Reversible Addition of Protic Molecules to Co-ordinated Di-2-pyridyl Ketone in Palladium(II), Platinum(II), and Gold(III) Complexes. *X*-Ray Crystal Structures of Dichloro(dihydroxy-di-2-pyridylmethane)palladium(II) and Dichloro(dihydroxy-di-2-pyridylmethane)gold(III) Chloride

By **Giuliano Annibale, Luciano Canovese,** and **Lucio Cattalini,** Istituto di Chimica Generale ed Inorganica, Università di Venezia, Italy
Giovanni Natile,* Cattedra di Chimica Generale ed Inorganica, Università di Bari, Italy
Marina Biagini-Cingi, Anna-Maria Manotti-Lanfredi, and **Antonio Tiripicchio,** Istituto di Chimica Generale ed Inorganica e Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Università di Parma, Italy

Palladium(II), platinum(II), and gold(III) species react with di-2-pyridyl ketone (dpk) to give complexes in which one or two ligand molecules in the original keto- or in a newly formed diolic form are co-ordinated to the metal cation, namely: [$PdCl_2$(dpk·HX)] [X = OH (1), OMe (2), or OEt (3)]; [$PdCl_2$(dpk)], (4); [Pd(dpk·H_2O)$_2$][ClO_4]$_2$, (5); [$PtCl_2$(dpk)], (6); [$AuCl_2$(dpk·H_2O)]Cl, (7); and [Au(dpk·H_2O)$_2$][ClO_4]$_3$, (8). In solution, all species undergo either addition or release of the protic molecules depending upon the HX concentration; the rates of reversible hydrolysis and the stability of the hydrated species increase going from Pt^{II} to Pd^{II} to Au^{III} thus paralleling both the electron-withdrawing properties of the metal cations and their ability to fill the apical position of a tetragonal-pyramidal co-ordination shell. The crystal and molecular structures of (1) and (7) have been determined by *X*-ray diffraction: (1) crystallizes in the tetragonal space group $P4_1$ with $Z = 4$, a = 10.597(8), and c = 11.468(9) Å; (7) crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$, a = 10.398(10), b = 7.249(8), c = 18.406(12) Å, and β = 91.6(8)°. The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares to R = 0.018 and 0.063 for (1) and (7) respectively. Neutral [$PdCl_2$(dpk·H_2O)] and cationic [$AuCl_2$(dpk·H_2O)]$^+$ are present in the crystals of (1) and (7) respectively; the co-ordination geometry of the metal atom is square planar in both cases and involves two Cl and two N atoms, the dpk·H_2O molecule acting as a chelating *N*-donor ligand. The ligand conformation is very similar in both complexes, the six-membered chelate being in a boat form with a dihedral angle between the pyridyl rings of 114.54 and 116.63° respectively; this allows a very favourable co-ordination angle of 87.1(2) and 86.4(6)°, and a short contact between the oxygen atom of a hydroxyl group and the metal cation of 2.824(6) and 2.77(1) Å for (1) and (7) respectively.

A MOLECULE of di-2-pyridyl ketone (dpk) can, in principle, act as a bidentate nitrogen donor capable of forming six-membered rings on co-ordination to metal ions. Therefore it is of interest to compare the structure of these rings with the analogous pseudo-aromatic five-membered rings formed on co-ordination of molecules such as 2,2'-bipyridyl and 1,10-phenanthroline.[1]

Moreover, literature data indicate that dpk, when co-ordinated to a number of metal ions, easily undergoes addition of various nucleophiles (HX), including water, at the carbon atom of the carbonylic group to produce the corresponding condensation product $(C_5H_4N)_2C(OH)X$.[2-9]

In this paper we report the chemical behaviour of dpk on interaction with Pd^{II}, Pt^{II}, and Au^{III} under a variety of experimental conditions. *X*-Ray structures of [$PdCl_2$(dpk·H_2O)] and [$AuCl_2$(dpk·H_2O)]Cl, determined in the course of this investigation, are also included.

EXPERIMENTAL

Dipotassium tetrachloroplatinate(II), palladium(II) chloride, and hydrogen tetrachloroaurate(III) trihydrate were obtained from Johnson Matthey and Co.; di-2-pyridyl ketone, the inorganic salts, and solvents were reagent-grade products.

Preparation of Complexes.—[$PdCl_2$(dpk·H_2O)], (1). To a solution of $PdCl_2$ (0.200 g, 1.1 mmol) in water (5 cm^3) containing a slight excess of LiCl (0.100 g, 2.4 mmol) was added slowly, with stirring, a solution of di-2-pyridyl ketone (0.208 g, 1.1 mmol) in the same solvent (2 cm^3) and a yellow precipitate formed immediately. This was filtered off, washed twice with cold water, and air dried. The yield was *ca.* 90% {Found: C, 35.0; H, 2.8; Cl, 18.6; N, 7.3. [$PdCl_2$(dpk·H_2O)] requires C, 34.8; H, 2.7; Cl, 18.7; N, 7.4%}.

The compound [$PdCl_2$(dpk·MeOH)], (2), was prepared in a similar way using methanol as solvent instead of water. The yield was *ca.* 85% {Found: C, 36.8; H, 3.0; Cl, 18.4; N, 7.0. [$PdCl_2$(dpk·MeOH)] requires C, 36.6; H, 3.1; Cl, 18.0; N, 7.1%}.

The compound [$PdCl_2$(dpk·EtOH)], (3), was prepared using ethanol as solvent. The yield was *ca.* 80% {Found: C, 38.6; H, 3.5; Cl, 17.3; N, 6.8. [$PdCl_2$(dpk·EtOH)] requires C, 38.3; H, 3.5; Cl, 17.4; N, 6.9%}.

The compound [$PdCl_2$(dpk)], (4), could be obtained by two different procedures. (*i*) A suspension of (1), (2), or (3) in water (0.1 g in 10 cm^3) was heated to reflux for 2 h then cooled to room temperature and filtered. The yellow solid was air dried. (*ii*) To a solution of [$PdCl_2$(NCMe)$_2$] (0.250 g, 1 mmol) in dichloromethane (15 cm^3) was added dropwise, with stirring, a solution of di-2-pyridyl ketone (0.185 g, 1 mmol) in the same solvent (5 cm^3) and a yellow precipitate started to appear. The precipitation was further increased by adding diethyl ether (40 cm^3) and the yellow precipitate was filtered off, washed with diethyl ether, and air dried. The yield was *ca.* 60% {Found: C, 36.5; H, 2.1; Cl, 19.5; N, 7.6. [$PdCl_2$(dpk)] requires C, 36.5; H, 2.2; Cl, 19.6; N, 7.7%}.

[Pd(dpk·H_2O)$_2$][ClO_4]$_2$, (5). A solution of $PdCl_2$ (0.100 g, 0.55 mmol) in water (3 cm^3) containing a slight excess of LiCl (0.050 g, 1.2 mmol) was added slowly, with stirring, to a solution of di-2-pyridyl ketone (0.208 g, 1.1 mmol) in water

(3 cm^3) containing an excess of Li[ClO$_4$] (1 g) and cooled to 0 °C; a white precipitate formed immediately. This was filtered off, washed twice with small portions of ice-cold water then with tetrahydrofuran and diethyl ether, and air dried. The yield was *ca.* 86% {Found: C, 37.3; H, 2.8; Cl, 10.8; N, 7.8. [Pd(dpk·H$_2$O)$_2$][ClO$_4$]$_2$ requires C, 37.2; H, 2.8; Cl, 10.0; N, 7.9%}.

[PtCl$_2$(dpk)], (6). A solution of di-2-pyridyl ketone (0.184 g, 1 mmol) in water (5 cm^3) was added slowly, with stirring, to a solution of K$_2$[PtCl$_4$] (0.415 g, 1 mmol) in the same solvent (5 cm^3); a yellow precipitate slowly separated out of the solution. After 1 d at room temperature this precipitate was filtered off, washed twice with water, and air dried. The yield was *ca.* 93% {Found: C, 29.4; H, 2.2; Cl, 15.4; N, 6.1. [PtCl$_2$(dpk)] requires C, 29.3; H, 1.8; Cl, 15.7; N, 6.2%}.

[AuCl$_2$(dpk·H$_2$O)]Cl, (7). To a solution of HAuCl$_4$·3H$_2$O (0.200 g, 0.5 mmol) in water (3 cm^3), neutralized by addition of Na$_2$[CO$_3$] and cooled to 0 °C, was added dropwise, with stirring, a solution of di-2-pyridyl ketone (0.092 g, 0.5 mmol) in water (3 cm^3). A yellow precipitate immediately formed. The solid was filtered off, washed twice with ice-cold water then with acetone and diethyl ether, and air-dried. The yield was *ca.* 90% {Found: C, 26.1; H, 2.0; Cl, 21.1; N, 5.4. [AuCl$_2$(dpk·H$_2$O)]Cl requires C, 26.1; H, 2.0; Cl, 21.0; N, 5.5%}.

[Au(dpk·H$_2$O)$_2$][ClO$_4$]$_3$, (8). To a solution of HAuCl$_4$·3H$_2$O (0.200 g, 0.5 mmol) in water (3 cm^3), neutralized by addition of Na$_2$[CO$_3$], was added dropwise, with stirring, a solution of di-2-pyridyl ketone (0.185 g, 1 mmol) in the same solvent (3 cm^3) containing an excess of Li[ClO$_4$] (3 g) and cooled to 0 °C. A white precipitate formed immediately and was filtered off, washed twice with small portions of ice-cold water, then with acetone and diethyl ether, and air dried. The yield was *ca.* 87% {Found: C, 29.6; H, 2.2; Cl, 12.0; N, 6.1. [Au(dpk·H$_2$O)$_2$][ClO$_4$]$_3$ requires C, 29.4; H, 2.2; Cl, 11.8; N, 6.2%}.

Orange crystals of [PdCl$_2$(dpk·H$_2$O)], (1), were obtained by slow evaporation of a dilute aqueous solution of (1). Orange crystals of [AuCl$_2$(dpk·H$_2$O)]Cl, (7), were grown by slowly cooling a solution obtained in hot water.

Apparatus.—Ultraviolet and visible spectra were recorded on a Perkin-Elmer 575 spectrophotometer. The reversible uptake of water followed a first-order rate law, plots of $\ln(A_t - A_\infty)$ against time (A_t and A_∞ are the absorbances at time t and after six half-lives respectively) being linear, and the first-order rate constants for approach to equilibrium were obtained from the slopes of these plots.

X-*Ray Analysis.*—An irregularly shaped crystal of (1) (*ca.* 0.18 × 0.22 × 0.22 mm) and an elongated prismatic crystal of (7) (*ca.* 0.07 × 0.19 × 0.40 mm) were used for the structure determinations. Unit-cell parameters for both compounds were first determined from rotation and Weissenberg photographs and then refined by least-squares fit to 13 (1) and 15 (7) θ values carefully measured on a Siemens AED single-crystal diffractometer.

Crystal data. (1). C$_{11}$H$_{10}$Cl$_2$N$_2$O$_2$Pd, $M = 379.52$, Tetragonal, $a = 10.597(8)$, $c = 11.468(9)$ Å, $U = 1\,288(2)$ Å^3, $Z = 4$, $D_c = 1.96$ g cm^{-3}, $F(000) = 744$, Mo-K_α radiation, $\lambda = 0.710\,688$ Å, $\mu = 18.3$ cm^{-1}, space group $P4_1$ (from systematic absences and structure determination).

(7). C$_{11}$H$_{10}$AuCl$_3$N$_2$O$_2$, $M = 505.54$, Monoclinic, $a = 10.398(10)$, $b = 7.249(8)$, $c = 18.406(12)$ Å, $\beta = 91.6(8)°$, $U = 1\,387(2)$ Å^3, $Z = 4$, $D_c = 2.42$ g cm^{-3}, $F(000) = 944$, Mo-K_α radiation, $\lambda = 0.710\,688$ Å, $\mu = 111.7$ cm^{-1}, space group $P2_1/c$ (from systematic absences).

Intensity data were collected at room temperature using a Siemens AED automated single-crystal diffractometer with niobium-filtered Mo-K_α radiation and the θ—2θ scan technique. 1 204 Independent reflections for (1) ($3 \leqslant \theta \leqslant 25°$) and 3 026 for (7) ($3 \leqslant \theta \leqslant 27°$) were measured; of these 1 091 for (1) and 2 505 for (7), having $I \geqslant 2\sigma(I)$, were used in the structure analysis. A standard reflection was periodically measured to check the stability of the sample and of the instrument. The intensities were corrected for Lorentz and polarization factors, but no absorption corrections were applied. Although absorption is undoubtedly important in the structure of (7), the correction for this effect was not made because the small and irregular size and the opacity of the crystal prevented the morphological measurement of it.

The first absolute scale and the mean temperature factor were determined by Wilson's method.

Both structures were solved by the heavy-atom technique and the refinements for the non-hydrogen atoms were carried out by least-squares full-matrix cycles using the SHELX system of computer programs [10] with initially isotropic and then anisotropic thermal parameters.

The hydrogen atoms of (1) were all located directly from a difference synthesis and refined isotropically; the hydrogen atoms of (7) (except those of the two hydroxyl groups which were located in a ΔF map) were placed in the geometrically calculated positions and included in the final structure factor calculations with isotropic thermal parameters. The final conventional R values were 0.018 for (1) and 0.063 for (7) (observed reflections only). Atomic scattering factors corrected for anomalous dispersion effect of Pd and Cl for (1) and Au and Cl for (7) were taken from ref. 11. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were chosen at each stage of the refinement after analysing the variation of $|\Delta F|$ with respect to $|F_o|$. Final atomic co-ordinates for non-hydrogen atoms are given in Tables 1 and 2 for (1) and (7) respectively, those of the hydrogen atoms of compound (1) are given in Table 3. Atomic thermal parameters and lists of observed and calculated structure factors for both compounds and the calculated atomic co-ordinates of the hydro-

TABLE 1

Fractional atomic co-ordinates (× 10^4) of the non-hydrogen atoms for compound (1) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Pd	4 724(1)	1 793(1)	2 500
Cl(1)	3 078(2)	425(2)	2 811(2)
Cl(2)	3 554(2)	3 453(2)	3 210(2)
O(1)	8 781(5)	1 165(5)	3 285(6)
O(2)	6 759(5)	1 301(5)	4 024(5)
N(1)	6 155(5)	2 982(5)	2 140(5)
N(2)	5 850(5)	380(5)	1 906(5)
C(1)	5 949(9)	4 068(8)	1 562(7)
C(2)	6 908(9)	4 859(8)	1 250(8)
C(3)	8 125(10)	4 544(9)	1 550(8)
C(4)	8 342(8)	3 447(8)	2 107(8)
C(5)	7 345(6)	2 662(6)	2 416(7)
C(6)	5 425(8)	−531(7)	1 197(7)
C(7)	6 189(8)	−1 444(8)	725(8)
C(8)	7 445(9)	−1 416(9)	995(9)
C(9)	7 900(8)	−517(7)	1 748(8)
C(10)	7 096(6)	366(6)	2 203(7)
C(11)	7 514(6)	1 400(6)	3 048(7)

TABLE 2

Fractional atomic co-ordinates ($\times 10^4$) of the non-hydrogen atoms for compound (7) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Au	1 577(1)	1 385(1)	1 921(1)
Cl(1)	2 669(5)	747(8)	2 968(3)
Cl(2)	253(6)	−1 017(8)	2 126(3)
Cl(3)	4 062(5)	−807(8)	−1 039(3)
O(1)	3 349(13)	2 622(20)	−181(7)
O(2)	3 098(12)	532(19)	754(7)
N(1)	570(15)	2 060(21)	966(8)
N(2)	2 721(14)	3 545(23)	1 707(7)
C(1)	−695(17)	2 078(28)	943(10)
C(2)	−1 360(19)	2 468(31)	297(11)
C(3)	−619(21)	2 708(30)	−324(11)
C(4)	682(20)	2 642(27)	−292(10)
C(5)	1 305(18)	2 309(24)	367(9)
C(6)	3 059(21)	4 798(30)	2 228(11)
C(7)	3 792(22)	6 324(30)	2 078(12)
C(8)	4 228(20)	6 585(30)	1 384(12)
C(9)	3 883(18)	5 292(29)	839(11)
C(10)	3 161(17)	3 781(28)	1 019(9)
C(11)	2 757(18)	2 250(25)	471(9)

TABLE 3

Fractional co-ordinates ($\times 10^3$) and isotropic thermal parameters ($\times 10^3$) of the hydrogen atoms for compound (1) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U
H(1)	517(9)	426(7)	141(8)	58(27)
H(2)	671(8)	562(8)	67(8)	68(24)
H(3)	886(8)	509(8)	136(8)	89(26)
H(4)	900(8)	318(7)	247(9)	54(23)
H(6)	453(8)	−50(8)	114(8)	105(25)
H(7)	596(7)	−199(7)	−6(9)	103(22)
H(8)	803(8)	−200(8)	73(9)	70(24)
H(9)	888(8)	−44(8)	190(8)	60(24)
H(11)	909(8)	169(8)	396(8)	76(24)
H(12)	681(8)	198(8)	423(8)	90(25)

gen atoms of compound (7) are given in Supplementary Publication SUP 23088 (26 pp.).*

All calculations were performed on a Cyber-76 computer of Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna).

RESULTS AND DISCUSSION

Palladium(II), platinum(II), and gold (III) species react with di-2-pyridyl ketone, dpk, under a variety of experimental conditions (see Experimental section) to give complexes in which one or two molecules of dpk in its keto- and/or hydrated form [$(C_5H_4N)_2C{=}O$ = dpk and $(C_5H_4N)_2C(OH)X$ = dpk·HX] are co-ordinated to the metal.

Palladium(II) species react with dpk in protic solvents, HX, to give either [$PdCl_2$(dpk·HX)] or [Pd(dpk·HX)$_2$][ClO_4]$_2$ depending upon the metal to ligand ratio, whereas in aprotic solvents only [$PdCl_2$(dpk)] is formed. Tetrachloroplatinate(II) reacts with dpk either in protic or in aprotic solvents to give exclusively [$PtCl_2$(dpk)]. Finally tetrachloroaurate(III) reacts with dpk in water to give either [$AuCl_2$(dpk·H_2O)]$^+$ or [Au(dpk·H_2O)$_2$]$^{3+}$ depending upon the metal : ligand ratio.

Reversible Uptake of Protic Molecules.—Palladium complexes. Both [$PdCl_2$(dpk·H_2O)], (1), and [$PdCl_2$(dpk)], (4), give similar u.v. and visible spectra when dissolved in an aprotic solvent such as acetonitrile or 1,2-dichloroethane [Figure 1(*a*)]. Their spectra in protic solvents, such as water or alcohols, are also similar [Figure 1(*b*)], but differ from the spectra in aprotic solvents. The addition of 10% v/v of water into a solution of either (4) or (1) in acetonitrile causes a complete spectral change from (*a*) to (*b*); for lower amounts of added water (3 or 6% v/v) intermediate spectra are obtained [spectra (*c*) and (*d*) in Figure 1]. This clearly indicates that a reversible uptake of a protic molecule, HX, occurs in solution as indicated by equation (1).

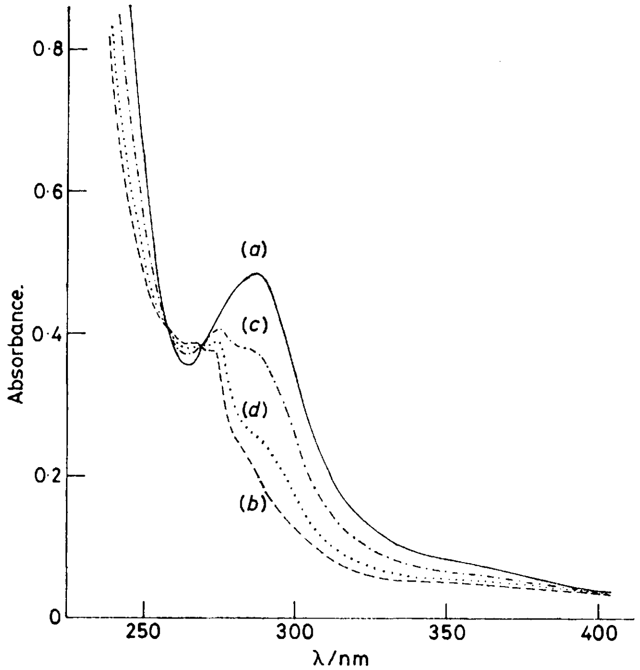

FIGURE 1 Absorption spectra of 5 × 10^{-5} mol dm^{-3} solutions of either [$PdCl_2$(dpk)] or [$PdCl_2$(dpk·H_2O)] in acetonitrile containing 0 (*a*), 3 (*c*), 6 (*d*), and 10 % v/v (*b*) water

$$[MCl_2\{C_5H_4N)_2C{=}O\}] + HX \rightleftharpoons [MCl_2\{(C_5H_4N)_2C(OH)X\}] \quad (1)$$

The kinetics of uptake and release of water in the palladium complexes could be measured from the spectral changes observed on dissolving either (4) or (1) in acetonitrile containing 3% v/v of water; in the former case the spectrum changed from (*a*) to (*c*) and in the latter case from (*b*) to (*c*) (Figure 1). Under these experimental conditions the forward and backward reactions of equation (1) have a similar rate constant of 1.5 × 10^{-4} s^{-1}.

The behaviour of the palladium complexes in solution accounts for the results obtained under preparative conditions. Lithium tetrachloropalladate(II) reacts with dpk in protic solvents, HX {X = OH, OCH_3, or OC_2H_5}, to give adducts with the ligand in the hydrated form, (1), (2), and (3) respectively; while dibenzonitriledichloropalladium reacts with dpk in aprotic solvents, such as dichloromethane,

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

to give a complex with the ligand in its original keto-form, (4). The quantitative interconversion of the hydrated to the keto-form can also be accomplished by keeping complex (1) at 100 °C for a few hours either in an oven or in boiling water in which (1) is sparingly soluble; in the latter case the protic solvent, present in large excess, does not interfere with the dehydration reaction which appears to be affected only by the temperature.

Platinum complexes. Only one complex, (6), the one with the ligand in its original keto-form, was isolated in the solid state. However, on dissolving this species in aprotic (acetonitrile, 1,2-dichloroethane) or in protic solvents (water, methanol) two different spectra were obtained [spectra (*a*) and (*b*) of Figure 2]. This is a clear indication that reversible uptake of a protic molecule [equation (1)] also occurs in this case. The equilibrium in the case of the platinum complex, however, is more shifted in favour of the keto-form than it was in the analogous palladium complex, and even in the presence of a large excess of water (50% v/v water–acetonitrile) both species are present in comparable concentration.

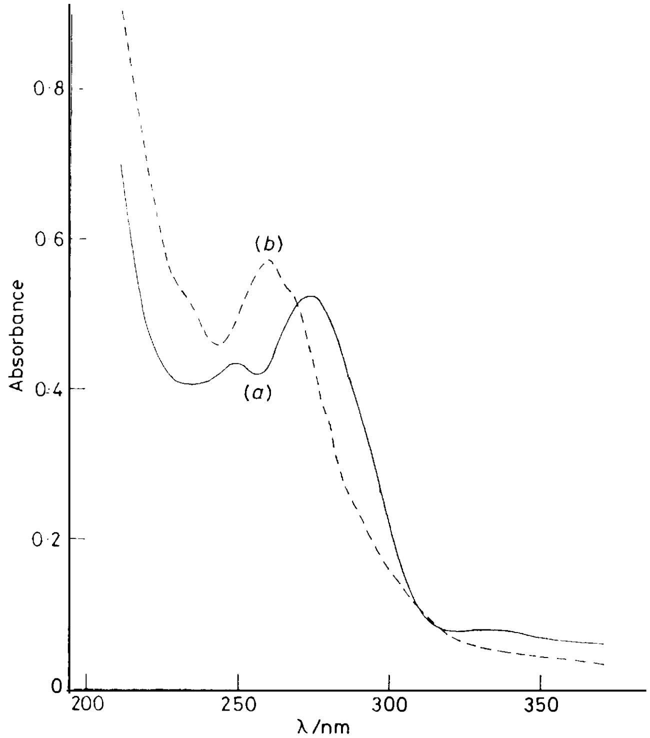

FIGURE 2 Absorption spectra of a 5 × 10^{-5} mol dm^{-3} solution of [PtCl$_2$(dpk)] in acetonitrile (*a*) and in water (*b*)

The rate constant for the conversion of the keto-form into the hydrated form in pure water is *ca.* 1 × 10^{-4} s^{-1} at room temperature; this slow rate combined with the almost complete insolubility of [PtCl$_2$(dpk)] in water explains why only this species could be isolated in the solid state.

Gold complexes. The behaviour of gold apparently differs from those of palladium and platinum in that only the complex having the ligand in its hydrated form could be isolated in the solid state, (7), and the spectra of solutions of this complex in commercial reagent-grade acetonitrile or in water were very similar. Addition of small aliquots of water to the acetonitrile solution did not cause any significant spectral change. However, complex (7) dissolved slowly in 1,2-dichloroethane to give a solution with a different spectrum which, on the addition of 0.1% v/v methanol, changed to one resembling that observed in acetonitrile or water (Figure 3). Therefore the obvious conclusion is that the equilibrium between the keto- and the hydrated form of dpk [equation (1)] also occurs in the gold case but lies well in favour of the hydrated form so that the presence of a very small quantity (0.1% v/v) of methanol in 1,2-dichloroethane, or water in acetonitrile (as is the case of commercial products), is sufficient to move equilibrium (1) completely to the right.

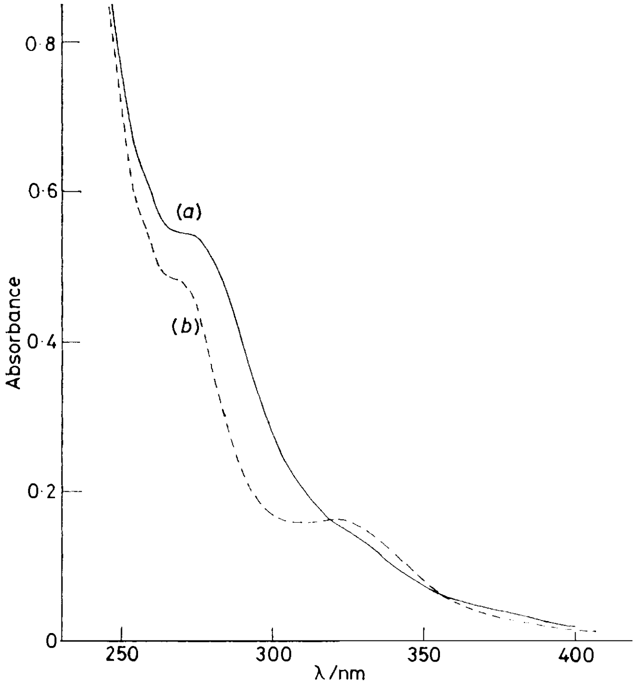

FIGURE 3 Absorption spectra of a 7 × 10^{-5} mol dm^{-3} solution of [AuCl$_2$(dpk·H$_2$O)]Cl in pure 1,2-dichloroethane (*a*) and after addition of 0.5% v/v methanol (*b*)

The equilibrium between the keto- and the hydrated form also exists in the bis adducts of palladium and gold [compounds (5) and (8)] but no detailed study on the solution chemistry of these species has been made.

From a comparison of the solution chemistry of these complexes, we conclude that the behaviour of palladium(II) is intermediate between those of platinum(II) and gold(III). Both the keto- and the hydrated form of the palladium(II) complexes coexist in comparable concentration in solution and can be isolated in the solid state, while the other two metal ions represent opposite extreme cases, platinum having much more affinity for the keto-form and gold more affinity for the hydrated one.

To ascertain if the uptake of the protic molecule occurs only after co-ordination of dpk to the metal ion or whether it can also occur during the process of co-ordination, the following experiments were carried out. Potassium trichloro(ethylene)platinate(II) was allowed to react in water with dpk and the progress of the reaction monitored spectrophotometrically. Under these extreme conditions (pure protic solvent) the complex with the ligand in its keto-form was formed first and then reacted with water to give the hydrated species quantitatively. Similarly, diacetonitrile(dichloro)palladium(II) was allowed to react with dpk in acetonitrile containing water (3% v/v) and in this case also the ratio of the keto- to the hydrated form of the complex was higher at the beginning than at equilibrium. Therefore, we conclude that dpk always reacts with the metal ion to give the complex in its keto-form which then reacts with HX to give the hydrated species.

Structure of Compound (1).—Crystals of (1) consist of neutral [$PdCl_2(dpk{\cdot}H_2O)$] molecules in which the palladium atom attains the usual square-planar co-ordination being bound to two chlorine and two nitrogen atoms of the chelating dpk·H_2O ligand. The Pd, Cl(1), Cl(2), N(1), and N(2) atoms are displaced from the mean plane passing through them by −0.001(1), 0.012(2), −0.008(2), 0.082(6), and −0.054(6) Å respectively. A view of the complex with the atomic numbering scheme is given in Figure 4; selected bond distances and angles are listed in Table 4. The Pd–Cl [2.296(3) and 2.301(3) Å] and the Pd–N [2.014(6) and 2.032(6) Å] bond lengths are in good agreement with those found in square-planar complexes of palladium(II) either *trans*- or *cis*-co-ordinated with uni- and bi-dentate *N*-donor ligands. Bond distances of 2.298(1) and 2.307(3) Å for Pd–Cl and 2.031(2) and 2.017(5) Å for Pd–N have been found in *trans*-dichlorobis(1-methylcytosine)- and *trans*-dichlorobis(2,3-dimethyl-1-t-butylisourea)-palladium(II) respectively.[12,13] In *cis*-complexes with bidentate chelating ligands forming five-membered rings [dichloro(*meso*-2,3-diaminobutane)- and dichloro(1,2-diaminoethane)-palladium(II)] [14,15] values of 2.317(2) and 2.309(3) Å for Pd–Cl and 2.029(6) and 1.978(12) Å for Pd–N have been determined, the chelating N–Pd–N bite angle being 83.6(2) and 83(1)° respectively. Because of the flexibility of the dpk·H_2O molecule (which differs from the rather rigid dpk) the chelation to the metal occurs with a very favourable N(1)–Pd–N(2) angle of 87.1(2)°. The six-membered chelate PdN(1)C(5)C(11)C(10)N(2) ring is in a boat conformation and the mean plane passing through N(1)C(5)C(10)N(2) leaves the Pd and C(11) atoms 0.865(1) and 0.746(1) Å out of the plane on the same side. The torsion angles in the ring are: PdN(1)C(5)C(11), −2.5; N(1)C(5)C(11)C(10), 64.5; C(5)C(11)C(10)N(2), −64.8; C(11)C(10)N(2)Pd,

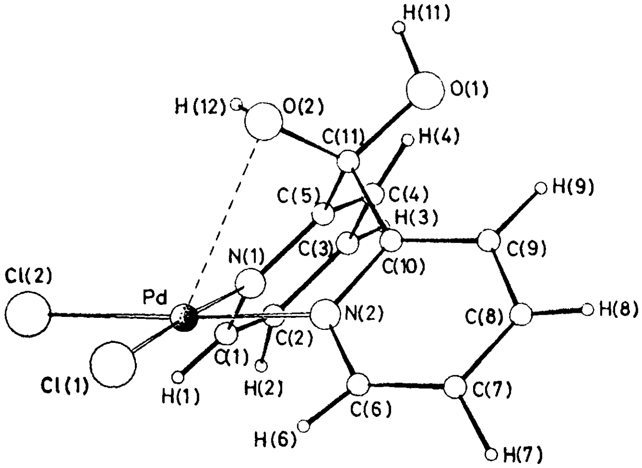

FIGURE 4 View of the molecular complex [$PdCl_2(dpk{\cdot}H_2O)$] with the atomic numbering scheme

TABLE 4

Selected bond distances (Å) and angles (°) of (1) and (7), with estimated standard deviations in parentheses (M = Pd for data in the first column, M = Au for those of the second column)

	(1)	(7)
M–Cl(1)	2.296(3)	2.257(6)
M–Cl(2)	2.301(3)	2.258(7)
M–N(1)	2.014(6)	2.08(1)
N–N(2)	2.032(6)	2.01(2)
N(1)–C(1)	1.346(10)	1.32(2)
N(1)–C(5)	1.344(8)	1.37(2)
C(1)–C(2)	1.365(11)	1.39(3)
C(2)–C(3)	1.376(12)	1.41(3)
C(3)–C(4)	1.346(11)	1.35(3)
C(4)–C(5)	1.391(10)	1.38(2)
C(5)–C(11)	1.532(9)	1.52(3)
C(10)–C(11)	1.528(10)	1.55(3)
N(2)–C(10)	1.364(8)	1.37(2)
N(2)–C(6)	1.340(9)	1.36(3)
C(6)–C(7)	1.373(11)	1.38(3)
C(7)–C(8)	1.367(11)	1.38(3)
C(8)–C(9)	1.373(11)	1.41(3)
C(9)–C(10)	1.369(10)	1.37(3)
O(1)–C(11)	1.392(8)	1.39(2)
O(2)–C(11)	1.380(9)	1.39(2)
Cl(1)–M–Cl(2)	91.0(1)	89.7(2)
Cl(1)–M–N(1)	177.1(2)	178.2(5)
Cl(1)–M–N(2)	91.9(2)	92.3(4)
Cl(2)–M–N(1)	90.0(2)	91.6(5)
Cl(2)–M–N(2)	176.6(2)	178.0(4)
N(1)–M–N(2)	87.1(2)	86.4(6)
C(1)–N(1)–C(5)	118.9(6)	123(2)
C(1)–N(1)–M	120.9(5)	121(1)
C(5)–N(1)–M	120.0(4)	116(1)
C(6)–N(2)–C(10)	118.0(6)	119(2)
C(6)–N(2)–M	122.5(5)	122(1)
C(10)–N(2)–M	119.5(4)	119(1)
C(2)–C(1)–N(1)	122.2(8)	120(2)
C(3)–C(2)–C(1)	118.9(8)	117(2)
C(4)–C(3)–C(2)	119.2(9)	122(2)
C(5)–C(4)–C(3)	120.5(8)	119(2)
C(11)–C(5)–N(1)	116.2(6)	118(1)
C(11)–C(5)–C(4)	123.6(6)	124(2)
N(1)–C(5)–C(4)	120.1(6)	118(2)
C(7)–C(6)–N(2)	123.3(8)	122(2)
C(8)–C(7)–C(6)	118.0(8)	120(2)
C(9)–C(8)–C(7)	120.0(9)	119(2)
C(8)–C(9)–C(10)	119.7(8)	119(2)
C(9)–C(10)–N(2)	121.0(7)	121(2)
C(9)–C(10)–C(11)	123.5(6)	124(2)
N(2)–C(10)–C(11)	115.5(6)	115(2)
C(10)–C(11)–C(5)	107.0(6)	108(1)
C(10)–C(11)–O(1)	106.0(5)	108(1)
C(10)–C(11)–O(2)	107.0(5)	110(1)
O(1)–C(11)–C(5)	111.2(5)	110(1)
O(2)–C(11)–C(5)	112.5(6)	108(1)
O(1)–C(11)–O(2)	112.8(6)	112(2)

4.1; C(10)N(2)PdN(1), 42.0; and N(2)PdN(1)C(5), −42.9°. The two pyridyl rings of the dpk·H_2O ligand are planar and make a dihedral angle of 114.54°.

The palladium atom is also involved in a weak intramolecular axial interaction with the O(2) atom of a hydroxyl group, the resulting Pd–O(2) distance [2.824(6) Å] being long compared to the sum of the covalent radii (*ca.* 2.0 Å) but less than the non-bonding distance (*ca.* 3.5 Å) for these atoms. The Pd–O(2) vector makes a 29.9° angle with the normal to the co-ordination plane.

The complexes are linked in the crystal by hydrogen bonds involving the chlorine and the hydroxylic hydrogen atoms (Figure 5) [O(2) ··· $Cl(2^{I})$, 3.080; H(12) ··· $Cl(2^{I})$, 2.40; O(1) ··· $Cl(1^{I})$, 3.196; H(11) ··· $Cl(1^{I})$, 2.20 Å; $H(12)O(2)Cl(2^{I})$, 22.4; $O(2)H(12)Cl(2^{I})$, 150.7; $H(11)O(1)Cl(1^{I})$, 6.3; and $O(1)H(11)Cl(1^{I})$, 170.7°].*

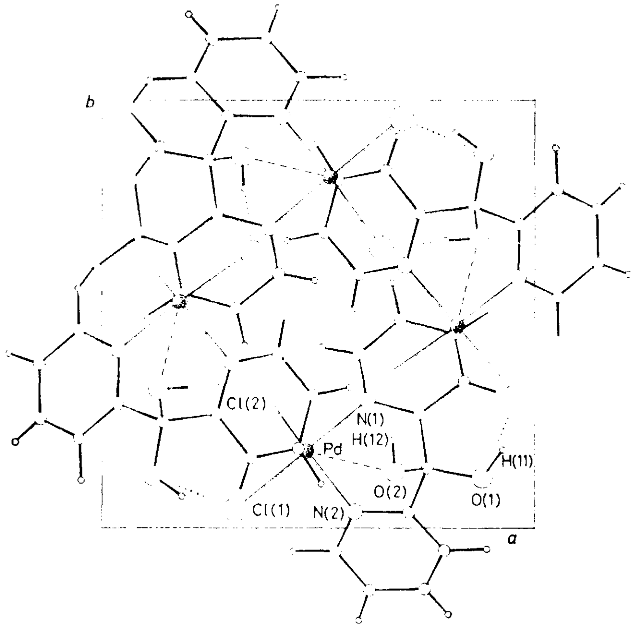

FIGURE 5 Projection along *c* showing the network of hydrogen bonds in crystals of $[PdCl_2(dpk{\cdot}H_2O)]$

Structure of Compound (7).—Crystals of (7) consist of $[AuCl_2(dpk{\cdot}H_2O)]^+$ cations and Cl^- counter ions. The cation has a square-planar geometry with two chlorine and two nitrogen atoms of a chelating dpk·H_2O ligand. Displacements of Au, Cl(1), Cl(2), N(1), and N(2) atoms from the mean plane passing through them are 0.002(2), −0.005(6), 0.001(6), −0.040(15), and 0.001(15) Å respectively. A view of the complex with the atomic numbering scheme is given in Figure 6, selected bond distances and angles are given in Table 4. The Au–Cl bond lengths [2.257(6) and 2.258(7) Å] are normal and equal, while the Au–N bonds [2.08(1) and 2.01(2) Å] differ but still lie in the usual range for square-planar gold complexes.

It is to be emphasized how the diolic form of dpk can assume a conformation suitable for chelation to the metal without preventing, through steric interactions, the co-ordination of two more chlorine atoms in the same plane. On the other hand the bulky planar organic ligands of the complexes $[AuCl_3(biquin)]$,[16] $[AuCl_3(dmphen)]$,[17] and $[AuCl_3(pquin)]$ [18] [biquin = 2,2′-biquinolyl, dmphen = 2,9-dimethyl-1,10-phenanthroline, pquin = 2-(2′-pyridyl)quinoline] which allow only one chlorine atom to be in the ligand plane lead to a structure in which three chlorine and one nitrogen atoms are in the co-ordination plane with the ligand perpendicularly disposed and necessarily bringing the other nitrogen within bonding distance.

The six-membered chelate ring AuN(1)C(5)C(11)C(10)-N(2) also adopts a boat conformation with the Au and C(11) atoms lying 0.993(2) and 0.708(18) Å above the plane passing through N(1)C(5)C(10)N(2). The torsion angles in the ring are: AuN(1)C(5)C(11), −5.6; N(1)-C(5)C(11)C(10), −59.2; C(5)C(11)C(10)N(2), 64.7; C(11)-C(10)N(2)Au, −2.6; C(10)N(2)AuN(1), −45.6; and N(2)AuN(1)C(5), 50.0°.

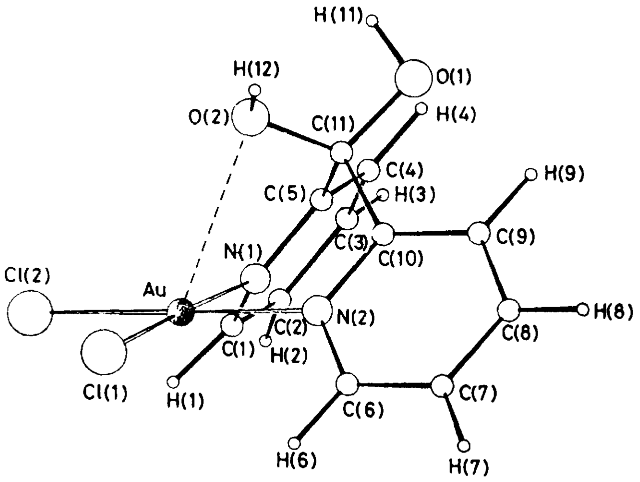

FIGURE 6 View of the cationic complex $[AuCl_2(dpk{\cdot}H_2O)]^+$ with the atomic numbering scheme

The chelate N(1)AuN(2) bite angle [86.4(6)°] is very favourable and close to the one found in the palladium complex. The two pyridyl rings are perfectly planar and the dihedral angle between them is 116.63°, very close to the value found in the palladium complex.

The gold atom is also involved in two long-range interactions, in the approximate octahedral sites of the metal, with the O(2) atom of one hydroxyl group [Au–O(2) = 2.77(1) Å] and the Cl(2) atom of an adjacent complex [$Au-Cl(2^{II})$ = 3.230(7) Å], this latter loosely joining the complexes in chains. The angles formed between the Au–O(2) and $Au-Cl(2^{II})$ vectors and the normal to the co-ordination plane are 27.2 and 3.0° respectively. Although these distances are much longer than those usually considered as bonding interactions (2.05 and 2.40 Å respectively) they are shorter than normal non-bonded distances (*ca.* 3.6 and 4.0 Å respectively). Long octahedral interactions with oxygen or chlorine atoms are

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* Roman numeral superscripts indicate the equivalent transformations: I; $1 - y, x, \frac{1}{4} + z$; II, $-x, \frac{1}{2} + y, \frac{1}{2} - z$; III, $1 - x, -y, -z$.

common in gold(III) complexes, for example in [bis(2-aminoethyl)amine]chlorogold(III) and [bis(2-aminoethyl)amido]chlorogold(III) axial interactions of the same type as the present ones have been found between the metal and Cl$^-$ and/or an oxygen of the perchlorate anion.[19]

The complex cations and the Cl$^-$ anions are linked in the crystal (Figure 7) by hydrogen bonds involving the hydroxylic hydrogens and the ionic chlorides [O(1) · · · Cl(3) = 3.048, H(11) · · · Cl(3) = 2.13, O(2) · · · Cl(3^{III}) = 2.991, and H(12) · · · Cl(3^{III}) = 2.08 Å; H(11)O(1)-Cl(3) = 13.7, O(1)H(11)Cl(3) = 160.2, H(12)O(2)Cl(3^{III}) = 10.0, and O(2)H(12)Cl(3^{III}) = 165.6°].

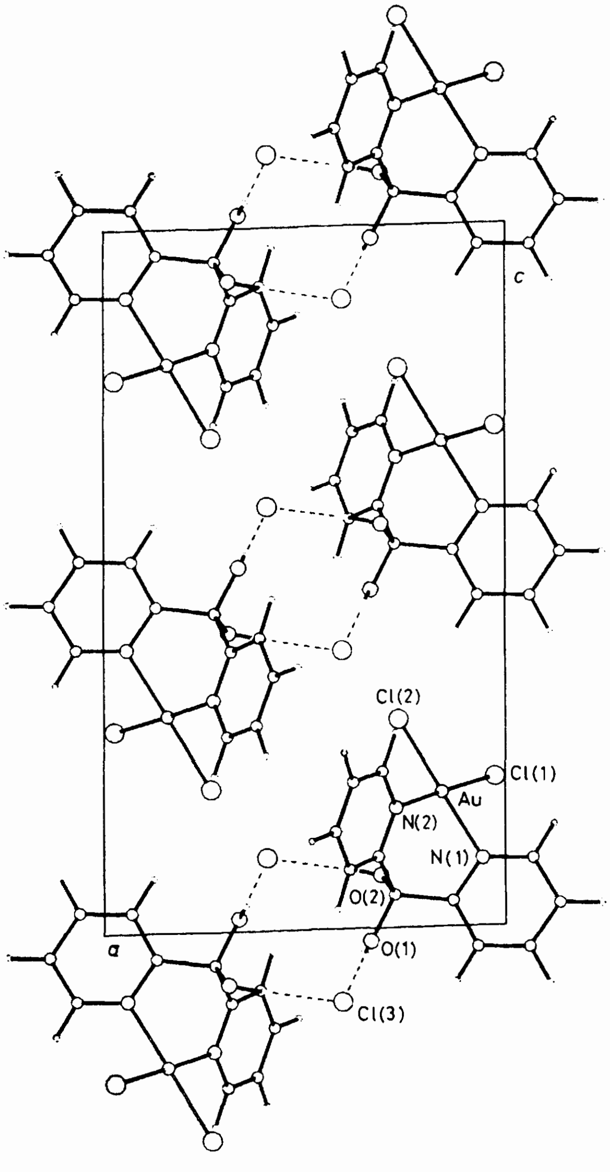

FIGURE 7 Projection along *b* showing the network of hydrogen bonds in crystals of [AuCl$_2$(dpk·H$_2$O)]Cl

Conclusions.—The question arises as to why the carbonyl group of dpk, $(C_5H_4N)_2C{=}O$, when co-ordinated to metal ions adds a protic molecule, HX, to give $(C_5H_4N)_2$-C(OH)X, while in general such addition products of ketones are rather unstable and exist only when the carbonyl group is flanked by strong electron-withdrawing groups.[20] In an earlier work the hydration of dpk in its 1 : 2 complexes was explained on the basis of the relief of non-bonding interactions between hydrogen atoms adjacent to the pyridine nitrogen atoms of *trans* ligands.[3,4] However, this cannot be the only reason as hydration also occurs in the 1 : 1 complexes where no such steric interaction is present.

Another possible explanation is that, in contrast to five-membered rings, the formation of a planar six-membered ring between dpk and a metal ion is difficult; the formation of a chelate in the boat form with the metal and the carbonyl carbon above the plane of the two nitrogen and the two 2-carbon atoms of the pyridine rings being more easily achieved.[21,22] In the latter case the coplanarity of the ligand and the conjugation over the carbonyl group would be destroyed and as a result the hydration of the keto-group would be facilitated. That the relief of strain within a ring may be important is in accord with the observation that while acetone has little or no tendency for hydration, cyclopropanone yields a stable hydrate.[23]

An additional driving force for the metal-promoted hydration might result from an interaction of the hydroxy- or the X-group of C(OH)X with the central metal. Evidence for terdentate behaviour of the $(C_5H_4N)_2C(OH)X$ ligand has been found in complexes with metal ions which form octahedral species, especially when X is a nitrogen base.[4]

We have observed that the stability of the hydrated species and the rates of reversible hydrolysis have similar trends, increasing on going from platinum(II) to palladium(II) to gold(III) and thus paralleling the reactivity towards ligand substitution in complexes of these metal ions. Several causes can contribute to this enhancement. For example; (*i*) the electron-withdrawing ability of the metal ion will affect the electrophilicity of the carbonyl carbon; (*ii*) the strain within a planar six-membered chelate will favour the sp^2 to sp^3 rehybridization of the carbon atom linking the pyridine rings; (*iii*) the ability of the metal ion to accumulate the reagent in the fifth position will facilitate the reaction by holding the two reactants in juxtaposition;[24] and (*iv*) the hydrated species will be stabilized by interaction of the hydroxy- (or X) group of $(C_5H_4N)_2C(OH)X$ with the central metal through the axial co-ordination site.

There are reports in the literature which indicate that the electron-withdrawing properties of the metal cation and the ability to make an apical position available for co-ordination by an extra donor in a tetragonal pyramid increase along the sequence $Pt^{II} < Pd^{II} < Au^{III}$.[25] Moreover, the *X*-ray diffraction data have shown that, in both complexes, there is a strong boat-like deformation of the six-membered chelate with a dihedral angle between the two pyridine planes of 114.5 and 116.6° for (1) and (7) respectively and a definite interaction between one hydroxy-group and the metal cation, as is apparent from the short M · · · O distances [2.824(6) and 2.77(1) Å respectively]. Therefore we conclude that the effects mentioned above certainly contribute to the stabilization of the hydrated species.

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