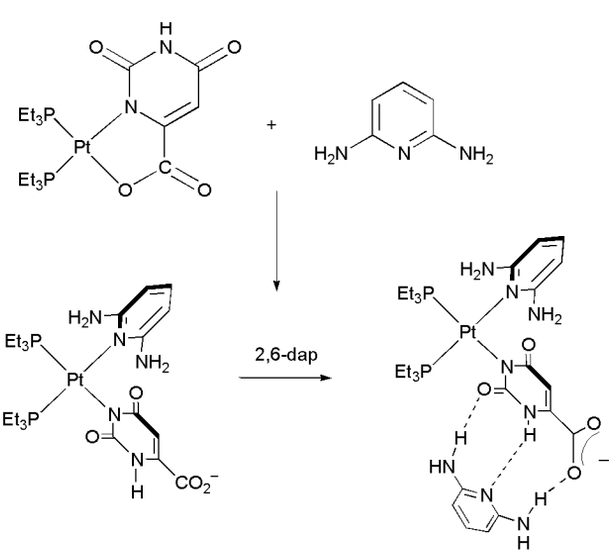
Neither the bridging hydroxo nor the amino groups are involved in hydrogen bonding interactions as both of these sites are obscured by the bulky phosphine rings, the closest approach to the amino hydrogen atom being to the π system of one of the phenyl rings, though the distance of the hydrogen to the centroid of the ring of 3.09 Å is too long for any significant N–H · · · π interaction. The non-co-ordinated amino group is also largely shielded by the phosphine rings, and the closest approach of either of these two hydrogen atoms is to one of the oxygen atoms of the triflate anions, though here again the H · · · O distance [2.56 Å] is too long for any significant hydrogen bonding interaction. There are no inter-complex interactions of note.

The marked difference in the co-ordination behaviours of 2-ap and 2,6-dap in these experiments may originate from the greater steric hindrance in 2,6-dap, disfavouring bis(*cis-endo*-nitrogen) co-ordination for this ligand. Alternatively, or additionally, it may be due to its arrangement of Brønsted basic sites. The deprotonation of 2,6-dap and water to give complex **3a** is presumably associated with double protonation of the second equivalent of 2,6-dap. Analogous double protonation of 2-ap would be expected to be less favoured than for 2,6-dap due to its lack of spacially well separated basic sites. The complex is also notable for being formed under relatively mild conditions compared to related previous μ-amido complexes reported by Mason,[7a] Park,[7b] and Pringle[7c] and co-workers.

The ^{31}P-{^{1}H} NMR spectrum (CH_2Cl_2) of these crystals confirmed them to be complex **3a** and the spectrum remained unchanged after one week, *i.e.* when pure it showed no tendency to convert into complex **3b**. However by adding a further excess of 2,6-dap to the 1 : 2 ratio of the [Pt(dppp)(OTf)$_2$] and 2,6-dap a clean ^{31}P-{^{1}H} NMR spectrum of **3b** was obtained. The reaction can be summarised as in Scheme 1. Complex **3b** was isolated as a yellow solid by diffusion of diethyl ether into the solution. The IR spectrum of this compound showed *ν*(C–H) stretching modes at 3056, 2962 and 2867 cm^{-1}, *ν*(N–H) stretching modes at 3357 and 3558 cm^{-1} and O–H at 3440 cm^{-1}. The positive ion FAB spectrum showed a peak for the ion {Pt(dppp)(OH)[NH(C_5H_3N)NH_2] + H}$^+$ at *m*/*z* 743. From the stoichiometry of the reaction and the physical properties exhibited by complex **3b** we suggest that a likely structure is that shown in Scheme 1, based on a mononuclear platinum complex.

Complex [Pt(PEt$_3$)$_2$(2,6-dap)(*N*-HL)] 4 and the co-crystal [Pt(PEt$_3$)$_2$(2,6-dap)(*N*-HL)]·2,6-dap 5

In addition to the above studies of aminopyridine co-ordination to the Pt(dppp)$^{2+}$ unit, we investigated the effect of adding excess 2,6-diaminopyridine to platinum complexes containing the orotate ligand. The complex [Pt(PEt$_3$)$_2$(2,6-dap)(*N*-HL)] **4** [*N*-HL = N(3)-bound orotate dianion] was obtained by adding an excess of 2,6-diaminopyridine to the previously reported orotate complex [Pt(PEt$_3$)$_2$(*N*,*O*-HL)][4] [*N*,*O*-HL = N(1)- and O-bound dianion of orotic acid] in $CHCl_3$ (see Scheme 2). The solution was allowed to stand at



Scheme 2 Reactions of [Pt(PEt$_3$)$_2$(HL)] with 2,6-dap.

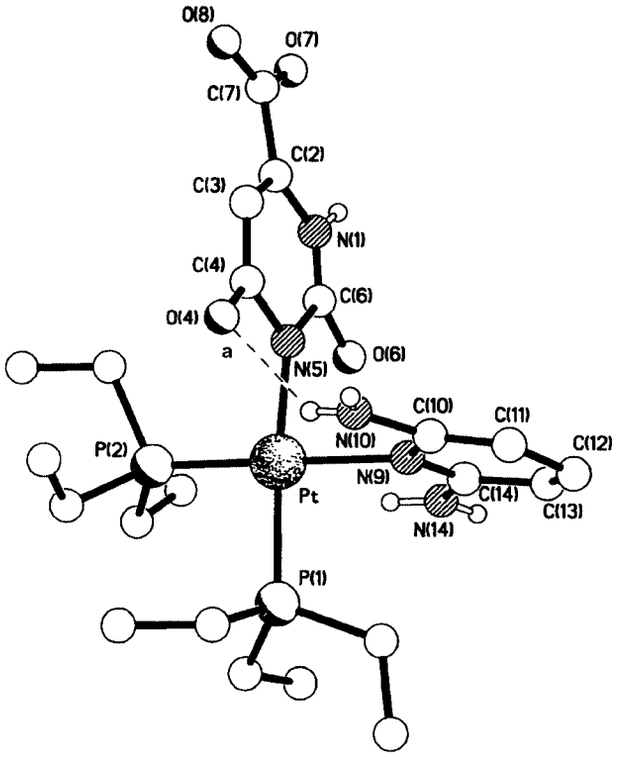


Fig. 6 The molecular structure of complex **4**. The geometry of the N–H···O hydrogen bond **a** is N···O 2.68, H···O 2.04 Å, N–H···O 128°.

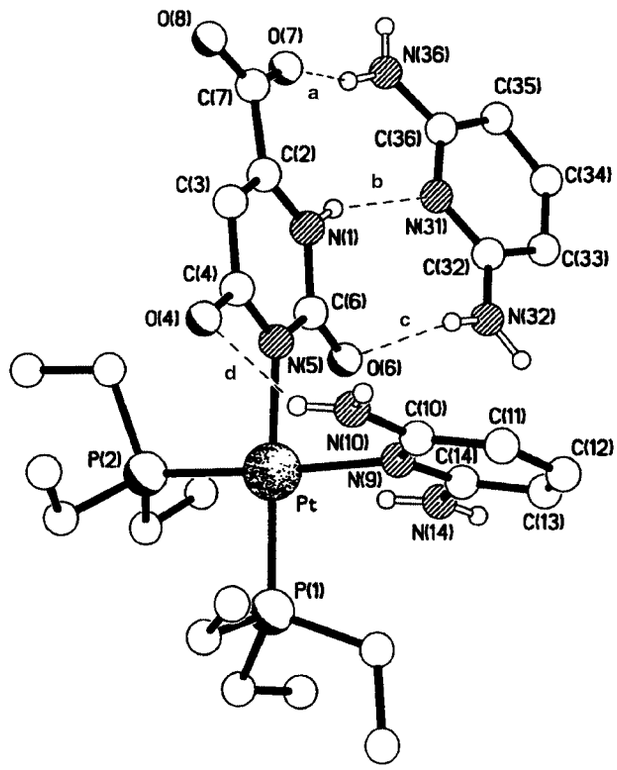


Fig. 7 The molecular structure of complex **5**. The geometries of the N–H···X hydrogen bonds [N···X, H···X distances (Å), N–H···X angle (°)] are: (**a**) 2.88, 2.02, 159; (**b**) 3.44, 2.58, 160; (**c**) 2.90, 2.06, 154; (**d**) 2.93, 2.15, 144.

room temperature in the dark for one week. The resulting off-white crystals were collected and analysed. The IR stretch of the C=O groups in the ligand occurs at 1625 cm^{-1} (broad) which is distinctly different from those of the complex [$Pt(PEt_3)_2$(*N*,*O*-HL)] where the C=O stretches occur at 1677, 1670 and 1650 cm^{-1}. The positive ion FAB mass spectrum shows the parent cation [$Pt(PEt_3)_2$(2,6-dap)(*N*-HL) + H]$^+$ at *m*/*z* 695. The ^{1}H NMR spectrum in d_6-DMSO shows the orotate C–H at δ 5.76 and the N–H at δ 8.30, in addition to the phosphine ethyl groups at δ 1.07–1.64, the protons of the aromatic ring of 2,6-diaminopyridine at δ 5.67 and 7.26 and its NH_2 protons at δ 5.74 and 5.92. The ^{31}P-{^{1}H} NMR spectrum shows an AB pattern due to two inequivalent phosphorus centres co-ordinated to platinum in *cis* positions with δ −0.2 and −1.0. The coupling constants are $^2J_{P\text{-}P} = 22.7$ and $^1J_{Pt\text{-}P} = 3104$ and 3267 Hz respectively.

Crystals of complex **4** were analysed by single crystal X-ray crystallography, and found to be heavily solvated with chloroform which was severely disordered and distributed over multiple partial occupancy sites. This fact, coupled with the crystallisation in a polar space group (with some evidence of racemic twinning), has led to an overall structure determination lacking the necessary precision to permit detailed analysis of the geometric parameters. The gross structure is, however, very similar to that of the 1:1 adduct with 2,6-diaminopyridine, **5** (see below), and has an intramolecular N–H···O hydrogen bond between one of the amino hydrogen atoms [N(10)] and one of the carbonyl oxygens [O(4)] of the orotate ligand (**a** in Fig. 6). Although the hydrogen atom positions have been calculated (and as such may not be totally reliable), the internuclear distance between the heteroatoms is compatible with a hydrogen bonding interaction. Similarly, there is evidence for the formation of loosely linked helical chains of molecules formed by N–H···O hydrogen bonds between the other hydrogen on N(10) in one molecule and one of the carboxyl oxygen atoms, O(7), in the next (the N···O and H···O distances are 3.24 and 2.42 Å, with an associated N–H···O angle of 154°). There are no close approaches to the other amino group, N(14). The relative identities (carbon or nitrogen) of N(1) and C(3) cannot unambiguously be defined, though the pattern of bond lengths favours the structure depicted in Fig. 6; there are approaches of *ca*. 2.6 Å of partial occupancy chlorine atoms to both H(1) and H(3).

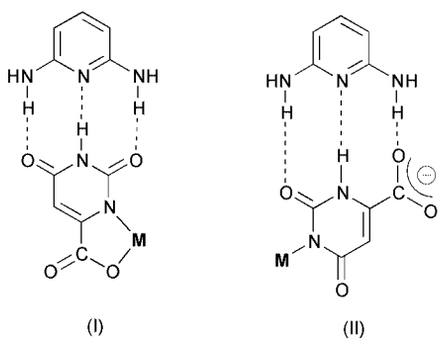
Despite the unconventional monodentate orotate co-ordination mode in complex **4**, it retains a potential ADA triple hydrogen bonding site, in common with conventional *N*,*O*-bound orotate complexes. We therefore investigated this aspect by attempting co-crystallisation of complex **4** with a further equivalent of 2,6-dap. Red-brown block co-crystals of [$Pt(PEt_3)_2$(2,6-dap)(*N*-HL)]·2,6-dap **5** were grown from a $CHCl_3$ solution of **4** and 2,6-diaminopyridine (see Scheme 2). There seems no obvious origin for the unusual colour of this hydrogen bonded adduct. The crystal structure of **5** (Fig. 7) shows that the platinum complex adopts a conformation virtually identical to that of **4** with one of the amino hydrogen atoms [N(10)] being intramolecularly hydrogen bonded to a carbonyl oxygen [O(4)] of the orotate ligand (**d** in Fig. 7). Here, there is no ambiguity in the position of the amino nitrogen N(1) within the orotate ligand, there being clear evidence for significant double bond character of the C(2)–C(3) linkage.‡ As postulated, the 2,6-diaminopyridine unit enters into a triple hydrogen bonding DAD:ADA interaction with the orotate ligand (**a**, **b** and **c** in Fig. 7) which uses its non-co-ordinated ring nitrogen atom, one of the carbonyl oxygens and one carboxylate oxygen atom. In the previously observed triple hydrogen bonding between a conventional *N*,*O*-co-ordinated orotate ligand and 2,6-diaminopyridine[2] the hydrogen bonds were between the two ring carbonyl oxygen atoms and the nitrogen atom that here is co-ordinated to the metal (see Scheme 3). The geometry at platinum is distorted square planar with *cis* angles ranging between 86.9(3) and 96.1(1)° (Table 3). The Pt–N and Pt–P distances are unexceptional.

‡ Exchanging the identities of N(1) and C(3) results in a marked worsening of R_1.

Adjacent 1:1 adducts are linked by pairs of N–H···O hydrogen bonds (**e** and **f** in Fig. 8) to form helical chains that extend in the crystallographic *b* direction. Although two of the potential hydrogen bonding donors [the hydrogen atoms on N(14)] and one of the potential acceptors [O(8)] are not utilised in chain formation, there is no cross-linking between chains. A probable reason for this is the formation of a strong C–H···O hydrogen bond between one of the included chloroform molecules and the exposed carboxylate oxygen atom O(8) that lies on the periphery of the chain (**g** in Fig. 8), thus utilising the only remaining potential acceptor for cross-chain linking not already involved in hydrogen bonding. This co-crystal **5** is similar to the co-crystals of metal-modified nucleobase complexes, platinum guanine and cytosine complexes, reported by Lippert and co-workers,[1,8] however, having helical chain packing.

Table 3 Selected bond lengths (Å) and angles (°) for complex **5**

Pt–N(5)	2.089(7)	Pt–N(9)	2.104(7)
Pt–P(2)	2.267(3)	Pt–P(1)	2.282(3)
N(5)–Pt–N(9)	86.9(3)	N(5)–Pt–P(2)	88.4(2)
N(9)–Pt–P(2)	173.1(2)	N(5)–Pt–P(1)	172.7(2)
N(9)–Pt–P(1)	89.1(2)	P(2)–Pt–P(1)	96.10(10)



Scheme 3 Simultaneous metal co-ordination and ADA:DAD triple hydrogen bonding by orotate in the conventional (I) and unconventional (II) modes.

Conclusion

Reactions between [Pt(dppp)(OTf)$_2$] with pyridine, 2-aminopyridine and 2,6-diaminopyridine were investigated, and straightforward bis(*cis*-*endo*-nitrogen) complexation was observed for py and 2-ap. However, reaction with 2,6-dap resulted in the unusual *exo*-nitrogen-co-ordinated μ-amido complex [(dppp)Pt(μ-OH)[μ-NH(C$_5$H$_3$N)NH$_2$]Pt(dppp)][OTf]$_2$ **3a**. *endo*-Nitrogen co-ordination of 2,6-diaminopyridine and simultaneous unconventional *N*-monodentate orotate co-ordination were observed in complex [Pt(PEt$_3$)$_2$(2,6-dap)(*N*-HL)] **4**. The retention of an ADA site in this orotate co-ordination mode allowed molecular recognition of the complementary DAD base 2,6-dap, *via* 'unconventional' orotate hydrogen bonding sites, as revealed in complex [Pt(PEt$_3$)$_2$(2,6-dap)(*N*-HL)]·2,6-dap **5**. The crystal structure of complex **5** reveals further association of adducts to form hydrogen bonded helical chains.

Experimental

IR spectra were recorded with a Perkin-Elmer 1720 Infrared FT Spectrometer between 4000 and 250 cm^{-1} as KBr pellets, NMR spectra on a JEOL JNM-EX270 FT NMR spectrometer. Mass spectroscopy was carried out by the respective services provided by the Chemistry Department at Imperial College and microanalyses by the respective services provided by the Analysis Department at the University College of London. Syntheses were conducted under nitrogen atmospheres using standard Schlenk techniques. The complexes [Pt(PEt$_3$)$_2$(*N*,*O*-HL)][2] and [Pt(dppp)(OTf)$_2$][5] were prepared according to published methods. Orotic acid, pyridine, 2-aminopyridine and 2,6-diaminopyridine were purchased from Aldrich, 2,6-diaminopyridine was recrystallised from chloroform prior to use.

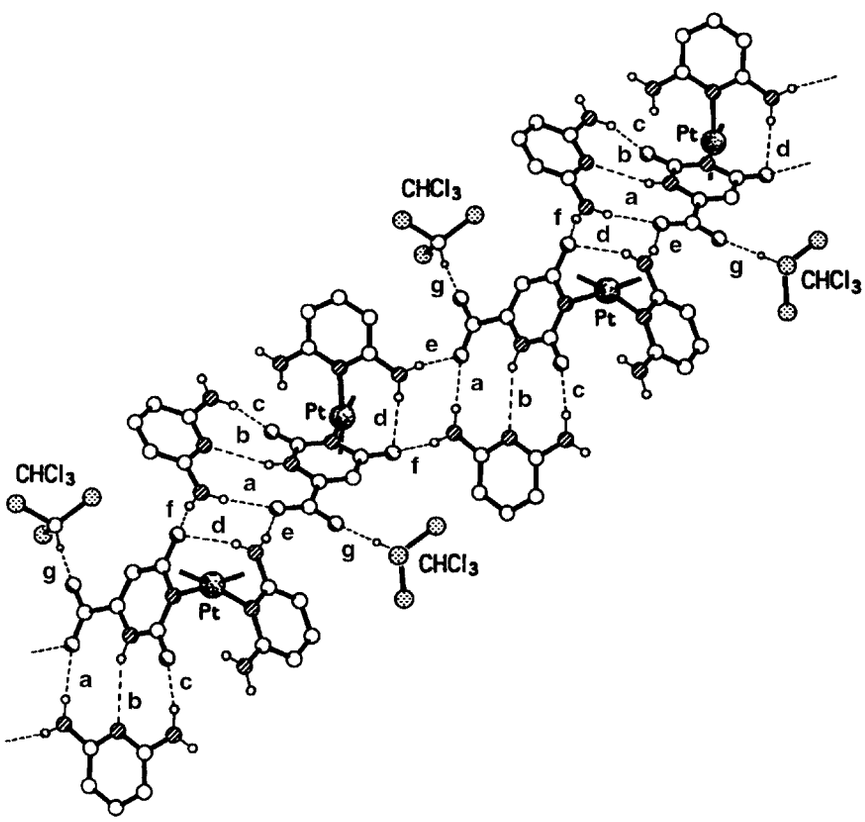


Fig. 8 Part of one of the helical chains of molecules present in the structure of complex **5**. The geometries of the X–H···Y hydrogen bonds [X···Y, H···Y distances (Å), X–H···Y angle (°)] are: (**e**) 2.88, 2.00, 166; (**f**) 2.93, 2.06, 163; (**g**) 2.98, 2.05, 161.

X-Ray crystallography

Crystal data for complex 2a. $[C_{37}H_{38}N_4P_2Pt][CF_3SO_3]_2 \cdot H_2O$, $M = 1111.9$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.854(1)$, $b = 28.854(2)$, $c = 13.197(1)$ Å, $\beta = 94.23(1)°$, $V = 4501.7(5)$ Å^3, $Z = 4$, $D_c = 1.641$ g cm^{-3}, μ(Cu-Kα) = 80.4 cm^{-1}, $T = 293$ K; clear prisms, 6688 independent reflections. The major occupancy non-hydrogen atoms of the cation and anions were refined anisotropically using full matrix least squares based on F^2 to give $R_1 = 0.051$, $wR_2 = 0.124$ for 5495 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$] and 554 parameters.

Crystal data for complex 3a. $[C_{59}H_{59}N_3OP_4Pt_2][CF_3SO_3]_2 \cdot 2CH_2Cl_2 \cdot 0.5Et_2O$, $M = 1845.2$, monoclinic, space group $P2_1/n$ (no. 14), $a = 20.233(5)$, $b = 15.050(2)$, $c = 25.667(4)$ Å, $\beta = 107.14(1)°$, $V = 7469(2)$ Å^3, $Z = 4$, $D_c = 1.641$ g cm^{-3}, μ(Mo-Kα) = 40.9 cm^{-1}, $T = 293$ K; yellow platy prisms, 8857 independent reflections. The major occupancy non-hydrogen atoms of the cation and anions were refined anisotropically using full matrix least squares based on F^2 to give $R_1 = 0.063$, $wR_2 = 0.142$ for 5409 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$] and 742 parameters.

Crystal data for complex 4. $C_{22}H_{39}N_5O_4P_2Pt \cdot 2CHCl_3$, $M = 933.4$, monoclinic, space group $P2_1$ (no. 4), $a = 8.755(1)$, $b = 17.979(3)$, $c = 14.108(1)$ Å, $\beta = 103.53(1)°$, $V = 2159.0(4)$ Å^3, $Z = 2$, $D_c = 1.436$ g cm^{-3}, μ(Cu-Kα) = 104.6 cm^{-1}, $T = 293$ K; orange/yellow blocks, 3320 independent reflections. The major occupancy non-hydrogen atoms were refined anisotropically using full matrix least squares based on F^2 to give $R_1 = 0.088$, $wR_2 = 0.229$ for 2728 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$] and 425 parameters. The polarity of the structure was indicated by a combination of *R*-factor tests [$R_1^+ = 0.0881$, $R_1^- = 0.0891$] and by use of the Flack parameter [$x^+ = -0.15(9)$], though the lack of a more definitive assignment may reflect some racemic twinning.

Crystal data for complex 5. $C_{22}H_{39}N_5O_4P_2Pt \cdot C_5H_7N_3 \cdot 2CHCl_3$, $M = 1042.5$, monoclinic, space group $P2_1/c$ (no. 14), $a = 14.072(3)$, $b = 17.826(3)$, $c = 17.462(4)$ Å, $\beta = 104.02(2)°$, $V = 4250(1)$ Å^3, $Z = 4$, $D_c = 1.629$ g cm^{-3}, μ(Mo-Kα) = 38.0 cm^{-1}, $T = 203$ K; brown blocks, 7454 independent reflections. The major occupancy non-hydrogen atoms were refined anisotropically using full matrix least squares based on F^2 to give $R_1 = 0.054$, $wR_2 = 0.123$ for 5309 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$] and 464 parameters.

CCDC reference number 186/1909.

See http://www.rsc.org/suppdata/dt/b0/b000974l/ for crystallographic files in .cif format.

Preparations

[Pt(dppp)(py)$_2$][OTf]$_2$ 1. Pyridine (7.9 mg, 0.1 mmol) was added to a stirred solution of [Pt(dppp)(OTf)$_2$] (45 mg, 0.05 mmol) in CH_2Cl_2 (10 cm^3). The mixture was stirred for 20 min, layered with pentane (20 cm^3) and left to stand to give the product as white crystals, yield 70%. Found: C 55.3; H 4.0; N 2.3. $C_{53}H_{46}F_6N_2O_4P_2Pt$ requires: C 55.6; H 4.1; N 2.4%. IR ($\tilde{\nu}$/cm^{-1}): 3072, 2928, 1609, 1437, 1281, 1256, 1115, 1030, 696, 637. +ve FAB MS: *m*/*z* 914, [Pt(dppp)(Py)$_2$(OTf)]$^+$. −ve FAB MS: *m*/*z* 149, [OTf]$^-$. ^{1}H NMR (d$_6$-DMSO): δ 2.24–2.38 (CH_2, m, 2 H), 3.28 (CH_2, m, 4 H), 7.30–7.67 (phenyl CH, m, 12 H), 7.03 (pyridine CH, m, 4 H), 8.59 (pyridine CH, m, 2 H) and 8.97 (pyridine CH, m, 4 H). ^{31}P-{H} NMR (CD_2Cl_2): δ −14.7, $^1J_{PtP}$ = 3034 Hz.

[Pt(dppp)(2-ap)$_2$][OTf]$_2$ 2a and 2b. The synthesis was as for complex **1**, using 2-aminopyridine (9.4 mg, 0.1 mmol) in place of pyridine, to give white crystals. The two isomers could not be separated on a large scale, combined yield 70%. Found: C 42.2; H 3.3; N 4.8. $C_{39}H_{38}F_6N_4O_6P_2PtS_2 \cdot H_2O$ requires C 42.1; H 3.6; N 5.0%. IR ($\tilde{\nu}$/cm^{-1}): 3424, 3334, 3212, 3062, 2962, 1643, 1249, 1029, 638, 516. +ve FAB MS: *m*/*z* 850, [Pt(dppp)(2-ap)(OTf)]$^+$. −ve FAB MS: *m*/*z* 149, [OTf]$^-$. ^{1}H NMR (CD_2Cl_2): one isomer, δ 2.30 (CH_2, m, 2 H), 2.93 (CH_2, m, 2 H), 3.68 (CH_2, m, 2 H), 5.69 (NH_2, m, 4 H), 7.08–7.64 (phenyl CH, m, 20 H), 5.92 [pyridine CH(3), d, 1 H], 6.08 [pyridine CH(4), t, 1 H], 6.28 [pyridine CH(5), t, 1 H] and 8.26 [pyridine CH(6), d, 1 H]; another isomer, δ 2.30 (CH_2, m, 2 H), 2.93 (CH_2, m, 2 H), 3.68 (CH_2, m, 2 H), 6.17 (NH_2, m, 4 H), 7.08–7.64 (phenyl CH, m, 20 H), 6.51 [pyridine CH(3), d, 1 H], 6.52 [pyridine CH(4), t, 1 H], 6.70 [pyridine CH(5), t, 1 H] and 8.89 [pyridine CH(6), d, 1 H]. ^{31}P-{H} NMR (CD_2Cl_2): one isomer, δ −15.25 $^1J_{PtP}$ = 2988 Hz; another isomer, δ −17.73, $^1J_{PtP}$ = 2986 Hz.

[(dppp)Pt(μ-OH){μ-NH(C$_5$H$_3$N)NH$_2$}Pt(dppp)][OTf]$_2$ 3a. The synthesis was as for complex **1**, using 2,6-diaminopyridine in place of pyridine, to give a yellow solid. Yellow crystals were obtained by diffusion of hexane into a dichloromethane solution of the mixture, yield 15%. A consistent elemental analysis was not obtained possibly owing to partial desolvation of the crystals. Characterisation was based on X-ray crystallography and the following data. IR ($\tilde{\nu}$/cm^{-1}): 3558w, ν(O–H); 3442w, 3351w (br), 3056w, ν(N–H); 2962w, 2923w, 2867w, ν(C–H); 1658m, 1617m, 1438, 1276s, 1259s, 1157m, 1103m, 1029s, 707w, 694m, 638m, 516m. +ve FAB MS: *m*/*z* 1488, [Pt$_2$(dppp)$_2$-(μ-OH)(μ-NH(C$_5$H$_3$N)NH$_2$)(OTf)]$^+$. −ve FAB MS: *m*/*z* 149 [OTf]$^-$. ^{31}P-{H} NMR (CD_2Cl_2): δ −6.39, −10.62, $^1J_{PtP}$ = 2910, $^1J_{PtP}$ = 3512, $^2J_{PP}$ = 27.4 Hz.

[Pt(OH)(2,6-dap)(dppp)][OTf] 3b. The synthesis was as for complex **3a**, using 3 equivalents of 2,6-diaminopyridine, to give a yellow powder, yield 40%. A consistent elemental analysis was not obtained possibly owing to partial desolvation of the crystals and the characterisation was based on the following data. IR ($\tilde{\nu}$/cm^{-1}): 3558w (br), ν(O–H); 3440s (br), 3357w (br), ν(N–H); 1617m, 1436m, 1261s, 1029s, 707w, 694m, 638m, 516m. +ve FAB MS: *m*/*z* 715, [Pt(dppp)(NH(C$_5$H$_3$N)NH$_2$)]$^+$. ^{31}P-{H} NMR (CD_2Cl_2): δ −12.42, −17.45, $^1J_{PtP}$ = 2829, $^1J_{PtP}$ = 3153, $^2J_{PP}$ = 26.7 Hz.

[Pt(PEt$_3$)$_2$(2,6-dap)(*N*-HL)] 4. A solution of 2,6-diaminopyridine (37.5 mg, 0.34 mmol) in $CHCl_3$ (2 cm^3) was added to a solution of [Pt(PEt$_3$)$_2$(HL)] (27 mg, 0.06 mmol) in $CHCl_3$ (2 cm^3). The colourless solution was kept dark and evaporated slowly at room temperature for one week to give pale yellow crystals, yield 17 mg, 40%. Found: C 36.1; H 5.6; N 9.6. $C_{22}H_{39}N_5O_4P_2Pt \cdot 0.33CHCl_3$ requires: C 36.5; H 5.4; N 9.5%. IR ($\tilde{\nu}$/cm^{-1}): 3180w (br), ν(N–H); 1625s, 1579s, ν(C=O); 1461m, 1359m, 769w. +ve FAB MS: *m*/*z* 695, [Pt(PEt$_3$)$_2$(C$_5$H$_2$N$_2$O$_4$)-(C$_5$H$_7$N$_3$) + H]$^+$. ^{1}H NMR (d$_6$-DMSO): δ 1.07 (CH_3, m, 6 H), 1.64 (CH_2, m, 2 H), 1.80 (CH_2, m, 2 H), 5.67 (pyridine CH, s, 1 H), 7.26 (pyridine CH, t, $^3J_{HH}$ = 7.6 Hz, 1 H), 5.74 (NH_2, m, 2 H), 5.92 (NH_2, m, 2 H), 5.76 (orotate CH, s, 1 H) and 8.30 (orotate NH, s, 1 H). ^{31}P-{H} NMR (d$_6$-DMSO): δ −0.2 (P1, d, $^2J_{PP}$ = 22.7, $^1J_{PtP}$ = 3103.9) and −1.01 (P2, d, $^2J_{PP}$ = 22.7, $^1J_{PtP}$ = 3267.5 Hz).

[Pt(PEt$_3$)$_2$(2,6-dap)(*N*-HL)]·2,6-dap 5. A solution of 2,6-diaminopyridine (4.4 mg, 0.04 mmol) in $CHCl_3$ (2 cm^3) was added to a solution of [Pt(PEt$_3$)$_2$(2,6-dap)(*N*-HL)] **4** (14.6 mg, 0.02 mmol) in $CHCl_3$ (2 cm^3). Light was excluded from the colourless solution which evaporated slowly at room temperature over three weeks to give a few red crystals in *ca*. 5% yield. A consistent elemental analysis was not obtained possibly owing to desolvation of the crystals, and characterisation was based on X-ray crystallography.

Acknowledgements

BP plc is thanked for endowing D. M. P. M.'s chair.

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