Inorganica Chimica Acta, 131 (1987) 253–257

Synthesis and Characterization of Platinum(II) and Palladium(II) Complexes with 2,5-Dimethyl-4-hydroxypyrimidine

A. ADEYEMO*

Department of Chemistry, University of Ibadan, Nigeria

and R. P. RAVAL

Department of Chemistry, Virginia Union University, Richmond, Va., U.S.A.

(Received October 2, 1986; revised February 3, 1987)

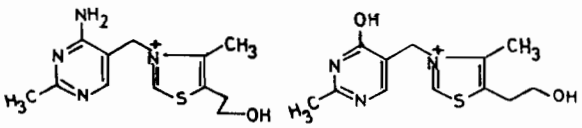
Abstract

The binding of Pt(II) and Pd(II) ions to 4-amino-2,5-dimethyl pyrimidine (ADMPY) has been compared with the binding of these same metal ions to 2,5-dimethyl-4-hydroxy pyrimidine (HDMPY), analogue of ADMPY in which the amino group has been replaced by a hydroxyl group. A brief comparison is made with the corresponding Pt(II) and Pd(II) complexes of thiamine and oxythiamine. In this paper we report the synthesis, elemental analyses, infrared spectral data, proton and carbon-13 nuclear magnetic resonance studies of these new complexes.

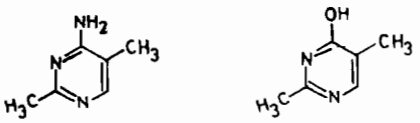
A complete assignment of ^{1}H and ^{13}C NMR spectra resonance is presented for both the ligand and the complexes. The results show that the metallation site is the N-1′ position of the ligand in agreement with earlier works [1–3], however, the chemical shifts observed for this ligand upon complexation are larger than the corresponding chemical shifts observed for the 4-amino-2,5-dimethyl pyrimidine analogue contrary to the thiamine/oxythiamine system.

Introduction

Recently we reported the synthesis and characterization of Pd(II) complexes of 4-amino-2,5-dimethyl pyrimidine [1] where we claimed the N-1′ position of the ligand as the coordination site in agreement with the previous reports [2, 3]. In another paper from our laboratory [4], we reported correlation between ligand basicity and chemical shifts upon metal coordination to thiamine and oxythiamine (structures **I** and **II**). Since then we have been curious as to whether this ligand basicity/chemical shift correlation is unique to the thiamine/oxythiamine system or if it could be extended to some similar systems. A very good example of such a system could be 4-amino-2,5-dimethyl pyrimidine and 2,5-dimethyl-4-hydroxypyrimidine (structures **III** and **IV**).



I **II**



III **IV**

Experimental

Potassium tetrachloroplatinate(II), potassium tetrachloropalladate(II) and deuterated dimethyl sulfoxide were purchased from Aldrich Chemical company and were used without further purification.

Preparation of 2,5-Dimethyl-4-hydroxypyrimidine

Five grams (40.60 mmol) of 4-amino-2,5-dimethyl pyrimidine were dissolved in 150 ml of 6 N HCl and refluxed for 10 h. Having been evaporated to dryness, the residue was dissolved in 80 ml of water. The pH of the resulting solution was then adjusted to 5 and evaporated to dryness. The residue was extracted with chloroform, evaporation of which yielded 92% of 2,5-dimethyl-4-hydroxypyrimidine. The melting point was determined to be 175 ± 0.5 °C [5].

Preparation of Pt(II) and Pd(II) Complexes

The platinum(II) and palladium(II) complexes were prepared as described earlier [1].

Anal. Calc. for $Pt(HDMPY)_2Cl_2 \cdot H_2O$, $C_{12}H_{18}N_4O_3PtCl_2$ (M_r = 532): C, 27.07; H, 3.38; N, 10.53; Cl,

*Author to whom correspondence should be addressed.

0020-1693/87/$3.50

13.33. Found: C, 26.78; H, 3.06; N, 10.47; Cl, 13.21%.

Anal. Calc. for $Pd(HDMPY)_2Cl_2 \cdot H_2O$, $C_{12}H_{18}N_4O_3PdCl_2$ (M_r = 443.3): C, 32.51; H, 4.06; N, 12.63; Cl, 15.99. Found: C, 32.62; H, 3.78; N, 12.61; Cl, 15.78%.

Proton and carbon-13 NMR spectra were run on a Varian FT-80A 20 MHz, using DMSO-d_6 as solvent and TMS as internal reference standard. The infrared spectra were recorded on a Perkin-Elmer IR NO 297 Spectrophotometer, employing KBr pellets with polystyrene as references. The melting points were determined in capillaries and were uncorrected.

Results and Discussions

^1H NMR Spectra

The proton NMR chemical shifts are given in Table I and Fig. 1. The assignments of the resonances are based on previous studies including off-resonance techniques [1, 2, 6]. Three resonances are observed for the free ligand and they were assigned as follows: a singlet at 1.85 ppm is due to 5′-CH_3 while the singlet at 2.20 ppm is ascribed to the 2′-CH_3 signal. The most downfield resonance is unequivocally assigned to the C6′-H proton.

TABLE I. ^1H NMR Chemical Shifts of the Ligand and its Pt(II) and Pd(II) Complexes

Proton	HDMPY	$Pt(HDMPY)_2Cl_2 \cdot H_2O$	$Pd(HDMPY)_2Cl_2 \cdot H_2O$
5′-CH_3	1.85	1.87	1.89
2′-CH_3	2.20	2.94	3.01
C6′-H	7.63	8.00	8.00

In the $Pt(HDMPY)_2Cl_2$ complex, the 5′-CH_3 signal hardly shifted (0.02 ppm), while 2′-CH_3 and C6′-H shifted downfield by 0.74 and 0.37 ppm, respectively. In the $Pd(HDMPY)_2Cl_2$ complex, 5′-CH_3, 2′-CH_3 and C6′-H protons shifted downfield by 0.04, 0.81 and 0.37 ppm, respectively. These downfield chemical shifts in Pt(II) and Pd(II) complexes compared to the free ligand are a strong indication for a N-1′–metal covalent bond. These chemical shifts are comparable to those observed in Pt(II)–nucleoside complexes reported by Kong and Theophanides [7, 8]. These findings are also consistent with the work of Adeyemo *et al.* [3, 9], Adeyemo and Raval [1], Theophanides *et al.* [2] and some other authors [6, 10]. In order to provide a sound argument for our claim that the N-1′ position of the ligand is the coordination site, we have considered other alternative binding sites (N-3′ and/or

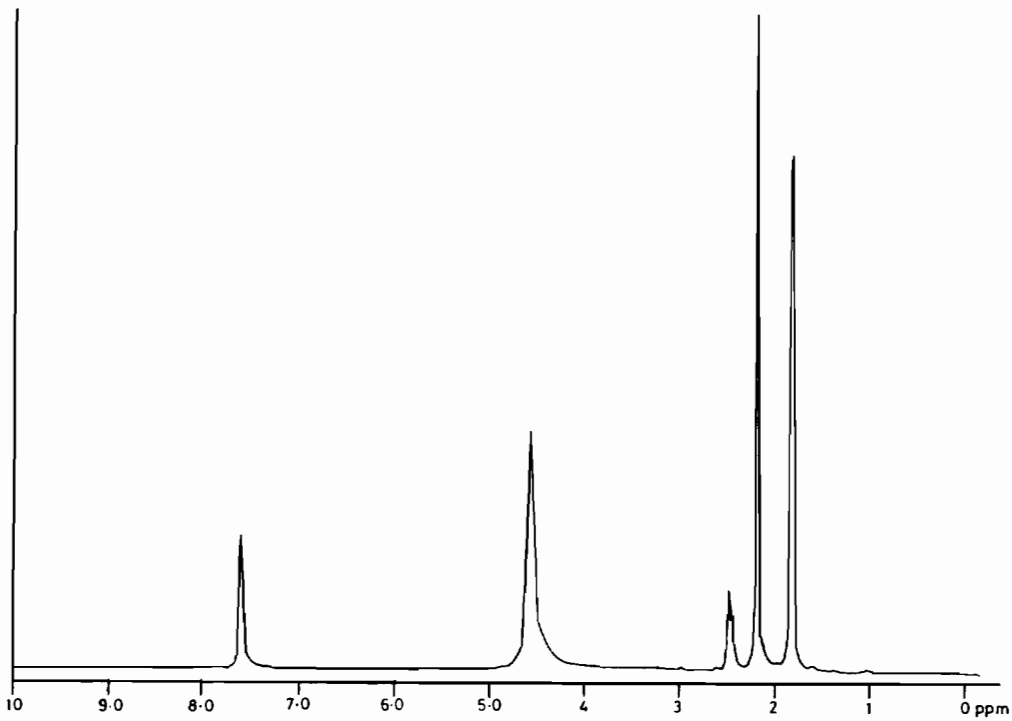


Fig. 1. ^1H NMR spectrum of HDMPY.

C4′-OH). If binding were through the phenolic group, one would expect 5′-CH_3 protons to be shifted downfield by about twice as much as 2′-CH_3 protons since 5′-CH_3 and 2′-CH_3 protons are *ortho* and *meta*, respectively, to the phenolic group. It has been suggested in a paper on Pt(II)–pyridine complexes that the downfield shifts of the *meta* and *para* protons are roughly only half of that of the *ortho* protons [11]. Since our observation is contrary to this hypothesis, we concluded that the phenolic group is not likely to be the coordination site. Another potential donor atom is the N-3′ position of HDMPY. Again, considering N-3′ as the coordination site, one would expect 2′-CH_3 and C4′-CH protons which are *ortho* to this assumed coordination site to be shifted downfield by about twice as much as 5′-CH_3 and C6′-H protons which are *meta* and *para*, respectively, to the N-1′ position. It is interesting to observe that a downfield shift of 0.37 ppm of the C6′-H proton is roughly half the downfield shift of 0.81 ppm of 2′-CH_3 protons. Along the same line of reasoning, one would expect the C4′-OH signal to shift downfield by about twice as much as 5′-CH_3 and C6′-H protons. Unfortunately, we could not observe the C4′-OH signal. Although, 5′-CH_3 protons were observed (0.02 or 0.04 ppm downfield shift), this was not a strong evidence in favour of N-3′ as a possible coordination site.

^{13}C NMR Spectra

The ^{13}C NMR chemical shifts are given in Table II and Fig. 2. The assignments for the free ligand and its Pt(II) and Pd(II) complexes are reported for the first time. The spectra for the ligand and its complexes were recorded in the same solvent (DMSO-d_6) for effective comparison. The free ligand shows six resonances as expected. The resonance at 162.50 ppm is assigned to the C4′ carbon while the signals at 157.07 and 150.48 ppm are attributed to C2′ and C6′ carbons, respectively. Other signals, C5′, 2′-CH_3 and 5′-CH_3 are assigned to 121.03, 20.82 and 12.58 ppm, respectively. Complexation causes downfield shift of carbons adjacent to the coordination site [12].

In the $Pt(HDMPY)_2Cl_2$ complex, C4′ shifted upfield to 160.98 ppm representing a shift of 1.87 ppm. Another upfield shifted resonance is 5′-CH_3 (0.32 ppm). All other signals experienced downfield shift. The C2′, C6′, C5′ and 2′-CH_3 carbons shifted by 3.41, 0.98, 2.05 and 2.26 ppm, respectively. The chemical shifts in $Pd(HDMPY)_2Cl_2$ complex are similar to those of $Pt(HDMPY)_2Cl_2$ except that the C6′ signal could not be observed. This finding is consistent with our experience in the $Pd(ADMPY)_2Cl_2$ complex reported [1] earlier. Thus ^{13}C NMR results provided additional support for the assumption that Pt(II) and Pd(II) are coordinated through the N-1′ position of the ligand.

TABLE II. ^{13}C NMR Chemical Shifts of the Ligand and its Pt(II) and Pd(II) Complexes

Carbon	HDMPY	$Pt(HDMPY)_2Cl_2 \cdot H_2O$	$Pd(HDMPY)_2Cl_2 \cdot H_2O$
C4′	162.85	160.98	160.60
C2′	157.07	160.48	160.45
C6′	150.48	151.46	–
C5′	121.03	123.08	122.53
2′-CH_3	20.82	23.08	23.04
5′-CH_3	12.58	12.26	12.20

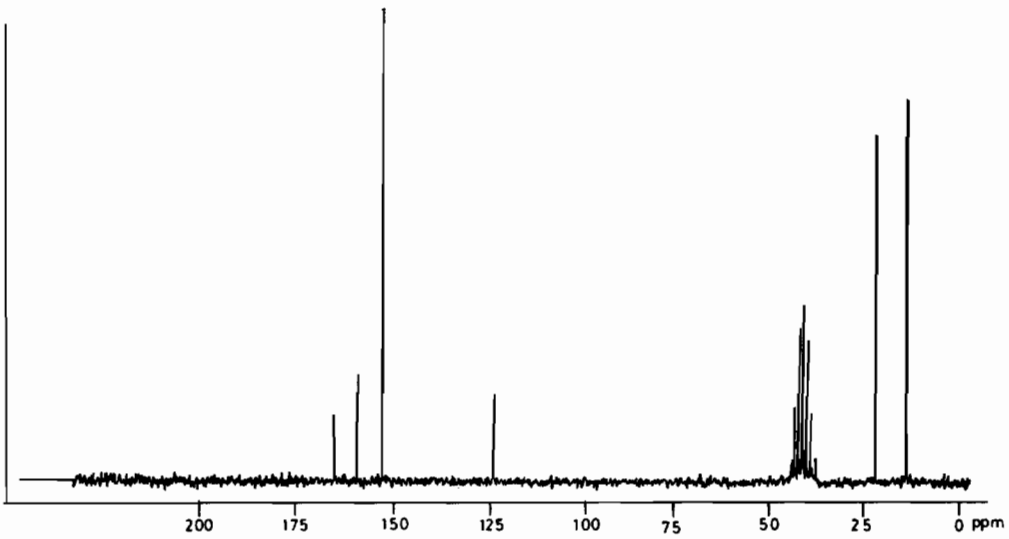


Fig. 2. ^{13}C NMR Spectrum of HDMPY.

TABLE III. Infrared Spectra Data (cm^{-1}) of the Compounds[a]

HDMPY	$Pt(HDMPY)_2Cl_2 \cdot H_2O$	$Pd(HDMPY)_2Cl_2 \cdot H_2O$	Assignments
3400–3200br	3600–3400br 3200–2850br	3600–3400br 3200–2850br	ν(HOH) + ν(OH) + ν(CH)
1665s	1685s 1675s	1675s 1670s	ring stretching coupling
1610s	1625sh 1575m	1625sh 1583m 1558m 1520m	skeletal C=C, C=N stretching
1490m	1490m		
1450m			
1435w	1430m	1430m	
1380s	1380m	1375m	
1318m	1340–1310br		
1285sh	1270w 1265w	1255w	
1200w			
1185s		1185w	
1170s	1165m	1164m 1130sh	
1045sh	1065m	1062w	
1030m	1040m	1040w	ν(C–OH) stretching
1020s	1025m	1025w	
950sh 935s	920w	930w	pyrimidinyl ring breathing
775s 764s	775m 770m	80m 770w	pyrimidinyl CH out of plane bending
743m	740w	700w	
594m	620m	630m	pyrimidinyl ring in plane vibration

[a]s, strong; m, medium; w, weak; sh, shoulder.

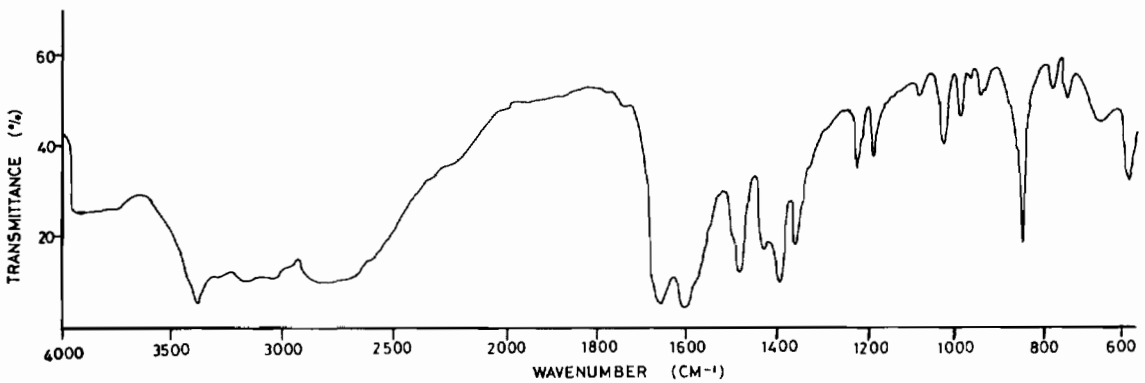


Fig. 3. IR spectrum of HDMPY.

Infrared Spectra

The IR tentative assignments are given in Table III and Fig. 3. Although the free ligand (HDMPY) and its Pt(II) and Pd(II) complexes show many bands between 1700 and 600 cm^{-1}, we shall concentrate on those bands which are relevant to our interpretation.

The appearance of a broad band around 3500 cm^{-1} supports the presence of water in Pt(II) and Pd(II) complexes. The non-involvement in bonding of the phenolic oxygen with metals is indicated by the non-removal of the ν(C–OH) band of the ligand in the complexes [2, 13, 14]. This band appears at 1045, 1030 and 1020 cm^{-1} in the ligand and at 1065, 1040 and 1025 cm^{-1} in $Pt(HDMPY)_2Cl_2$ and at 1062, 1040 and 1025 cm^{-1} in $Pd(HDMPY)_2Cl_2$ complexes.

Strong evidence for the involvement of the ring nitrogen in the complexes can be appreciated by considering the bands around 1600 cm^{-1}. The free ligand and its complexes show two bands in this region. At 1665 and 1610 cm^{-1} for the ligand, at 1675 and 1625 cm^{-1} for the Pt(II) complex and at 1673 and 1625 cm^{-1} for the Pd(II) complex. This observation is in very good agreement with Pt(II) and Pd(II) complexes of thiamine reported earlier [2] and also consistent with the Pt(II) and Pd(II) complexes of pyridine previously reported [15]. It is interesting to observe that the corresponding bands in pyridine and its Pt(II) and Pd(II) complexes occur at lower frequencies than in the pyrimidine moiety in very good agreement with other independent studies [16, 17].

In summary, the absence of complex ^{1}H and ^{13}C NMR spectra eliminates the possibility of having polymeric units [18]. Three proton resonances were observed for the Pt(II) and Pd(II) complexes. Six carbon-13 resonances were observed for the free ligand as well as in the Pt(II) complex while five resonances were observed for the Pd(II) complex. These facts coupled with the elemental analysis strongly suggest that our complexes are simple and symmetric 2:1 (ligand:metal) complexes. The fact that 2′-CH_3 and C6′-H proton which are adjacent to the assumed coordination site (N-1′) shifted downfield by about 0.80 and 0.37 ppm, respectively, confirmed coordination through the N-1′ position of the ligand. The most downfield shifted carbon resonances are C2′ (3.41 ppm), 2′-CH_3 (2.26 ppm) and C6′ (0.98 ppm) carbons, which are adjacent to the assumed coordination site, also lends support to our assumption that Pt(II) and Pd(II) are coordinated through the N-1′ position of the ligand. Finally, the IR spectra indicate the involvement of the ring nitrogen and more specifically the N-1′ position through a shift to higher frequencies of the bands around 1600 cm^{-1} as HDMPY goes to Pt(II) and Pd(II) complexes. All these findings are in good agreement with earlier reports [1–18]. The Kurnakov [19] test was performed on these new complexes and this was found to be positive, establishing the fact that *cis* isomers are preferred to *trans* isomers. This finding is in very good agreement with an earlier report [18].

Acknowledgement

We thank A. H. Robins and Company of Richmond, Va, U.S.A. for the elemental analyses, infrared, proton and carbon-13 NMR spectra of the ligand and its Pt(II) and Pd(II) complexes.

References

1 A. Adeyemo and R. P. Raval, *Inorg. Chim. Acta, 66*, L1 (1982).
2 N. Hadjiliadis, J. Markopoulos, G. Preumatikakis, D. Katakis and T. Theophanides, *Inorg. Chim. Acta, 25*, 21 (1977).
3 A. Adeyemo, Y. Teklu and T. Williams, *Inorg. Chim. Acta, 51*, 19 (1981).
4 A. Adeyemo, A. Shamim and A. Turner, *Inorg. Chim. Acta, 78*, L23 (1983).
5 R. P. Raval, *Ph.D. Dissertation*, Howard University, 1978.
6 A. A. Gallo and H. Z. Sable, *J. Biol. Chem., 249*, 1382 (1974).
7 P. C. Kong and T. Theophanides, *Inorg. Chem., 13*, 1167 (1974).
8 P. C. Kong and T. Theophanides, *Inorg. Chem., 13*, 1981 (1974).
9 A. Adeyemo, A. Shamim and A. Turner, *Inorg. Chem. Acta, 91*, L23 (1984).
10 A. Adeyemo, A. Shamim, A. Turner and K. Akinade, *Inorg. Chim. Acta, 78*, 191 (1983).
11 J. Chatt and A. D. Westland, *J. Chem. Soc. A*, 88 (1968).
12 T. Yasui and T. Ama, *Bull. Chem. Soc. Jpn., 48*, 3171 (1975).
13 A. Marzotto, G. Bandoll, D. A. Clements, F. Benetollo and L. Galzigna, *J. Inorg. Nucl. Chem., 35*, 2769 (1973).
14 G. V. Fazakerley and J. C. Russel, *J. Inorg. Nucl. Chem., 37*, 23 77 (1975).
15 S. Haghigh, C. A. McAuliffe, W. E. Hill, H. H. Kohl and M. E. Friedman, *Inorg. Chim. Acta, 43*, 113 (1980).
16 R. Poddar and U. Agaruila, *J. Inorg. Nucl. Chem., 35*, 3769 (1973).
17 W. R. McWhinnie, *J. Inorg. Nucl. Chem., 27*, 1063 (1973).
18 A. Shamim, A. Adeyemo, M. T. Shamim, J. Wheeler, A. Turner and A. B. Hussein, *Inorg. Chim. Acta, 91*, 179 (1984).
19 N. Kurnakov, *J. Russ. Phys. Chem. Soc., 25*, 565 (1893).