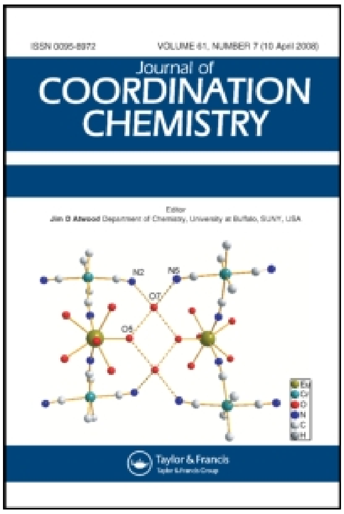

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Spyridoula Kasselouri[a]
[a] Department of Chemistry, Physics and Material Technology, Technological Institute of Athens, Egaleo, Greece

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF COMPLEXES OF 1,2-*BIS*-(2-PYRIDYLMETHYLENEIMINO)BENZENE WITH PLATINUM(II) AND PALLADIUM(II)

SPYRIDOULA KASSELOURI

Department of Chemistry, Physics and Material Technology, Technological Institute of Athens, 12210 Egaleo, Greece

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The synthesis and characterization of new square planar platinum and palladium complexes of general formula $[ML]Cl_2$ [M = Pt(II) and Pd(II), L = 1,2-*bis*(2-pyridylmethyleneimino)benzene] are reported. By using high resolution ^1H NMR spectroscopy it has been shown that the ligand L acts as a tetradentate through all four nitrogen atoms and prefers the *syn* orientation for both pyridine rings.

Keywords: Schiff base; platinum; palladium; ^1H NMR; *syn syn* conformation

INTRODUCTION

Chelate compounds of N_4 Schiff bases are models for metal enzymes and group-B vitamins[1,2]. Furthermore, these compounds have remarkable fungicidal and antimicrobial activity[3] and find applications in organic synthesis and catalysis (*i.e.*, palladium compounds[4]); they also form metal complexes with novel structural types[5].

Such Schiff bases as free ligands, are not always planar. The energetically preferred conformation is such that the aryl moiety is twisted along the C-N bond, while the pyridine groups are practically coplanar with the azomethine group[6,7] (Figure 1). The orientation of the pyridyl groups of 1,2-*bis*-(2-pyridylmethyleneimino)benzene (L) enables the existence of three different conformational isomers, *syn syn*, *syn anti* and *anti anti* in statistic ratio 1:2:1 (Figure 1). The present work is concerned with the synthesis, characterization

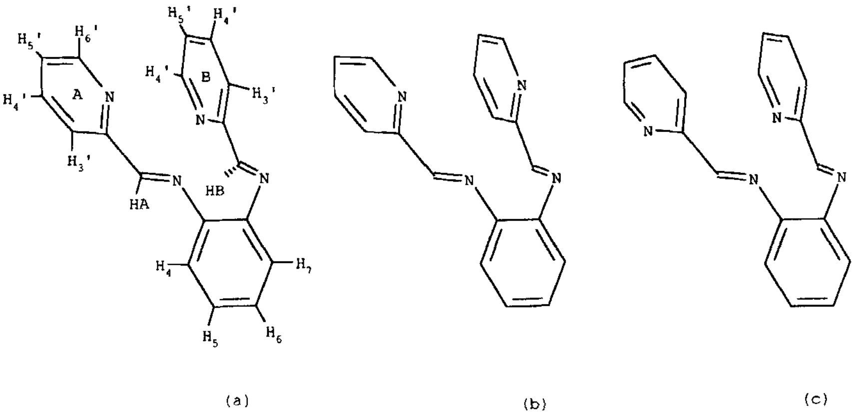

FIGURE 1 The *syn anti* (a), *syn syn* (b) and *anti anti* (c) conformations of the ligand L. In *syn anti* conformation (a), the differences between the pyridine groups A and B, are denoted, with respect to the text.

and NMR studies of the novel compounds [PdL]Cl$_2$ and [PtL]Cl$_2$ as models for the *syn syn* conformation of the acyclic, neutral, N$_4$-chelate ligand L.

EXPERIMENTAL

Synthesis

Ligand L was obtained from the condensation of 1,2-phenylenediamine with 2-pyridyl carboxaldehyde in *n*-PrOH, as described earlier[8].

[PdL]Cl$_2$

To a solution of Na$_2$PdCl$_4$ (1 mmol) in MeOH (20 cm^3), 1 mmol of L dissolved in MeOH (10 cm^3) was added. The resulting solution was stirred at room temperature and soon began to deposit a yellow precipitate. Stirring was continued for 2h when the precipitate was collected by filtration, washed with cold MeOH and Et$_2$O and dried *in vacuo* over silica gel. The yield was *ca* 60%. *Anal.* Calcd. for $C_{18}N_4H_{14}PdCl$(%): C, 50.5; N, 13.1; H, 3.3; Pd, 24.9; Cl, 8.3. Found: C, 50.3; N, 13.4; H, 3.3; Pd, 24.7; Cl, 8.6; Λ_M = 160 S cm^{-1} mol^{-1}.

[PtL]Cl$_2$

To a solution of K$_2$PtCl$_4$ (0.4 mmol) in a water-methanol mixture 1:1 (30 cm^3), 0.4 mmol of L dissolved in MeOH (5 cm^3) were added. The resulting solution

TABLE I Diagnostic IR Bands (cm^{-1}) for L and its Metal Complexes.

Compound	*ν (C=N)$_{Schiff}$*	*δ (Py)*	*γ (Py)*	*ν (M-N)$_{Schiff}$*	*ν (M-N)$_{ring}$*
[a]L	1618 m	613 m	408 m		
$[PdL]Cl_2$	1642 sh	636 m	433 m	472 w	272 w
				462 sh	278 w
$[PtL]Cl_2$	1651 m	640 w	438 m	479 w	268 w
				473 w	274 w

[a]Taken from ref. 8; abbreviations: γ = out of plane deformation; δ = in plane deformation; m = medium; sh = shoulder; w = weak; ν = stretching; Py = pyridine rings.

was refluxed for 24h and a pale yellow precipitate was deposited after cooling to room temperature. The precipitate was collected by filtration, washed with a cold mixture of water methanol (1:1) and dried *in vacuo* over P_4O_{10}. The yield was *ca* 55%. *Anal.* Calcd. for $C_{18}N_4H_{14}PtCl$(%): C, 41.8; N, 10.8; H, 2.7; Pt, 37.7; Cl, 6.9. Found: C, 42.1; N, 10.6; H, 2.9; Pt, 37.6; Cl, 6.8; Λ_M = 172 S cm^{-1} mol^{-1}.

Physical Measurements

Elemental analysis were carried out using published methods[9]. The electrical conductivity measurements were performed using a E365B Conductscope (Metrohm Ltd) for *ca* 10^{-3} solutions at 25°C in DMF. IR spectra in CsBr pellets were recorded on a Perkin Elmer 783 spectrometer (4000-200 cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Brucker AM 400 WB spectrometer in DMSO-d_6. The DMSO-d_6 solvent resonances were used as chemical shift references for ^1H (CH_3 = 2.62 ppm) spectra.

RESULTS AND DISCUSSION

The complexes were obtained as microcrystalline solids which were partially soluble in hot MeOH and MeCN and soluble in cold DMF and DMSO. Λ_M values for both complexes are in accord with them being 1:2 electrolytes[10].

Table I gives some diagnostic IR bands. Assignments have been made from the literature[8,11-13] and by comparing the complex spectra with that of the free ligand. The band assigned to ν(C=N) in the free ligand shifts upon complexing to higher frequencies for both palladium and platinum complexes. This suggests coordination through the nitrogen atoms of the azomethine group[11-13]. The shift of the characteristic in-plane and out-of-plane deformation bands of the pyridine rings to higher frequencies in both complexes indicates coordination through the

TABLE II ^{1}H NMR chemical shifts (ppm) for L and its metal complexes at 400.13 MHz in DMSO-d_6 at 310 K.

Compound	*H6'A* *H6'B*	*CHA* *CHB*	*H3'A* *H3'B*	*H4'A* *H4'B*	*H5'A* *H5'B*	*H3*	*H6*	*H5*	*H4*
L	8.81 d	8.73 s	8.42 d	8.02 t	7.61 t	7.32 d	6.80 d	7.12 t	6.72 t
	8.82 d	8.62 s	8.21 d	7.42 t	7.62 t				
[PdL]Cl$_2$	9.45 d	10.01 s	8.77 d	8.42 t	8.31 t	7.80 d		7.48 t	
[PtL]Cl$_2$	9.10 d	9.62 s	8.67 d	8.40 t	8.25 t	7.76 d		7.42 t	

d = doublet; s = singlet; t = triplet.

nitrogen atoms of the pyridines[8,13]. The number of ν(M-N)$_{\text{schiff}}$ and ν(M-N)$_{\text{ring}}$ bands is expected to be two for each mode[14,15]. Indeed, two ν(M-N)$_{\text{schiff}}$ and two ν(M-N)$_{\text{ring}}$ bands confirm their *cis* structure. Also, the absence of bands in the region 200-400 cm^{-1}, which can be assigned to MCl stretching frequencies, denotes that L coordinates as a tetradentate.

^{1}H NMR chemical shifts for both the free ligand and the metal complexes are given in Table II. The ^{1}H NMR spectrum of the free ligand at 400 MHz in DMSO-d_6 at 310 K exhibits double resonances for all the protons. Assignments were assisted by resonance decoupling experiments. Two different single resonances, in approximate ratio 1:1, were observed for $H_{2''}$ of the azomethine group, suggesting magnetically nonequivalent environments for these protons (Figure 1). $H_{2''A}$ in the *anti* conformation of pyridine, is close to the nitrogen electrons, while $C_{2''B}$ in the *syn* conformation is close to $C_{3'}$ and as such, should be expected to show a significant difference in chemical shifts. The shift of $H_{2''A}$ to fields lower than $H_{2''B}$, may arise from pure electronegativity, due to the pyridine nitrogen atom.

The appearance of double resonances for all protons confirms the existence of both *syn* and *anti* orientations of the pyridine moieties of the ligand. With increasing or decreasing temperature over a range of 50 K, no significant change was observed in the double resonances. This indicates that there is a significant energy barrier to fast rotation of the pyridine groups around the C-N bond.

In contrast, single resonances appear for both [PdL]Cl$_2$ and [PtL]Cl$_2$ complexes for all protons, indicating that only one isomer of L exists. In both complexes the protons of the 6-pyridyl position, $H_{6'}$, and azomethine group, $H_{2''}$, show a downfield shift compared with the free ligand, and which is much larger in the palladium complex. This suggests coordination through all four nitrogen atoms of the ligand L to the same metal centre, giving L the *syn syn* conformation.

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