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Palladium(II) complexes of 2-acylpyridines. The crystal structure of dibromo bis(phenyl-2-pyridyl ketone)palladium(II)

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Abstract

Reaction of Pd(II) with 2-pyridine-carboxaldehyde (PC), methyl 2-pyridyl ketone (MPK) and phenyl 2-pyridyl ketone (PPK) in methanolic solutions gave six new complexes which have been characterized by elemental analysis, conductivity measurements, and IR and UV–Vis spectroscopic techniques. The ligands PC and PPK behave as monodentate and exhibit nitrogen coordination while MPK exhibits N, O ligation through the ring nitrogen and carbonylic oxygen atom in the production of a five membered chelate ring. The crystal structure of the Pd(II) complex of PPK has been determined by single crystal X-ray diffraction methods. Crystal data are: monoclinic space group $P2_1/n$, $a=8.707(3)$, $b=14.394(3)$, $c=8.967(3)$ Å, $\beta=93.45(2)°$, $D_{calc}=1.871$ g cm^{-3}, $V=1121.8$ Å^3, $R_F=0.062$; $R_w=0.068$, $GOF=2.0$. The complex molecule is the *trans*-isomer of a square planar structure and the central Pd(II) lies on a center of symmetry and is coordinated by two bromides and two pyridine ring nitrogen atoms.

Introduction

During the past few years, in addition to platinum compounds, the coordination compounds of palladium(II) and (IV) seem to be promising in cancer chemotherapy [1]. Many palladium(II) and (IV) neutral and ionic complexes with *trans* structures, e.g. *trans*-[Pd(NH$_3$)$_2$Cl$_2$], were found to exhibit antitumor activity [2–5]. The transition metal complexes of pyridines have been extensively studied because of their interesting properties and applications [6], while a few studies have been reported on the complexes of 2-acylpyridines [7–9]. Previous studies in the coordination chemistry of 2-acylpyridines have involved first row transition metal ions [7–9], as well as one investigation involving tin(IV) [10]. The ligands can potentially exhibit two modes of coordination; the pyridine nitrogen atom could coordinate alone or the carbonyl oxygen atom could coordinate along with the pyridine nitrogen atom.

As a part of our systematic investigation on the platinum group metals [11–17], we report here the preparation and characterization of Pd(II) complexes with PC, MPK and PPK, Fig. 1.

Experimental

PdCl$_2$, PC, MPK and PPK were purchased from Fluka Chemical Company. All the solvents and chemicals used were of high purity. Elemental analyses of the samples were performed in the Centre National de la Recherche Scientifique, Vernaison, France. Analyses of the elements palladium and halogens, and physical measurements were carried out using published methods [11–17].

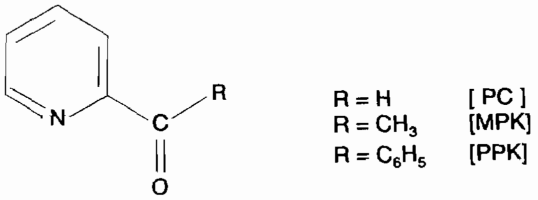

Fig. 1. The structures of the ligands.

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Synthesis

Pd(PC)$_2$X$_2$, Pd(MPK)X$_2$ and Pd(PPK)$_2$X$_2$ where X = Cl, Br

The complexes were prepared by mixing methanolic solutions of the ligands and lithium tetrahalogen-palladate prepared *in situ* from $PdCl_2$ and 2LiX (1.5:3 and 4:2 ligand to metal molar ratio). The reaction mixture was stirred for 24 h at room temperature. Then it was left in the refrigerator for one day. The powders were filtered off, washed with cold methanol and ether and dried *in vacuo* over silica gel. They were redried at 90 °C *in vacuo* over P_4O_{10}.

Attempts to isolate the complexes $Pd(MPK)_2X_2$, $Pd(PC)X_2$ and $Pd(PPK)X_2$ were unsuccessful.

Crystal and molecular structure determination

Crystals were obtained by slow evaporation of a methanolic solution of the complex. X-ray data were collected at room temperature in the $\omega/2\theta$ scan mode ($2\theta < 25°$) on an Enraf-Nonius CAD4 diffractometer with incident-beam (Ag Kα) graphite monochromator. Intensity data were corrected for Lorentz and polarization effects. The absorption was disregarded. Weissenberg photographs were used for investigating space group and approximate unit-cell dimensions. Cell dimensions together with other experimental parameters are indicated in Table 1. Only reflections with $I > 3\sigma(I)$ were retained for the solution of the structure. The structure was solved by using the SDP package and SHELX-76 [18, 19]. Final coordinates and B_{eq} values for the non-hydrogen atoms are listed in Table 2.

Refined parameters were calculated by using anisotropic thermal parameters for non-hydrogen atoms and isotropic factors for hydrogen atoms. See also 'Supplementary material'.

TABLE 1. Crystal data for $Pd(PPK)_2Br_2$

Formula	$PdBr_2N_2O_2C_{24}H_{20}$
M_r	632.2
a (Å)	8.707(3)
b (Å)	14.394(3)
c (Å)	8.967(3)
β (°)	93.45(2)
V (Å^3)	1121.8
Z	2
D_x (g cm^{-3})	1.871
Space group	$P2_1/n$
Total reflections	1781
Significant reflections, $I > 3\sigma(I)$	1278
Refined parameters	142
Residual factors	
R	0.062
R_w	0.068
GOF	2.0

TABLE 2. Fractional coordinates and B_{eq} (Å^2) of the non-hydrogen atoms

Atom	x	y	z	B_{eq}
Pd	0.000	0.000	0.000	1.69(3)
Br	0.9207(2)	0.1002(2)	0.1971(2)	4.57(5)
O	0.280(1)	0.106(1)	−0.352(1)	5.4(4)
N	0.211(1)	0.0575(7)	0.017(1)	2.0(2)
C1	0.296(2)	0.044(1)	0.147(2)	3.0(3)
C2	0.441(2)	0.074(1)	0.178(2)	3.6(4)
C3	0.510(2)	0.122(1)	0.075(2)	4.1(4)
C4	0.426(2)	0.139(1)	−0.064(2)	3.8(4)
C5	0.282(2)	0.104(1)	−0.087(2)	2.5(3)
C6	0.206(2)	0.118(1)	−0.242(2)	3.4(4)
C7	0.038(2)	0.147(1)	−0.263(2)	2.6(3)
C8	0.956(2)	0.126(1)	−0.395(2)	3.0(3)
C9	0.807(2)	0.151(1)	−0.423(2)	3.7(4)
C10	0.740(2)	0.202(1)	−0.316(2)	4.5(5)
C11	0.819(2)	0.228(1)	−0.180(2)	3.6(4)
C12	0.968(2)	0.197(1)	−0.152(2)	3.0(3)

Results and discussion

Colours, analytical data and molar conductivity values are given in Table 3. The complexes are microcrystalline or powder like, stable in atmospheric conditions, and soluble in DMF and DMSO. Some of the complexes have moderate solubility in methanol. Elemental analysis of the PC and PPK products suggested a 1:2 adduct. The analytical results of the reaction product with MPK show 1:1 adduct formation.

The conductivity measurements for all the complexes in 10^{-3} M dimethylformamide solutions give values of Λ_m between 2.0–39.0 Ω^{-1} cm^2 mol^{-1} indicating the non-ionic nature of the complexes [20]. The higher values of the conductance for some complexes in this solvent could be attributed to the strong donor capacity of the solvent, which frequently leads the solvent molecule to enter the coordination sphere and knock the anion out of the coordination sphere [13, 20].

The principal IR bands of interest and the proposed assignments are given in Table 4. The proposed assignments are supported by literature reports [7–10, 21–23].

The weak bands at 3060 and 3030 cm^{-1} which appear in all the compounds are assigned to the C–H stretching motion of the rings [22], while the weak bands at 2850 and 2820 cm^{-1} which appear in PC are assigned to the C–H stretching mode of the formyl group –CHO. The complexes **4** and **5** show a very broad band at 3400 cm^{-1} which is probably due to hydrogen bonding. The disappearance of the νCH(CHO) stretching mode and the appearance of the new νOH stretching band suggest tautomerization (enolization) of the labile formyl group for complexes **4** and **5**.

TABLE 3. Analytical and molar conductivity data of the compounds

Compound	Serial number	Colour	Anal. Found (calc.) (%)					Λ_m[a] (S cm^2 mol^{-1})
			C	H	N	Pd	X	
$Pd(PC)_2Cl_2$	**4**	brown–yellow	36.94 (36.80)	2.60 (2.55)	5.95 (7.15)	25.68 (27.13)	17.90 (18.11)	30.0
$Pd(PC)_2Br_2$	**5**	red–brown	27.53 (29.99)	2.07 (2.08)	5.19 (5.83)	19.92 (22.14)	33.10 (33.26)	36.0
$Pd(MPK)Cl_2$	**6**	yellow	28.28 (28.17)	2.55 (2.34)	4.79 (4.69)	35.7 (35.6)	24.10 (23.79)	27.5
$Pd(MPK)Br_2$	**7**	orange–yellow	21.77 (21.70)	2.00 (1.80)	3.94 (3.62)	28.30 (27.46)	41.40 (41.25)	37.0
$Pd(PPK)_2Cl_2$	**8**	light yellow	52.38 (52.97)	3.28 (3.31)	5.09 (5.15)	20.01 (19.57)	13.15 (13.04)	2.5
$Pd(PPK)_2Br_2$	**9**	yellow	46.06 (45.57)	2.90 (2.85)	4.37 (4.43)	17.30 (16.82)	25.50 (25.26)	3.2

[a]Values of molar conductance for ac. 10^{-3} M solutions DMF at 25 °C.

TABLE 4. IR spectra data of the ligands and some representative complexes

Assignments	PC	MPK	PPK	**4**	**6**	**8**
νOH				3400br	3090ms	3110m
νCH	3060m	3060m	3082m	3060sh	3022m	3090w
		3010m	3060m			3062ms
			3010m			3030w
νCH(CHO)	2850mw					
	2820mw				2900w	
νCH_3		2925w				
		2862w			1618m	1670vvs
νC=O	1720vs	1700vs	1670vs	1712w		
				1670m	1588vs	1595s
I Ring stretching	1589s	1585ms	1582ms	1625s		
				1600vs	1572s	1580ms
II Ring stretching	1572ms	1570m	1570m	1572w		1568w
					1442m	1450vs
III Ring stretching	1472m	1468m	1468m	1480ms		1442sh
IV Ring stretching	1440ms	1438ms	1450s	1438ms	1430sh	
δCH_3 as		1420w	1438ms		1352ms	
δCH_3 sym		1360s				
δCH(CHO)	1390w			1385m	1320s	1321s
V Ring stretching in plane	1300m	1300m	1302m	1290m	1295s	1305s
	1260w	1282s	1285s	1240sh	1255mw	1285vs
	1218ms	1240s	1242s	1215ms		1246s
δCH	1150mw	1150w	1150sh	1158m	1165s	1165s
nCH	1089mw	1100m	1092m	1080s	1094s	1105ms
VI Ring breathing	995ms	996ms	992s	1032m	1031s	1002m
δCH out of plane deformation	760s	780s	780s	765vs	785vs	770s
	707mw	742m	750s	710sh	758m	752s
VII in plane ring bending	611ms	593s	575mw	612w	592ms	572w
VIII out of plane ring bending	408m	412w	400m	445m	432m	430mw

The carbonyl stretching frequency appears as a strong band in the region 1720–1670 cm^{-1} in all the complexes. In the metal ion complexes **4** and **5** there is an apparent splitting of this band, the lower energy band is probably caused by the formation of a hydrogen bond. In the metal ion complexes **6** and **7** the carbonyl stretching frequency is shifted appreciably (52 cm^{-1}) to lower frequency, indicating an interaction between the metal ion and the oxygen atom while in the case of the PPK the carbonyl stretching frequency is uneffected upon complex formation. The stretching frequencies of C=N and C=C in the pyridine ring appear at 1589–1582 and 1572–1570 cm^{-1} in the ligands **1**, **2** and **3**. Upon complex formation the peak at 1589–1582 cm^{-1} shifts to a slightly higher frequency, however the peak at 1572 cm^{-1} does not shift at all. The higher frequency shift of the peak at 1589–1582 cm^{-1} suggests bond formation between the metal ion and the ring nitrogen [8]. In the case of complexes **6** and **7**, the frequency shifts of the carbonyl group and the pyridine ring may suggest chelate ring formation which can also be confirmed by far-IR data.

The band of the ligands at 996–992 cm^{-1} is assigned to the breathing motion of the pyridine ring, which is expected to shift to higher frequencies when the pyridine nitrogen is involved in bonding with metal ions [24]. In all the complexes prepared this band is found between 1030–10002 cm^{-1} consistent with N coordination.

The far-IR spectra of the complexes in the region 400–200 cm^{-1} are given in Table 5. In complex **8** the strong band at 342 cm^{-1} appears in the spectrum of the bromo analogue at 297 cm^{-1}. These are assigned to the Pd–Cl and Pd–Br stretchings, respectively. The presence of one Pd–X motion implies a *trans* configuration for the complexes. The ratio ν(Pd–Br)/ν(Pd–Cl) is 0.86 [21, 25]. Among the palladium complexes the bands at *c*. 280 cm^{-1} are consistent and may be assigned to the stretching bands of palladium–nitrogen [26, 27]. Complex **6** exhibits two bands at 368 and 342 cm^{-1} while the bromo analogue shows bands at 310 and 295 cm^{-1}. These are assigned to Pd–Cl and Pd–Br, respectively. The presence of two Pd–X motions implies a *cis* configuration. In planar Pt(II) and Pd(II) complexes, ν(MX) is sensitive to the ligand *trans* to the M–X bond [21]. The metal–halogen stretching frequency ν(M–X) becomes lower as a ligand with stronger *trans*-influence is introduced *trans* to the M–X bond [28]. Since the *trans*-influence of the N-donor is expected to be stronger than that of the O-donor, in complex **6** the higher frequency at 368 cm^{-1} could be attributed to the ν(Pd–Cl) *trans* to the O-donor with the lower frequency at 342 cm^{-1} to the ν(Pd–Cl) *trans* to the N-donor [21, 28]. In complexes **6** and **7**, the common bands at *c*. 290 and 276 cm^{-1} are assigned to the chelate ring vibrations, the former mainly due to the stretching vibration of palladium–nitrogen, and the latter to that of palladium–oxygen. Because of the chelate ring formation in these complexes of MPK, the bond distances between the palladium ions and the nitrogen atom will be shortened and the stretching vibrations Pd–N appear at higher frequencies than those of PC and PPK [8].

TABLE 5. Experimental assignments of 2-acylpyridine metal complexes in the far-IR region

Compound	νPd–X	νPd–N	νPd–O
4	340mbr	287m	
5	300m	288m	
6	368s 342vs	295w	276mw
7	310s 295sh	288w	278m
8	342vs	286m	
9	297s	278m	

The electronic spectral data of the complexes and the ligands are given in Table 6. In the visible spectra of the square planar complexes of Pd(II) and for d^8 configurations in general, three d–d spin allowed, singlet–singlet and three spin forbidden singlet–triplet transitions are predicted [29]. Strong charge transfer transitions may interfere and prevent the observation of all the expected bands [29]. The intense bands at 20.000–25.000 cm^{-1} are assigned to d–d spin allowed transitions while the band at 26.000–28.000 cm^{-1} may be due to n$\rightarrow\pi^*$ transitions of the ligands [9, 12, 23, 29, 30].

Description of the structure of Pd(PPK)$_2$Br$_2$

The structure of the complex and the atomic numbering scheme are shown in Figs. 2 and 3. Table 7 lists selected bond distances and angles. The Pd(II) atom is four-coordinated and is surrounded in a strictly planar fashion by two *trans* nitrogen atoms of the PPK

TABLE 6. Electronic spectral data

Compounds	DMF	D Reflectance	Assignment
1	26.550		n$\rightarrow\pi^*$
2	29.990		n$\rightarrow\pi^*$
3	28.040		n$\rightarrow\pi^*$
4		25.000sh	$^1A_{1g}\rightarrow{}^1E_g$
	28.570	27.030	n$\rightarrow\pi^*$
	31.900		LMCT
5		20.830sh	$^1A_{1g}\rightarrow{}^3B_{1g}$
		23.090	$^1A_{1g}\rightarrow{}^1E_g$
	28.170br	26.810sh	n$\rightarrow\pi^*$
	32.150sh		LMCT
6		23.620sh	$^1A_{1g}\rightarrow{}^3B_{1g}$
		25.000	$^1A_{1g}\rightarrow{}^1E_g$
	28.410	27.780sh	n$\rightarrow\pi^*$
	30.860sh		LMCT
7		24.800	$^1A_{1g}\rightarrow{}^1E_g$
	27.930	27.780	n$\rightarrow\pi^*$
	31.640		LMCT
8	24.940	24.630	$^1A_{1g}\rightarrow{}^1E_g$
		26.810sh	
		28.570	n$\rightarrow\pi^*$
9	24.800	23.720	$^1A_{1g}\rightarrow{}^1E_g$
		28.850	n$\rightarrow\pi^*$
			LMCT

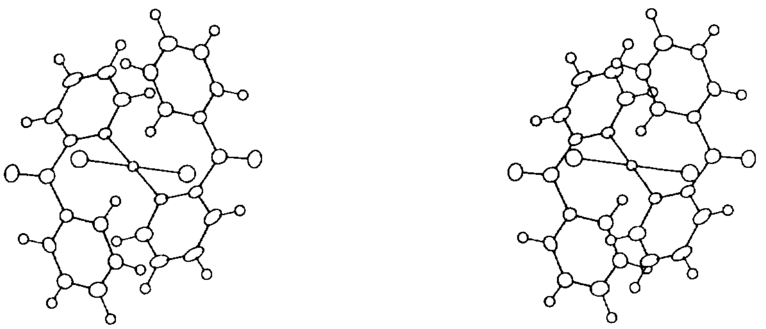

Fig. 2. Stereoview of the structure of the complex Pd(PPK)$_2$Br$_2$.

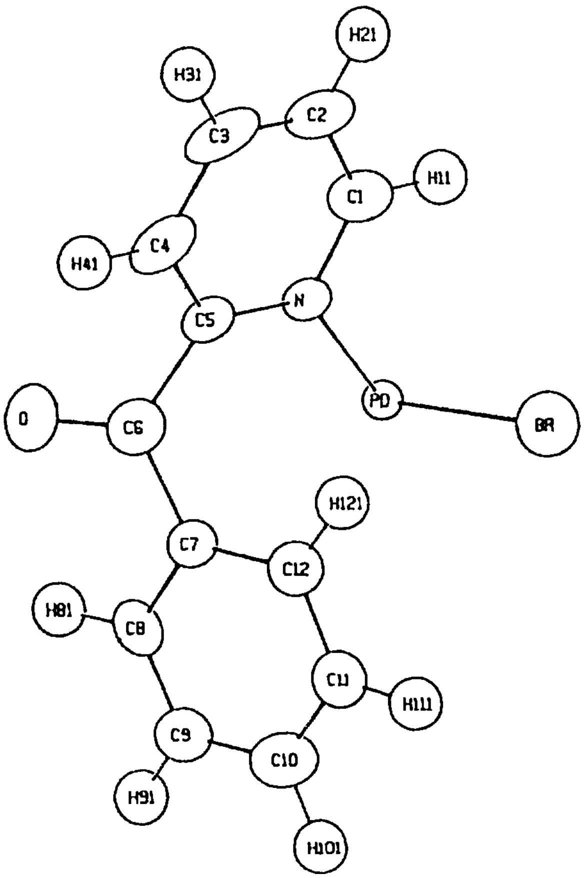

Fig. 3. Atomic numbering scheme (assymetric unit).

TABLE 7. Bond lengths (A) and angles (°)

Pd-Br	2.414(2)	C(4)-C(5)	1.36(2)
Pd-N	2.01(1)	C(5)-C(6)	1.52(2)
N-C(l)	1.35(2)	C(6)-C(7)	1.52(2)
N-C(5)	1.33(2)	C(7)-C(8)	1.38(2)
O-C(6)	1.22(2)	C(7)-C(12)	1.40(2)
C(1)-C(2)	1.35(2)	C(8)-C(9)	1.35(2)
C(2)-C(3)	1.32(3)	C(9)-C(10)	1.37(3)
C(3)-C(4)	1.43(3)	C(10)-C(11)	1.41(2)
		C(11)-C(12)	1.38(2)
Br-Pd-N	89.9(3)	C(5)-C(6)-C(7)	121(1)
C(1)-N-C(5)	115(1)	C(7)-C(6)-O	119(1)
N-C(1)-C(2)	126(2)	C(6)-C(7)-C(12)	121(1)
C(1)-C(2)-C(3)	119(2)	C(6)-C(7)-C(8)	119(1)
C(2)-C(3)-C(4)	118(1)	C(12)-C(7)-C(8)	120(1)
C(3)-C(4)-C(5)	119(2)	C(7)-C(8)-C(9)	123(1)
C(4)-C(5)-N	123(1)	C(8)-C(9)-C(10)	117(1)
C(4)-C(5)-C(6)	116(1)	C(9)-C(10)-C(11)	123(2)
N-C(5)-C(6)	121(1)	C(10)-C(11)-C(12)	119(2)
C(5)-C(6)-O	120(1)	C(11)-C(12)-C(7)	118(1)

and two bromide atoms. The bond distances and angles in the PPK ligand are normal in the structure. The C-C bond lengths in the phenyl groups are all normal.

Pyridine in the gas phase has equal C-C bond lengths of 1.392(1) Å; the C-N bond lengths are 1.340(1) Å and the C-N-C angle is 116” 50’ [31]. The average C-C bond distance of the pyridine ring atoms is 1.365 Å for the Pd(II) complex, which is comparable to the accepted value of 1.395(1) Å [32]. The average C-N bond distance 1.340(2) Å is the same as the accepted value of 1.340(1) Å. The average bond angles within the rings are 120.0”. There is usually very little change in the bond lengths of the pyridine ring on coordination to a metal ion [33].

The Pd-N (sp”) bond distance of 2.01(1) Å is comparable with the values of 2.026(12) Å in bis (L-prolinato)palladium(II) [34] and 2.024(7) Å in *trans*-(2-methylindole)$_2$Cl$_2$ [35]. The Pd-Br distance of 2.414(2) Å is similar to that found in other square planar *trans* complexes of Pd(II) [36].

Conclusions

From the overall study presented above it is concluded that the ligands PC and PPK exhibit monodentate behaviour, the bonding site being the pyridine nitrogen atom, while MPK behaves as a bidentate chelated ligand bonding through both pyridine nitrogen and carbonyl oxygen. Tautomerization (enolization) of the labile formyl group (PC) appears on coordination with Pd(II). Monomeric square planar structures are assigned for all the complexes in the solid state.

All data suggest that the complexes **4**, **5**, **8** and **9** exhibit a square planar *trans* configuration. In accordance with the *trans* effect the *cis* Pt(II) and Pd(II) complexes can be synthesized directly from the $[MCl_4]^{2-}$ ions by reaction with an N-donor ligand in methanolic or aqueous media, indicating that Cl^- has a greater *trans* effect compared to the nitrogen donor ligands [37]. The replacement of the halogen ions from $[MX_4]^{2-}$ by L molecules gives the *cis*-isomer in the case of the Pt(II) complexes, while when $[PdX_4]^{2-}$ react with N-donor ligands *cis*–*trans* isomerization takes place because of the higher stability of the *trans*-isomer [13, 38, 39]. This would explain why the *cis*-isomers of palladium are quite rare. It is worth noting that MPK reacts in a different manner with $[PdX_4]^{2-}$, giving only 1:1 adducts. The Pauling Electroneutrality Principle could provide a reasonable explanation for the failure to isolate 1:2 complexes with MPK. The inductive effect of the methyl group transfer charge to the carbonyl oxygen and a large transfer of charge to the central atom is possible, so one molecule of MPK is needed to bring about 'electroneutrality', in the presence of less basic anionic ligands, e.g. Cl^- and Br^- [40, 41].

Acylpyridines can be coordinated in monodentate or bidentate fashion. Both possibilities arise in Pd(II) which forms strong bonds to nitrogen and weaker to oxygen, contrary to organotin derivatives which give strong bonds to oxygen and weaker to nitrogen [10].

Supplementary Material

Tables of anisotropic thermal parameters, coordinates of the hydrogen atoms and a complete list of bond angles can be obtained upon request from the authors.

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