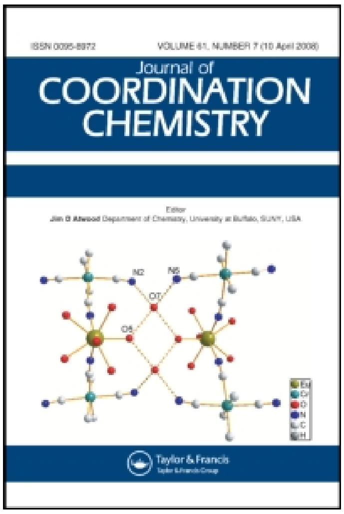

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Spectroscopic and thermal studies of some Palladium complexes with certain Heterocyclic Nitrogen ligands

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To cite this Article Ramadan, Ramadan M. , El-Medani, Samir M. , Ali, Omyma A. M. and Mohamed, Hassan A.(2004) 'Spectroscopic and thermal studies of some Palladium complexes with certain Heterocyclic Nitrogen ligands', Journal of Coordination Chemistry, 57: 5, 373 — 379

To link to this Article: DOI: 10.1080/00958970410001680363

URL: http://dx.doi.org/10.1080/00958970410001680363

J. Coord. Chem., Vol. 57, No. 5, 20 March 2004, pp. 373–379

SPECTROSCOPIC AND THERMAL STUDIES OF SOME PALLADIUM COMPLEXES WITH CERTAIN HETEROCYCLIC NITROGEN LIGANDS

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(Received 24 June 2003; Revised 8 September 2003; In final form 9 February 2004)

Mono- and binuclear palladium complexes were isolated from reactions of $[PdCl_4]^{2-}$ with heterocyclic nitrogen donor ligands depending on the type of ligand. Bidentate ligands L–L, where L–L = 2-(2′-pyridyl)-benzimidazole (PBI), 2-pyrazinecarboxylic acid (PC) and 2-pyrazinecarboxamide (PCA) gave the monosubstituted $[Pd(L\text{-}L)Cl_2]$ complex. Binuclear palladium complexes $[Pd(L)Cl_2]_2$ were obtained from reactions with the monodentate ligands 2-aminothiazole (AT) or 2-aminobenzimidazole (ABI). Elemental analyses and spectroscopic studies of the reported complexes allowed structures to be proposed. The thermal properties of the complexes were also investigated by thermogravimetric techniques.

Keywords: Palladium; Nitrogen ligands; Complexes; Spectra; Thermal analysis

INTRODUCTION

Interest in transition metal complexes of heterocyclic compounds containing nitrogen as a donor atom such as pyridines, bi- and polypyridines, azines and their derivatives has been stimulated by their electrochemical properties, magnetic coupling interactions, and catalytic and photocatalytic processes [1–5]. In the last decade, complexes of azines, especially those of pyrazines, such as 2,3-bis(2′-pyridyl)pyrazine, 2,3-bis(2′-pyridyl)quinoxaline and 2-pyrazinecarboxamide and their derivatives, have found applications in the fields of photochemistry and catalysis [6–9]. On the other hand, the chemistry of Pd(II) and Pt(II), and their applications in catalysis, is versatile [10,11]. Many azine derivatives have a vital role in biology. Some azines act as anticancer or antiallergic reagents [12,13]. Coordination compounds of Pd(II) and Pt(II) have found application

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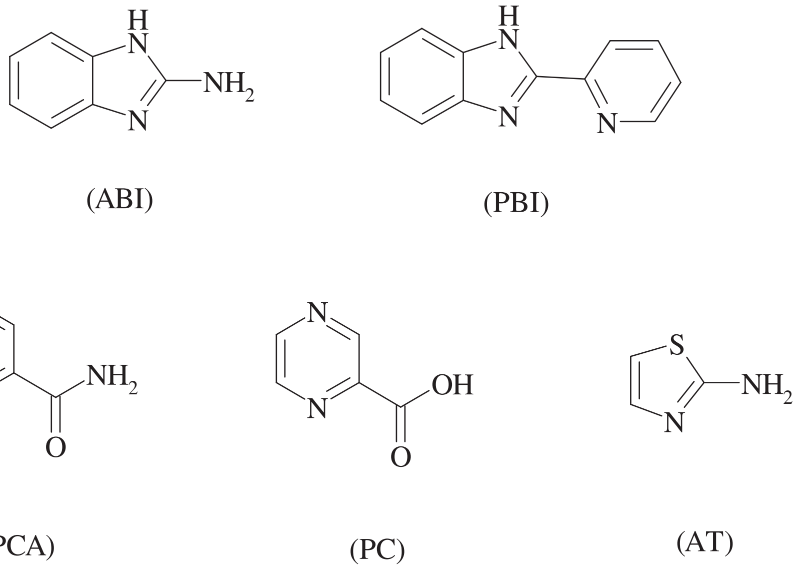
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001680363



SCHEME 1 The molecular structures of ligands.

as antitumor reagents [14]. Cisplatin analogs of some benzimidazole derivatives as well as their equivalent palladium compounds have been characterized by X-ray structure analysis. The antitumor activities of the corresponding platinum compounds were compared to the activity of cisplatin in one fibroblast and eight brain tumor cell lines [15]. Also, complexes of the type [M(bpy)(L-L)]NO_3 [M = Pd(II) or Pt(II), bpy = 2,2′-bipyridine, L–L = anion of 2-pyridinecarboxylic acid or 2-pyrazinecarboxylic acid] have been found to bind calf thymus DNA, possibly through hydrogen bonding [16].

Mono- and binuclear Pd(II) and Pt(II) complexes are known. For example, the [M(dithiocarbamato)(L)]Cl complexes (M = Pd or Pt, L = methioninol) have been prepared by reacting methioninol with the appropriate $[M(dithiocarbamato)Cl]_n$ complex in a 1 : 1 molar ratio. At a 1 : 2 molar ratio, the binuclear species $[M_2(dithiocarbamato)_2(L)Cl_2]$ were obtained [17]. Mononuclear complexes with the general formula $M(L)_2Cl_2$ (M = Pd or Pt, L = functionalized nitrogen-containing tertiary phosphine ligands namely *o*-, *m*- and *p*-dimethylphosphinyl-methylene-oxyaniline) have been reported [18]. Vibrational studies, physical and analytical data indicated that the ligands in the complexes coordinated through the amino group to form square-planar platinum and palladium complexes.

Our interest in the coordination chemistry of heterocyclic ligands containing nitrogen atoms such as pyrazines and imidazoles [19–22] has prompted us to investigate the reactions of Pd(II) with some selected heterocyclic ligands (Scheme 1).

EXPERIMENTAL

Materials

$PdCl_2$, 2-(2′-pyridyl)benzimidazole (PBI), 2-aminobenzimidazole (ABI), 2-pyrazinecarboxylic acid (PC), 2-pyrazinecarboxamide (PCA) and 2-aminothiazole (AT) were

TABLE I Elemental analysis, color, yield and mass spectrometry data for the palladium complexes

Complex	*Color*	*Yield* (%)	*Found* (*Calcd.*) (%)			*Mass Spectrometry*	
			C	*H*	*N*	*Mol. Wt*	*m/z*
$[Pd(PBI)Cl_2]\cdot 3H_2O$	Yellow	79	33.7 (33.8)	3.6 (3.5)	9.7 (9.9)	426.58	373 $[P-3H_2O]^+$
$[Pd(PC)Cl_2]\cdot 5H_2O$	Yellowish brown	84	15.1 (15.3)	3.9 (3.6)	7.0 (7.2)	391.48	302 $[P-5H_2O]^+$
$[Pd(PCA)Cl_2]\cdot 2H_2O$	Pale brown	92	17.5 (17.8)	2.9 (2.7)	12.8 (12.5)	336.47	301 $[P-3H_2O]^+$
$[Pd(AT)Cl_2]_2\cdot H_2O$	Dark brown	76	12.4 (12.6)	2.0 (1.8)	9.6 (9.8)	573.73	456 $[P-H_2O-AT]^+$
$[Pd(ABI)Cl_2]_2\cdot H_2O$	Dark brown	77	26.1 (26.3)	2.4 (2.5)	12.9 (13.2)	638.98	604 $[P-H_2O-NH_3]^+$

purchased from Aldrich. $[PdCl_4]^{2-}$ solutions were prepared by heating a solution of 0.083 g $PdCl_2$ (0.50 mmol) in 50 cm^3 H_2O and 0.5 cm^3 HCl (37%) at 70°C. The clear solution of $[PdCl_4]^{2-}$ was filtered and left to cool.

Instruments

IR measurements (KBr pellets) were carried out on a Shimadzu 8000 FT-IR spectrophotometer. NMR measurements were performed on a Varian-Mercury 300 MHz spectrometer. Samples were dissolved in $(CD_3)_2SO$ with TMS as internal reference. Thermogravimetric analyses (TG and DTG) were carried out under N_2 atmosphere with a heating rate of 10°C/min. using a Shimadzu DT-50 thermal analyzer. The complexes were also characterized by elemental analysis (Perkin-Elmer 2400 CHN instrument) and mass spectroscopy (Finnigan MAT SSQ 7000). Table I gives the elemental analysis, color, yield and mass spectrometric data for the complexes.

Syntheses of Complexes

A ligand solution (0.5 mmol dissolved in minimum ethanol) was added dropwise with constant stirring to a $[PdCl_4]^{2-}$ solution (0.5 mmol). Immediate precipitation of the complexes occurred. (Complexes of AT and ABI ligands required heating (60°C) to precipitate). The solid was filtered off, washed by ethanol and then recrystallized from hot ethanol. The complexes were dried on a vacuum line.

RESULTS AND DISCUSSION

Depending on the ligand, mono- or binuclear palladium complexes were isolated from the reactions of $[PdCl_4]^{2-}$ solution with heterocyclic nitrogen donor ligands in ethanol [Eqs. (1) and (2), Scheme 1].

$$[PdCl_4]^{2-} + L-L \rightarrow [Pd(L-L)Cl_2] + 2Cl^- \qquad (1)$$

$$L-L = \text{PBI, PC and PCA}$$

$$2[PdCl_4]^{2-} + 2L \rightarrow [Pd(L)Cl_2]_2 + 4Cl^- \qquad (2)$$

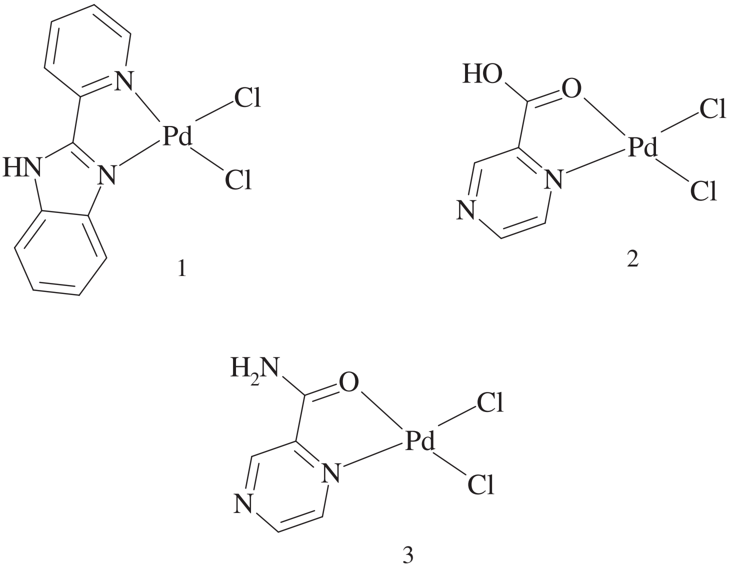
$$L = \text{AT and ABI}$$

TABLE II Important IR and NMR data for ligands and their palladium complex

Compound	*IR data* (cm^{-1})[a]			^1H *NMR data* (ppm)[b]
	$\nu(NH)$	$\nu(C{=}N)$	$\nu(C{=}C)$	
PBI[c]	3061(s)	1600(m) 1568(w)	1462(m) 1445(s)	12.70(s), 8.48(d), 8.15(d), 7.61(m), 7.12(m)
$[Pd(PBI)Cl_2] \cdot 3H_2O$[d]	3100(m)	1612(m) 1520(s)	1482(m) 1458(s)	12.73(s), 8.53(d), 8.18(d), 7.62(m), 7.15(m)
PC[e]	3062(m)	1666(s)	1528(m)	9.29(d), 8.96(s), 8.90(d),
$[Pd(PC)Cl_2] \cdot 5H_2O$	–	1666(s)	1460(m)	9.12(d), 9.04(d), 8.74(b,s)
PCA[f]	3410(s) 3287(m) 3163(s)	1612(s) 1590(m)	1528(m)	9.28(d), 8.95(d), 8.81(dd), 8.42(b,s), 8.02(b,s)
$[Pd(PCA)Cl_2] \cdot 2H_2O$	3433(s) 3186(m) 3071(m)	1630(m) 1589(s)	1435(m)	9.20(d), 9.02(d), 8.83(dd), 8.23(b,s), 7.86(b,s)
AT	3410(s) 3294(s) 3148(m)	1628(s)	1489(s)	7.39 (b,s), 6.90(d), 6.45 (d)
$[Pd(AT)Cl_2]_2 \cdot H_2O$	3395(s) 3287(m) 3225(w)	1600(m)	1512(s)	7.85(b,s), 7.21(b,s), 7.06(d), 6.66(d)
ABI	3387(s) 3310(s) 3055(m)	1651(s) 1558(s)	1458(s)	10.83(b,s), 7.12(m), 6.87(m), 6.15(b,s)
$[Pd(ABI)Cl_2]_2 \cdot H_2O$	3310(s) 3155(m)	1666(s)	1474(m)	7.12(m), 6.86(m), 6.22(b,s)

[a] s, strong; m, medium; w, weak. [b] s, singlet; d, doublet; m, multiplet. [c] $\delta(py) = 620$–$540\,cm^{-1}$. [d] $\delta(py) = 687$–$579\,cm^{-1}$. [e] $\nu(OH) = 3425\,cm^{-1}$, $\nu(C{=}O) = 1720\,cm^{-1}$. [f] $\nu(C{=}O) = 1713\,cm^{-1}$.

Interaction of bidentate ligands L–L [L–L = 2-(2′-pyridyl)-benzimidazole (PBI), 2-pyrazinecarboxylic acid (PC) and 2-pyrazinecarboxamide (PCA)] with $[PdCl_4]^{2-}$ resulted in immediate precipitation of the monosubstituted derivative $[Pd(L\text{-}L)Cl_2]$. Elemental analysis and mass spectral data confirmed the proposed formula (Table I). The PBI derivative was crystallized with three water molecules, the PC derivative isolated with five H_2O, while the PCA species separated with two H_2O molecules. The number of waters of crystallization was determined from the TG analysis (*vide infra*). The IR spectra of the complexes showed the characteristic bands of the ligands due to functional groups such as NH, C=N, C=O and C=C with the appropriate shifts (Table II). The ^1H NMR spectra of the complexes also displayed signals due to the different proton nuclei in ligands (Table II). The existence of the band due to the NH group in the IR spectrum of the $[Pd(PBI)Cl_2]$ complex, which was also confirmed by NMR, indicated that coordination of ligand occurred without proton displacement. For the $[Pd(PC)Cl_2]$ complex, no NMR signal was observed for the OH of the carboxylic moiety. However, this signal was not observed in the spectrum of the ligand itself. Reactions of $M(CO)_6$ (M = Mo and W) with PBI resulted in the formation of $[M(CO)_4(PBI)]$ complexes [23]. Also, reactions of $[M_3(CO)_{12}]$ (M = Ru and Os) with PBI gave $[Ru(CO)_3(PBI)]$ and $[Os(CO)_2(PBI)_2]$ [21]. Spectroscopic studies of these complexes showed that the ligand occupied equatorial positions without proton displacement. Interaction of $[M_3(CO)_{12}]$ (M = Ru and Os) with either PCA or PC gave the tricarbonyl derivatives $[M(CO)_3(L\text{-}L)]$. The two ligands are bidentate and occupied equatorial sites [24]. Scheme 2 gives the proposed structures of the palladium complexes

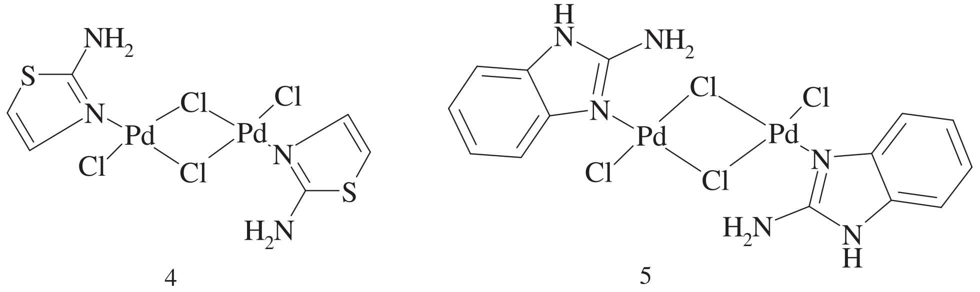


SCHEME 2 The palladium complexes of the bidentate ligands.

(**1**–**3**). The structure of **1** was previously determined by crystal structure analysis, which showed that the PBI ligand is bidentate and the two chlorines are *cis*.

In order to gain more insight into the structure and thermal stability of the palladium complexes, thermal studies on the solid complexes using thermogravimetric (TG) and differential thermogravimetric (DTG) techniques were performed. The TG and DTG plots of the mononuclear complexes exhibited well-defined and non-overlapping decomposition steps. The TG plot of the [Pd(PBI)Cl_2] complex showed that it decomposed in a single step. This occurred in the 690–790 K temperature range with a net weight loss of 58.2%. The percentage weight loss was consistent with the elimination of three H_2O molecules and the PBI group. A metal-containing residue of $PdCl_2$ was left (41.8%). Investigation of the [Pd(PC)Cl_2] complex showed that the TG and DTG plots exhibited two well-defined and non-overlapping decomposition steps. The first decomposition step occurred in the 505–585 K range with a net weight loss of 23.2%, which corresponds to the elimination of five H_2O molecules. The percentage weight loss in the second stage (31.5%) occurred in the 585–705 K range and is consistent with the elimination of the pyrazinecarboxamide molecule. The TG plot of the [Pd(PCA)Cl_2] complex showed a similar decomposition pattern to that of the [Pd(PC)Cl_2] complex with two decomposition steps in the temperature range 496–718 K with a total net weight loss of 47.6%. The first decomposition step occurred at 496–572 K (weight loss 10.6%) corresponding to elimination of two H_2O molecules. The second step, a loss of 37.0%, was consistent with elimination of the PCA ligand leaving a metal-containing residue, $PdCl_2$.

The binuclear palladium complexes [Pd(L)Cl_2]$_2$ [L = 2-aminothiazole (AT) or 2-aminobenzimidazole (ABI)] were obtained from reactions of ethanolic solutions of $[PdCl_4]^{2-}$ with L at elevated temperature. The mass spectral data of the two complexes, Table I, indicated dimers. Both complexes crystallized with a water molecule/mol of compound as determined from TG analysis. The IR and ^{1}H NMR spectra of the two complexes displayed the appropriate shifts due to complex formation (Table II).



SCHEME 3 The palladium complexes of the monodentate ligands.

As expected from the structure of the two ligands, the ν(C=N) band in the IR spectrum of $[Pd(AT)Cl_2]_2$ complex was shifted to lower frequency while it was shifted to higher frequency in the case of $[Pd(ABI)Cl_2]_2$. For example, the IR spectra of the 1 : 1 molecular adducts derived from 2-aminobenzimidazole as a donor and either trinitrobenzene or picric acid as an acceptor showed that the ν(C=N) bands were shifted to higher frequency [25]. On the other hand, similar charge-transfer complexes with 2-aminothiazole exhibited shifts to lower frequencies [26]. The proposed structures of the two palladium complexes (**4**, **5**) are given in Scheme 3.

Thermal studies of the two binuclear palladium complexes provided further insight into the proposed structures as well as their thermal stability. The TG plot of the $[Pd(AT)Cl_2]_2$ complex showed three decomposition steps in the temperature range 442–763 K. The first two steps were overlapping with unresolved peaks. These two peaks occurred at 442–582 K with a net weight loss of 19.9%, due to elimination of a water molecule and an AT ligand. The third decomposition step (660–762 K, 17.3%) could be due to elimination of the second AT ligand. Thermal decomposition of the $[Pd(ABI)Cl_2]_2$ complex exhibited a similar pattern to that observed for $[Pd(AT)Cl_2]_2$. However, a different thermal decomposition mechanism occurred. Two decomposition peaks are observed in the temperature range 430–792 K with a net weight loss of 44.2%. The first decomposition peak (430–492 K, 8.1%) could be due to elimination of a water molecule and two NH_3 groups. The second decomposition peak, which occurred at 500–792 K with a net weight loss of 36.1%, corresponded to material decomposition to leave a $PdCl_2$ residue (55.8%).

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