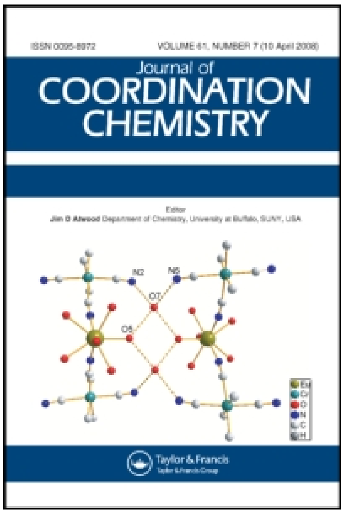

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COMPLEXES OF THE PLATINUM METALS WITH HYDRAZONES. PART I. PALLADIUM(II) COMPLEXES WITH 2-ACETYL-AND 2-BENZOYLPYRIDINE HYDRAZONES

Dimitra Kovala-demertzi[a]; David Nicholls[b]
[a] Laboratory of Inorganic and General Chemistry, University of Ioannina, Ioannina, Greece [b] Donnan Laboratories, The University, Liverpool, U.K.

To cite this Article Kovala-demertzi, Dimitra and Nicholls, David(1988) 'COMPLEXES OF THE PLATINUM METALS WITH HYDRAZONES. PART I. PALLADIUM(II) COMPLEXES WITH 2-ACETYL-AND 2-BENZOYLPYRIDINE HYDRAZONES', Journal of Coordination Chemistry, 17: 4, 297 — 303

To link to this Article: DOI: 10.1080/00958978808073920

URL: http://dx.doi.org/10.1080/00958978808073920

J. Coord. Chem. 1988, Vol. 17, pp. 297–303
Reprints available directly from the publisher
Photocopying permitted by license only

COMPLEXES OF THE PLATINUM METALS WITH HYDRAZONES. PART I. PALLADIUM(II) COMPLEXES WITH 2-ACETYL- AND 2-BENZOYLPYRIDINE HYDRAZONES

DIMITRA KOVALA-DEMERTZI

Laboratory of Inorganic and General Chemistry, University of Ioannina, Ioannina, Greece

and DAVID NICHOLLS*

Donnan Laboratories, The University, Liverpool L69 3BX, U.K.

(Received November 9, 1987)

Mono-ligand complexes derived from 2-acetylpyridine hydrazone (APH) and 2-benzoylpyridine hydrazone (BPH) have been prepared with palladium(II) salts. Their physical properties including molar conductance measurements and spectral (IR, ^{1}H-nmr and d–d) data are discussed in terms of possible structural types and the nature of bonding. No bis-ligand complexes have been prepared. The ligands appear to coordinate in the solid state *via* both pyridine and methylene nitrogen atoms but a change of bonding mode appears to occur when the solid complexes are dissolved in DMSO. A paramagnetic green species has been reproducibly prepared from Li_2PdCl_4 and APH.

Keywords: Palladium, “palladium-green”, hydrazones, pyridine, complexes

INTRODUCTION

We have recently described[1] complexes of cobalt(II) and zinc(II) with the ligands 2-acetylpyridine hydrazone (APH) and 2-benzoylpyridine hydrazone (BPH). In these, the ligands invariably act in a bidentate fashion forming mono or bis complexes. The mono-ligand complexes are tetrahedral while the bis complexes are octahedral. The ligands appeared to coordinate *via* both pyridine and methylene nitrogen atoms and thus belong to the class of chelating ligands containing the –N=C–C=N– grouping.

As part of a study of the compounds formed between hydrazones and the platinum metals we describe in this paper results on palladium(II) complexes. Mono-ligand complexes have been prepared and characterized, but surprisingly no bis-ligand complexes have been isolated.

EXPERIMENTAL

Materials and methods

$PdCl_2$ and K_2PdCl_4 were purchased from Fluka Chemical Company. All the solvents and chemicals used were of high purity. Analyses and physical measurements were carried out using published methods.[1–4]

---

* Author for correspondence.

Preparation of compounds

APH and BPH were prepared according to known procedures.[1]

Pd(APH)Cl$_2$, Pd(BPH)Cl$_2$

A solution of the ligand (1.8 mmol in ethanol) was added dropwise with stirring to a solution of lithium tetrachloropalladate(II) prepared *in situ* from 2.0 mmol of palladium chloride(II) and 4.0 mmol of lithium chloride in 30 ml of ethanol. A yellow powder precipitated. The reaction mixture was stirred for 24 h at room temperature, then it was left in the refrigerator for one day. The powder was filtered off, washed with EtOH and Et_2O and dried under vacuum over silica gel and finally at 90°C under vacuum over P_4O_{10}. Pd(APH)Cl$_2$: yellow powder, yield 65%. Anal. (%) Found: Pd, 34.4; Cl, 22.9. Calcd: Pd, 34.05; Cl, 22.69. Pd(BPH)Cl$_2$: orange powder, yield 70%. Anal. (%) Found: Pd, 28.9; Cl, 19.1. Calcd: Pd, 28.40; Cl, 18.93.

Pd(APH)Br$_2$, Pd(BPH)Br$_2$

The ligands and $PdCl_2$ or K_2PdCl_4 were dissolved separately in HBr (10 cm^3, 0.1M aqueous; heating was necessary for $PdCl_2$). The two solutions were mixed at room temperature and the precipitated complexes isolated as above. Pd(APH)Br$_2$: yellow powder, yield 82%. Anal. (%) Found: Pd, 26.9; Br, 39.2. Calcd: Pd, 26.51; Br, 39.82. Pd(BPH)Br$_2$: yellow powder, yield 87%. Anal. (%) Found: Pd, 22.5; Br, 34.10. Calcd: Pd, 22.95; Br, 34.48.

Efforts to prepare complexes with 1 : 2 stoichiometries, using various metal salt: ligand molar ratios, solvents (H_2O, CH_3OH and C_2H_5OH) and pH regions (1–10) met with failure. In all cases $PdLX_2$ complexes were isolated. Attempts to obtain the 1 : 2 complexes using an excess of ligand and slight heating, according to the equation $PdLX_2 + L \rightarrow PdL_2X_2$ were also unsuccessful.

Palladium green

A solution of the ligand APH (2.4 mmol) in ethanol was added dropwise with stirring to a solution of lithium tetrachloropalladate(II) in ethanol. The reaction mixture was stirred for 3 days at room temperature. The pH of the reaction mixture was kept at 5.0–5.3 and the product isolated as for the other complexes. Found for the green compound: C, 28.55; H, 2.93; N, 13.45; Pd, 31.77; Cl = 20.82%. Pd : Cl : C : H : N = 1.00 : 1.97 : 7.97 : 9.80 : 3.20.

RESULTS AND DISCUSSION

When solutions of the hydrazones of 2-acetyl- and 2-benzoylpyridines were stirred with ethanolic or aqueous solutions of palladium(II) salts, coloured air-stable complexes of the formula $PdLX_2$ (X = Cl, Br) were precipitated. The molar conductances of the complexes in dimethylformamide solutions are in accord with their formulation as non-electrolytes, thus excluding the alternative Magnus-salt type structures $[ML_2][MX_4]$.

TABLE I

Important infrared bands (cm^{-1}) in APH, BPH and their complexes.

Compound	$\nu(NH_2)$	$\nu(ND_2)$	$\delta(NH_2)$	$\delta(ND_2)$	$\nu(C{=}N_2)$	$\nu(N{-}N_2)$	breathing mode	C–H (o.p)	C–H (in.p)	M–N	M–N$_{ring}$	M–X
APH	3360 vs 3300 vs 3205 vs	2520 vs 2460 vs 2375 vs	1640 vs	1235 vs	1579 vs	1149 vs	995 m	620 m	408 m			
Pd(APH)Cl$_2$	3330 vs 3240 vs 3190 vs		1620 s		1590 vs	1162 vs	1038 m	662 w	425 m	410 m	270 m 267 sh	370 sh 350 vs
Pd(BPH)Br$_2$	3325 s 3240 s 3180 s	2500 s 2380 s 2340 s	1620 vs		1589 vs	1165 vs	1032 m	660 w	426 m	400 m	272 sh 269 m	284 m 280 w
BPH	3380 s 3290 s 3202 s	2522 s 2460 s 2362 s	1640 vs	1238 vs	1565 vs	1151 m	990 s	625 m	407 m			
Pd(BPH)Cl$_2$	3340 s 3260 s 3200 w		1598 vs		1580 vs	1170 w	1033 s	661 m	430 m	390 m 372 m	275 s 273 sh	350 sh 330 vs
Pd(BPH)Br$_2$	3340 s 3250 s 3200 sh		1600 s		1578 s	1168 w	1030 s	657 m	428 m	400 m 387 m	273 s 269 s	282 s 263 s

Infrared Spectra

The significant bands observed in the i.r. spectra of the ligands and their complexes are presented in Table I, along with their tentative assignments. In APH, the NH stretching frequencies occur at 3358, 3298 and 3182 cm^{-1} while in BPH they occur at 3355, 3281 and 3190 cm^{-1}. The complexes of APH show N–H stretching frequencies in the regions 3330–3325, 3250–3240 and 3205–3190 cm^{-1}. This reduction in the observed value of ν(NH_2) is thus not as large as expected if coordination of the NH_2 nitrogen atom occurs; it is indicative however of the presence of intermolecular hydrogen bonding of the NH protons with the bonded anions.[5]

The ν(C=N) stretching vibrations[6] observed at 1579 cm^{-1} (APH) and 1560 cm^{-1} (BPH) in the spectra of the free ligands are shifted to higher frequencies in the spectra of the complexes suggesting coordination through the nitrogen atom of the azomethine group.[1,7,8] The increase in ν(NN) in the spectra of complexes is again indicative of coordination from one of the nitrogen atoms of the N–N fragment.[1,9]

Finally, the bonding of the pyridine ring nitrogen to palladium(II) is suggested by the shifts in a number of bands, namely the stretching vibrations of the pyridine ring, and the in-plane and out-of-plane bending modes of the pyridine ring. The ν(C=N) and ν(C=C) stretching vibrations are shifted to higher energy by 20 cm^{-1} while in-plane and out-of-plane vibrations are shifted to higher energy by 20–40 cm^{-1} confirming bonding by the pyridine nitrogen.[10] The ring breathing frequencies in APH and BPH are located at 995 cm^{-1} and 990 cm^{-1} respectively and shift to higher frequencies upon complex formation.[11,12]

The assignment of bands in the region 500–200 cm^{-1} is very helpful in formulating and deducing the stereochemistry of the complexes. The ν(M–N) stretching frequencies for azomethine nitrogen are usually observed in complexes at 390–410 cm^{-1}.[9] We thus assign the new bands in the 390–400 cm^{-1} region in our complexes to ν(Pd–N) (methylene nitrogen atom). The bands at 275–267 cm^{-1} may be assigned to ν(Pd–N_{ring}), where N refers to the coordinated pyridine nitrogen atom.[11] The i.r. spectra also display strong bands at 370, 350 and 289, 260 cm^{-1} for the chloro and bromo complexes, respectively. The presence of two ν(Pd–X) vibrations in each spectrum confirms their cis structures. The ν(Pd–X) frequencies are also consistent with terminal rather than bridging halogens.

Proton Magnetic Resonance Spectra

The ^{1}H NMR spectrum of the ligand APH in d_6-DMSO shows a complex of peaks at δ 7.30, 7.78, 7.85 and 8.60 ppm downfield from TMS assigned to the pyridine protons, a sharp singlet at 6.87 ppm assigned to the –NH_2 protons and another sharp singlet at 2.23 ppm assigned to the –CH_3 group protons; the integrations of the signals were in the ratio 4 : 2 : 3. In the ^{1}H NMR spectra of the diamagnetic Pd(APH)X_2 complexes in d_6-DMSO the signals of the C_5H_4N and –NH_2 hydrogen atoms shift *ca* 1.0 and 1.1 ppm, respectively, downfield compared with those of free ligand, while the CH_3 proton resonances shift slightly (*ca* 0.3 ppm) downfield compared with those of the free ligand. The integrations of these three groups of peaks is again 4 : 2 : 3.

The spectrum of BPH shows a complex of peaks between δ 7.14 and 8.40 ppm downfield from TMS assigned to the pyridine and benzene protons and a sharp singlet at 6.57 ppm assigned to the –NH_2 protons. The integrations of these signals were in the ratio 9 : 2. In the ^1H NMR spectra of the diamagnetic complexes of BPH the signals of the C_5H_4N, C_6H_5 and $-NH_2$ hydrogen atoms shift *ca* 1.0 and 1.1 ppm, respectively, downfield compared with those of the free ligand.

The protons of the amino groups of the hydrazones exhibit characteristic downfield shifts by *ca* 1.1 ppm in all the complexes indicating protonation and/or coordination.[13] The spectra of these complexes in DMSO thus clearly suggest coordination from both the amino nitrogen atom and pyridine nitrogen atom.[14]

TABLE II

Proton chemical shifts[a] (δ in p.p.m., downfield from $SiMe_4$) of free and complexed hydrazones.

Compound	$C\text{–}CH_3$	$N\text{–}NH_2$	$C_5H_4N + C_5H_5$ (ring and benzene protons)
APH	2.23	6.78	7.3–8.6[b]
$Pd(APH)Cl_2$	2.58	7.84	8.2–9.1[b]
$Pd(APH)Br_2$	2.44	7.72	8.3–9.2[b]
BPH		6.57	7.1–8.4[c]
$Pd(BPH)Cl_2$		7.68	6.9–9.1[c]
$Pd(BPH)Br_2$		7.70	6.9–9.1[c]

[a] All the spectra were recorded in d_6-DMSO solution. [b] These signals integrate for four protons. [c] These signals integrate for nine protons.

TABLE III

Electronic spectral data and molar conductivities of the Pd(II) complexes.

	Electronic spectra			
Compound	Solid State (D.R.) energy, cm^{-1}	Solution (DMF) energy, cm^{-1} (ε, $l\,cm^{-1}mol^{-1}$)	Assignment	Λ_m ($ohm^{-1}cm^2mol^{-1}$)
$Pd(APH)Cl_2$	23,720 sh	22,100 (600)	$^1A_{1g} \rightarrow {}^1E_g$	12.1
	25,640 sh			
	28,570	29,900 (7,000)	C.T	
		37,450 (14,500)	$n \rightarrow \pi^*$	
$Pd(APH)Br_2$	22,730 sh	22,600 (650)	$^1A_{1g} \rightarrow {}^1E_g$	4.6
	25,220			
	28,300	29,895 (7,900)	C.T	
		37,037 (14,300)	$n \rightarrow \pi^*$	
APH		35,090 (10,000)	$n \rightarrow \pi^*$	
$Pd(BPH)Cl_2$	21,060 sh	21,980 (700)	$^1A_{1g} \rightarrow {}^1E_g$	3.6
	24,800			
	26,550 sh	29,330 (6,250)	C.T	
		36,830 (12,500)	$n \rightarrow \pi^*$	
$Pd(BPH)Br_2$	23,630 sh	21,980 (750)	$^1A_{1g} \rightarrow {}^1E_g$	8.2
	26,320			
	27,650 sh	29,850 (7,500)	C.T	
		36,968 (14,500)	$n \rightarrow \pi^*$	
BPH		35,400 (12,000)	$n \rightarrow \pi^*$	

Electronic Spectra

The electronic spectral data for the complexes and the ligands and the assignments of the observed bands[15] are given in Table III. 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. Strong charge transfer transitions may interfere and prevent the observation of all the expected bands. The band at 37,000 cm^{-1} is assigned to the $n \rightarrow \pi^*$ transition[16] while the band at 30,000 cm^{-1} is assigned to a charge transfer transition ($M \rightarrow L$).[17]

Spectral Properties of the Green Complex

Beside the bands of the i.r. spectrum of the complex Pd(APH)Cl_2 (Table I), new bands appear in the green complex at 1540 w, 1520 w, 1468 m, 1458 m, 1335 s, 1249 s, 1136 s cm^{-1} and the band at 1620 cm^{-1} is split.

In addition to the absorption characterizing the ligand, the visible spectrum in the solid state of this compound displays a broad transition centered at 13,100 cm^{-1} and a second transition at 16,220 cm^{-1}. These bands may be due to formally forbidden d–d transitions, but gain intensity by vibrational perturbation and by borrowing from the intense allowed bands. The spectrum of the green compound is similar to those of other platinum blues.[17,18] In dimethylformamide solution, the green complex gives an initially green solution which becomes light brown. The visible spectrum of this solution is essentially identical to that observed in the other diamagnetic complexes Pd(APH)X_2, showing that the electronic nature of the green compound is strongly altered upon dissolution.

E.s.r. signals are observed for the green complex in the solid state. A strong absorption is attributed to the perpendicular component $g_\perp = 2.03$ and a weaker one to the parallel component $g_\parallel = 1.95$. The e.s.r. spectrum of PdAPH is similar to those of other blue compounds with $g_\perp > 2 > g_\parallel$.

We thus report *a palladium analogue of the platinum blues*. I.r., vis and e.s.r. data are consistent with a bidentate ligand and oxidized metal centres.

CONCLUSIONS

In the solid cis-planar complexes $PdLX_2$ (X = Cl, Br; L = APH, BPH,), APH and BPH act as bidentate chelates bonding through the pyridine and methylene nitrogen atoms.

^1H NMR data obtained for the diamagnetic complexes in d_6-DMSO solution suggest a different coordination mode in which APH and BPH act as bidentate chelates and appear to coordinate *via* both the pyridine and amino group nitrogen atoms.

REFERENCES

1. D. Kovala-Demertzi and D. Nicholls, *Inorg. Chim. Acta*, **73**, 37 (1983).
2. D. Kovala-Demertzi, J.M. Tsangaris, H.O. Desseyn and B.J. Van der Veken, *Bull. Soc. Chim. Belg.*, **96**, 17 (1987).

3. D. Kovala-Demertzi, N. Hadjiliadis and J.M. Tsangaris, *J. Less. Comm. Metals*, **115**, 1 (1986).
4. D. Kovala-Demertzi, J.M. Tsangaris and N. Hadjiliadis, *Trans. Met. Chem.*, **8**, 140 (1983).
5. P. Souza, J.A. Carcia Vazquez and J.R. Masaguer, *Trans. Met. Chem.*, **9**, 318 (1984).
6. W.C. Harris, F.L. Glenn and L.B. Knight, *Spectrochim. Acta*. **31A**, 11 (1975).
7. C.N. Elgy and D. Nicholls, *J. Inorg. Nucl. Chem.*, **43**, 2025 (1981).
8. G.K. Sandhu and S.S. Sandby, *Synth. React. Inorg. Met. Org. Chem.*, **12**, 215 (1982).
9. S.K. Jain, B.S. Garg and Y.K. Bhoon, *Spectrochim. Acta*, **42A**, 9, 959 (1986).
10. R.J.H. Clark and C.S. Williams, *Inorg. Chem.*, **4**, 350 (1965).
11. C.F. Bell and D.R. Rose, *Inorg. Chem.*, **8** 161 (1969).
12. A. El-Dissouky and A. Kasem, *Trans. Met. Chem.*, **11** 449 (1986).
13. V.G. Fazakerley and R.K. Koch, *Inorg. Chim. Acta.*, **35**, 13 (1979); C.G. Vandralingen and J. Reedifk, *J. Inorg. Nucl. Chem.*, **41**, 1935 (1979); V. Ravindar, P. Lingalah and K.V. Reddy, *Inorg. Chim. Acta.*, **87**, 35 (1984).
14. M. Nonoyama, *Trans. Met. Chem.*, **7**, 282 (1982).
15. A.B.P. Lever, "Inorganic Electronic Spectroscopy", (Elsevier, New York, 1984).
16. A. Kaito, M. Hatano and A. Tafiri, *J. Amer. Chem. Soc.*, **99**, 5241 (1984); D. Kovala-Demertzi and J.M. Tsangaris, *Inorg. Chim. Acta.*, **125**, L31 (1986).
17. A.A. Zaki, C.A. McAuliffe, M.E. Friedman, W.E. Hill and H.H. Kohl, *Inorg. Chim. Acta*, **69**, 93 (1983).
18. F.A. Arrizabalanga, P. Castan and J.P. Laurent, *Inorg. Chim. Acta*, **92**, 203 (1984).