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Complexes of Platinum(II) and Palladium(II) with *N*-(2-methyl-4-aminopyrimidinyl-5)methylaniline

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Abstract

The reactions of K_2MX_4, where M = Pt(II), Pd(II) and X = Cl, with thiamine derivative, L, *N*-(2-methyl-4-aminopyrimidinyl-5)methylaniline have been studied in aqueous medium (1:2 molar ratio). The products of the general formula MLX_2 have been isolated and characterized by elemental analyses, infrared, proton and carbon-13 nuclear magnetic resonance spectra. A complete assignment of ^1H and ^{13}C NMR spectra resonances for both the free ligand and its metal complexes is presented for the first time. The results show that this ligand behaves like a bidentate ligand, coordinating through either the exocyclic amino group and the side chain nitrogen donor atom or the endocyclic nitrogens, N-1′ and N′-3′.

Introduction

In a recent publication from our laboratory [1] we reported the reactions of K_2MX_4 (M = Pt(II) or Pd(II), X = Cl) with a thiamine derivative, (4-amino-2-methyl-5-pyrimidinyl-methylthio)acetic acid. The isolated complexes from these reactions were perhaps the first examples of complexes of thiamine derivatives in which alternative sites to N-1′ position of the pyrimidine moiety are preferrentially coordinated. Neither the ring nitrogen nor the exocyclic amino group were found to react with metals, most probably due to the large difference between the basicities of these donor sites on the one hand and the sulfur and carboxylate group of the side chain on the other. That report was the first example of such complexes, aside from thiamine pyrophosphate complexes [2] where the ligand behaves like a bidentate ligand, coordinating through the sulfur and oxygen donor atoms. Continuing our studies on the reactions of Pt(II) and Pd(II) with thiamine derivatives which are potential bidentate ligands, we report the synthesis and characterization of Pt(II) and Pd(II) complexes of *N*-(2-methyl-4-aminopyrimidinyl-5)methylaniline.

This ligand which was first prepared by Matsukawa and Yurugi in 1954 was chosen for our studies since it affords a direct comparison of the donor properties of the wide variety of coordination

sites it offers (N-1′, N-3′, C4′–NH_2 and –N–). It should be remembered that in thiamine [4, 5], direct comparison of the donor properties of the various potential coordination sites was difficult, if not impossible, since the nitrogen atom of the thiazolium moiety of thiamine carries a positive charge which presumably adversely affects the coordinating ability of the sulfur atom with metals. It is interesting to compare the donor properties of this ligand with those of (4-amino-2-methyl-5-pyrimidinyl-methylthio)acetic acid [1].

Experimental

Potassium tetrachloroplatinate(II) and potassium tetrachloropalladate(II) were purchased and used without further purification.

Preparation of N-(2-methyl-4-aminopyrimidinyl-5)-methylaniline (NAMMPTA)

NAMMPTA (Fig. 1) was prepared according to the literature method [3]. *Anal.* Calc. for NAMMPTA,

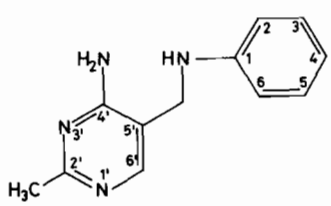

Fig. 1. Numbering-scheme of NAMMPTA.

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$C_{12}H_{14}N_4$ ($M = 214$): C, 67.29; H, 6.54; N, 26.17. Found: C, 66.94; H, 6.56; N, 25.96%.

Preparation of Pd(NAMMPTA)Cl_2

Approximately 2.14 g of NAMMPTA (1.0×10^{-2} mol) was dissolved in 50 ml of warmed distilled water and then mixed with 0.326 g of K_2PdCl_4 (5.0×10^{-3} mol) which was also dissolved in 50 ml of warmed distilled water after the individual solution had been filtered to remove any undissolved material. The reaction mixture was further heated to reduce its volume by about one-third of the original volume while being magnetically stirred. Upon cooling, a yellow precipitate was formed, filtered, and rinsed with cold distilled water, acetone and diethyl ether. The yellow compound was dried first at room temperature for a few days and then in the oven (120 °C) for five hours. Finally, the yellow compound was dried in a dessicator under calcium chloride for about a week. *Anal.* Calc. for Pd(NMMPTA)Cl_2, $PdCl_2C_{12}H_{14}N_4$: C, 36.80; H, 3.58; N, 14.31. Found: C, 36.94; H, 3.63; N, 14.37%.

Preparation of Pt(NAMMPTA)Cl_2

This compound was prepared by the same method used for the Pd(II) analogue. *Anal.* Calc. for Pt(NAMMPTA)Cl_2, $PtCl_2C_{12}H_{14}N_4$: C, 30.00; H, 2.92; N, 11.67. Found: C, 30.12; H, 2.98; N, 11.72%.

Instrumentation

Proton and carbon-13 NMR spectra were recorded on a Varian FT-80A spectrometer at 20 MHz, using DMSO-d_6 as solvent with TMS as internal reference standard. The infrared spectra were recorded between 4000 and 600 cm^{-1} on a Perkin-Elmer IR 297 spectrophotometer, as KBr pellets using polystyrene as reference. The elemental analyses were performed by A. H. Robins and Company of Richmond Virginia, U.S.A.

Results and Discussion

Proton NMR Spectra

The ^1H NMR assignments of the ligand, NAMMPTA and its Pt(II) and Pd(II) complexes are reported for the first time based on the known ^1H NMR spectra of thiamine [4–7] and its Pt(II) and Pd(II) complexes (Table I).

The free ligand shows six different resonances. The singlet at 2.33 ppm is assigned to 2′-CH_3 while the doublet at 4.00–4.08 ppm is ascribed to the 5′-CH_2 signal. The doublet of the 5′-CH_2 resonance is apparently due to the proton on the adjacent nitrogen atom. The signal which looks like a triplet

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centred at 5.97 ppm is assigned to the –N– resonance. The triplet arises from the adjacent 5′-CH_2 protons as expected. The doublet resonance at 6.53–6.67 is assigned to the phenyl protons. Integration shows that the area under this peak corresponds to five protons. What appears to be a doublet may be two different peaks which are close together and perhaps due to all the five phenyl protons being unequivalent. The resonance between 6.97 and 7.20 ppm is attributed to the exocyclic amino protons. This signal appears like a doublet perhaps due to hindered rotation about C4′ carbon or some kind of coupling. The most downfield resonance (7.97 ppm) is unequivocally assigned to the C6′–H proton. There is a marked difference between the ^1H NMR spectrum of the free ligand and those of the complexes.

In Pt(NAMMPTA)Cl_2 complex, 2′-CH_3 occurs at 1.80 ppm, with an upfield shift of 0.53 ppm, while 5′-CH_2 is shifted upfield from about 4.00 to 2.31

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ppm, with a shift of about 1.70 ppm. The –N– signal appears at around 6.30 ppm, with a downfield shift of 0.33 ppm. The resonance of the amino protons is the most downfield-shifted (0.63 ppm), while C6′–H signal is shifted downfield by about 0.43 ppm. Similarly in Pd(NAMMPTA)Cl_2 complex, 2′-CH_3 and 5′-CH_2 resonances are shifted upfield by 0.48 and 1.73 ppm, respectively. The other reso-

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nances, –N–, the phenyl protons, C4′–NH_2 and C6′–H, are shifted downfield by about 0.33, 0.25,

TABLE I. ^1H NMR Spectra of NAMMPTA and its Pt(II) and Pd(II) Complexes[a]

Type of proton	NAMMPTA	Pt(NAMMPTA)Cl_2	Pd(NAMMPTA)Cl_2
2′-CH_3	2.33s	1.80s	1.85s
5′-CH_2	4.00–4.08d	2.31s	2.35s
–NH–	5.97t	6.30	6.30
C2–C6	6.67–6.53d	6.95	6.75–6.85
C4′–NH_2	6.97–7.20	7.85	7.90
C6′–H	7.97s	8.40s	8.40s

[a]Abbreviations: s = singlet, d = doublet, t = triplet.

TABLE II. ^{13}C NMR Spectra of NAMMPTA and its Pt(II) and Pd(II) Complexes

Type of carbon	NAMMPTA	$Pt(NAMMPTA)Cl_2$	$Pd(NAMMPTA)Cl_2$
$2'$-CH_3	25.22	27.50	27.19
$5'$-CH_2	111.04	124.48	124.37
C3,C4,C5	112.59	112.48	112.67
C2,C6	116.26	116.59	116.63
C1	129.00	128.97	129.06
C5′	148.44	148.29	148.26
C6′	153.84	153.59	153.35
C4′	161.83	160.65	161.02
C2′	165.28	165.28	165.23

0.70 and 0.43 ppm, respectively. Since the most shifted resonances are $5'$-CH_2 (1.7 ppm) and C4′–NH_2 (0.70 ppm), we concluded that both the exocyclic amino group and the side chain nitrogen are involved in coordination.

Carbon-13 NMR Spectra

The ^{13}C NMR spectra resonance assignments of the free ligand and the complexes are reported for the first time based on previous work and off-resonance techniques [4–9]. Table II shows the chemical shifts of the ligand and its complexes.

In the free ligand, nine resonances are observed as opposed to the twelve resonances that one would expect were some of the resonances not equivalent. The resonance at 25.22 ppm is assigned to $2'$-CH_3, while the one at 111.04 ppm is assigned to $5'$-CH_2–. The resonance at 112.59 ppm is attributed to the C3, C4 and C5 carbons of the phenyl ring, while the signal at 116.26 ppm is assigned to C2 and C6 carbons. The C1 carbon of the phenyl ring should occur further downfield than all others in the ring due to the influence of the side chain nitrogen atom. The signal at 129.00 ppm is therefore assigned to C1 carbon of the phenyl ring. The resonances at 148.44, 153.84, 161.83 and 165.28 ppm are unequivocally assigned to C5′, C6′, C4′ and C2′, respectively.

In $Pt(NAMMPTA)Cl_2$ and $Pd(NAMMPTA)Cl_2$ complexes, the $2'$-CH_3 and $5'$-CH_2 resonances are shifted downfield by about 2.28 and 13.44 ppm and about 1.97 and 13.33 ppm, respectively. Other resonances either are shifted slightly or remained practically unchanged. A downfield shift of 13.44 and 13.33 ppm for the $5'$-CH_2 signal in $Pt(NAMMPTA)Cl_2$ and $Pd(NAMMPTA)Cl_2$, respectively, is a strong indication for coordination through the side chain nitrogen atom. These downfield chemical shifts are comparable to those reported earlier [4, 5, 10].

Infrared Spectra

Table III lists the IR spectra data of the free ligand and the Pt(II) and Pd(II) complexes. Although both the ligand and its complexes show many absorption bands, especially between 1700 and 600 cm^{-1}, only those that are important to spectral analysis and hence the possible stereochemistry of the complexes will be discussed in detail. The involvement of the exocyclic amino group and the non-involvement of the ring nitrogen in coordination is inferred by considering the bands around 1600 cm^{-1}. Both NAMMPTA and its Pt(II) and Pd(II) complexes show two bands in this region: at 1640 and 1602 for the ligand, at 1625 and 1600 for the $Pt(NAMMPTA)Cl_2$ complex and at 1620 cm^{-1} for the $Pd(NAMMPTA)Cl_2$ complex. A shift of these bands to lower frequencies in the complexes confirms the non-involvement of the ring nitrogen [8] and may suggest coordination through the exocyclic amino group [11–13].

TABLE III. The Infrared Frequencies of NAMMPTA and its Pt(II) and Pd(II) Complexes[a]

NAMMPTA

3458s, 3380m, 3310m, 3130br, 3050sh, 2920w, 2880w, 2850w, 2740w, 1640s, 1602s, 1585s, 1560s, 1512m, 1455s, 1410s, 1380w, 1360sh, 1330s, 1302m, 1278s, 1250w, 1235-w, 1175w, 1165w, 1150sh, 1090w, 1036w, 988m, 962w, 863m, 815w, 770s, 746s, 690s, 630w, 610w

$Pt(NAMMPTA)Cl_2$

3458br, 3320br, 3200br, 3150br, 2920w, 2845w, 1625s, 1600sh, 1560sh, 1543s, 1510sh, 1490w, 1468s, 1370s, 1350-m, 1260br, 1178m, 1025w, 990br, 753s, 693s

$Pd(NAMMPTA)Cl_2$

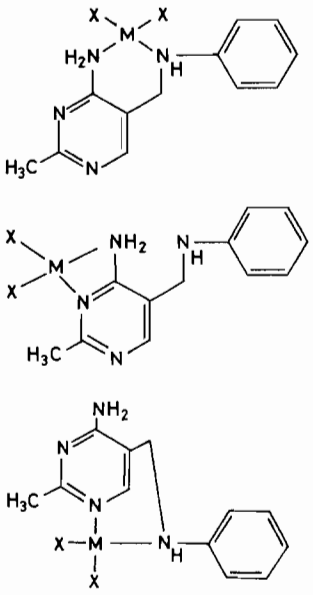
3460br, 3340br, 3160br, 3050br, 2910w, 1620s, 1547s, 1490s, 1460s, 1025sh, 990br, 925br, 753s, 693s

[a]Abbreviations: s = strong, m = medium, w = weak, sh = shoulder.

In conclusion, the fact that the –N–, C4′–NH_2 and $5'$-CH_2 protons shifted by 0.33, 0.70 and about 1.7 ppm, respectively, supports our assumption that

coordination is through the exocyclic amino group and the side chain nitrogen atom. The downfield shift of about 13.44 ppm experienced by the 5'-CH_2 carbon is a strong indication that coordination is through the side chain nitrogen atom, as this is consistent with previous studies [4, 5, 10].

The 20 cm^{-1} shift of NH_2 on coordination may be due to hydrogen bonding in the complex or as a result of complexation. Although the ^1H and ^{13}C chemical shifts are significant, the actual coordination site could not be established due to the random nature of the shift. In the absence of any suitable crystals for X-ray analysis, we propose the following possible structures:



Acknowledgements

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