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Metal Complexes of Alkyl Pyrazines-I

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Pyrazines are an important constituent of plants and insects. We report the synthesis, elemental analysis, mass spectra, ^{13}C nmr and I.R. studies of Pt(II) complexes of dimethyl pyrazine isomers (DMP). A trend in cluster formation of Pt(II)–DMP complexes is observed. Based on the ^{13}C chemical shifts, we postulate that in all the complexes Pt–pyrazine bonding is through N-1 rather than N-4.

Introduction

Pyrazines, especially alkylated ones, have been found to be an important constituent of plants like cocoa, coffee, *etc.* [1], as well as of the insect world [2]. Our group has been involved in the extraction, identification and synthesis of alkyl pyrazines [3] which are used as pheromones in several insects [4, 5]. In our continuous effort to synthesize and characterize potential anti-tumor compounds we extended our studies to investigate platinum(II) (and other noble metals) complexes with nitrogenous ligands. This report is concerned with the investigation of dimethyl pyrazine complexes of platinum(II) chloride.

Experimental

The three dimethyl pyrazines (DMP) namely, 2,3-DMP, 2,5-DMP and 2,6-DMP were purchased from Pyrazine Specialties, Atlanta, Georgia and Aldrich Chemical Co. and were used without further purification. Potassium tetrachloroplatinate(II), dimethyl sulfoxide and deuterated dimethylsulfoxide were bought from Aldrich Chemical Co. and were used as such. ^1H and ^{13}C nmr were recorded on a Nicolet 200 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) with respect to TMS, for ^1H spectra and with respect to TMSO-d_6 for ^{13}C spectra. Infrared spectra were recorded on a Perkin Elmer spectrometer model 621 in the 4000–200 cm^{-1} range using samples as KBr pellets. Elemental analysis was carried out by Mid-Atlantic Micro Lab. Inc., Atlanta, Georgia. Mass spectra were recorded at the Mid-West Center for Spectrometry, Department of Chemistry at the University of Nebraska, Lincoln, using high resolution fast atom bombardment (FAS) technique. The samples for mass spectra were dissolved in thioglycerol. Melting points were determined using a Thomas–Hoover melting point apparatus and were uncorrected.

Analysis: 2,6-Dimethyl pyrazine Pt(II) chloride (m.p. 225 °C), $[Pt(2,5\text{-}DMP)_2Cl_2]$. Calc. C, 29.88, H, 3.32; N, 11.62. Found C, 29.63, H, 3.25, N, 11.43, 2,5-Dimethyl Pt(II) chloride: (Fig. 2) (m.p. ~270 °C), Calc. C, 25.23; H, 2.80; N, 9.81. Found C, 24.12; H, 2.76; N, 9.27. 2,3-Dimethyl Pt(II) chloride: (Fig. 2) (m.p. 195 °C, decomposed), Calc. C, 15.50; H, 1.79; N, 6.03. Found C, 15.14, H, 1.93, N, 5.74.

Synthesis

Typically, the DMP was dissolved in a minimum amount of water and mixed in aqueous solution of K_2PtCl_4 in a 2:1 ratio with constant stirring. The mixture was warmed slightly for five minutes and then kept stirring overnight at room temperature. The 2,6-DMP complex precipitated much more quickly compared to the complexes with the 2,3- and 2,5-DMP isomers. The yellowish product (the color varied from pale to bright yellow) was filtered, washed with ice-water and then with ether. The products were slightly soluble in hot water, moderately so in acetone and dimethyl sulfoxide.

Results and Discussion

Tables IA and IB summarize the ^1H and ^{13}C nmr while Table II shows the I.R. data. Extensive work

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TABLE IA. ^{1}H Nmr Chemical Shifts for the Free Ligand and DMP–Pt(II) Complexes.

Ligand	Type of Protons	Chemical Shifts	
		Free Ligand	Metal Complex
2,6-DMP[a]	CH_3	2.20(s)	2.25(m)
	C-H	8.15(s)	8.15(s)
2,5-DMP[b]	CH_3	2.57(s)	2.25(m)
	C-H	8.33(s)	8.25(s)
2,3-DMP[a]	CH_3	2.30(s)	2.30(m)
	C-H	8.20(s)	8.15(s)

[a]This work, in deuterated DMSO. [b]Reference [18], in deuterated chloroform. Slight change in chemical shift is probably due to solvent effect.

TABLE IB. ^{13}C Chemical Shifts for the Free Ligands and DMP–Pt(II) Complexes.

Ligand	Type of Carbon	Chemical Shifts	
		Free Ligand	Metal Complex
2,6-DMP	C_2 C_6	152.353	156.058
	C_3 C_5	141.209	143.247
	C_2-CH_3, C_6-CH_3	20.866	21.060
2,5-DMP[a]	C_2 C_5	150.186	156.106, 153.389, 150.138
	C_3 C_6	143.150	147.420, 146.159, 143.538
	C_2-CH_3, C_5-CH_3	20.526	23.001, 21.011, 20.429
2,3-DMP	C_2 C_3	152.273	145.236, 144.996 144.412
	C_5 C_6	141.160	143.150, 143.587 142.016
	C_2-CH_3, C-CH_3	21.646	24.311, 24.117, 23.826, 23.636, 23.146, 22.807

[a] ^{13}C chemical shifts reported for 2,5-DMP ligand in reference 17 as neat liquid are very close to our values in DMSO solvent.

has been done on the metal–DMP complexation reactions [6–8, 15, 16, 20]. In the present investigation it appears that the three isomers interact differently with the Pt(II) chloride. Apparently the steric hindrance due to the positions of the two methyl groups (Fig. 1) plays an important role in the formation of these types of complexes.

TABLE II.[a] IR Data (in cm^{-1}).

2,6-DMP–Pt(II) Complex	2,5-DMP–Pt(II) Complex	2,3-DMP–Pt(II) Complex
3030(bd)	3015(bd)	3030(bd)
1590(s)	1583(bd)	1420(s)
1520(s)	1475(bd)	1395(bd)
1406(bd)	1425(bd)	1170(bd)
1370(bd)	1375(bd)	1140(bd)
1290(s)	1330(s)	1090(w)
1250(s)	1240(bd)	1000(s)
1173(s)	1150(s)	968(s)
1155(s)	1060(s)	825(bd)
1015(bd)	1030(bd)	740(w)
947(s)	970(bd)	325(bd)
875(s)	870(bd)	275(bd)
730(s)	735(w)	
560(w)	425(bd)	
520(w)	325(bd)	
440(w)	265(w)	
325(bd)		
260(w)		

[a]Abbreviations: s, sharp; bd, broad; w, weak.

^{13}C *Nmr*

The proton nmr did not show any remarkable changes *vis-à-vis* the proton nmr of the free ligands to warrant any discussion. Of the three isomers, 2,6-DMP appears to form a 2:1 ligand to metal complex. ^{13}C nmr (Table 1B) indicates that the chemical shifts for C_2 and C_6 carbons in the 2,6-DMP–Pt(II) complex is 3.7 ppm different from the free ligand C_2 and C_6. For C_3 and C_5 the shifts are about 2 ppm. Methyl carbons at 2,6- positions show minimum change. The larger chemical shifts for C_2 and C_6 carbons strongly suggest that metal–ligand bonding is through N_1 (as N_1 is in between the two said carbons) and not through N_4 despite the steric hindrance created by the close proximity of the two methyl groups to N_1. One possible explanation for the metal–ligand bonding through N_1 could be due to the large difference in the basicities of N_1 and N_4. It has been shown earlier [9] that the basicity of N_1 is much greater than the one for N_4. It is to be noted that in this complex only three chemical shifts are obtained for ^{13}C nmr as are found in the free ligand; this indicates the formation of a simple, non-polymeric complex unit in the present set of complexes (see below).

With 2,5-Pt(II) complex nine ^{13}C chemical shifts are obtained while for the 2,3-DMP–Pt(II) complex a total of twelve shifts are found. This could be due to the presence of polymeric units of the complexes. Any metal–pyrazine polymeric unit has the possibility of various types of pyrazines to be present. One that is bonded to the metal through one nitrogen

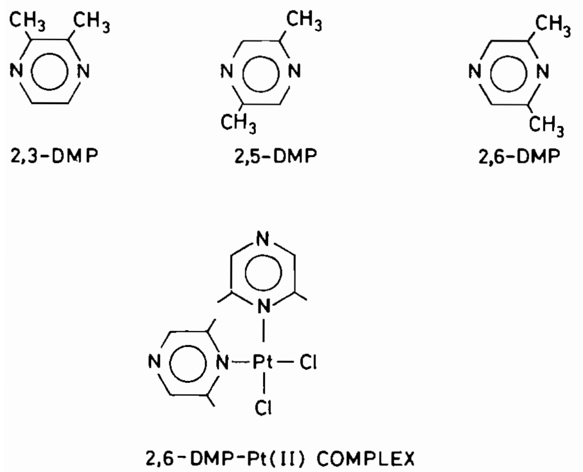

Fig. 1. The pyrazines and the 2,6-DMP complex.

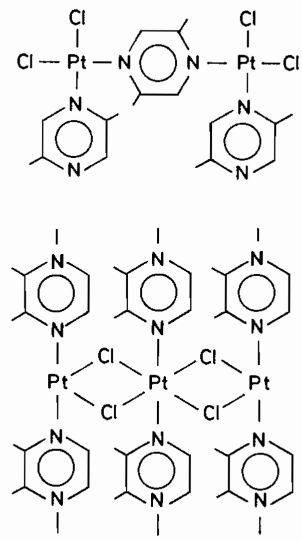

Fig. 2. Possible structures for 2,3- and 2,5-DMP complexes.

only (called terminal pyrazine), the other that is bonded to two separate metal ions through both nitrogens of the same pyrazine molecule (called bridging pyrazine) and the third, where Cl atoms are used as bridges. If our assumption for the formation of polymeric DMP–Pt(II) units is true, then ^{13}C nmr should show a number of chemical shifts as well as more than one shift for each type of carbon atom in the pyrazine molecule. It is our contention that in both the 2,3- and 2,5-DMP–Pt(II) complexes terminal as well as bridging pyrazines are present in each set of polymeric units and each set of carbons is in a different chemical environment and hence shows different chemical shifts. Figure 2 shows possible structures for Pt(II) 2,3-DMP and Pt(II) 2,5-DMP complexes. Due to the complicated ^{13}C spectra for the 2,3- and 2,5-DMP complexes, it is perhaps academic to make an absolute assignment for ^{13}C chemical shifts for each carbon involved.

Mass Spectra

Unfortunately, fast atom bombardment (FAS) mass spectra did not result in securing the molecular ions for the complexes. However it does confirm the presence of high molecular weight polymeric or cluster units. Detailed mass spectral analaysis for these and related compounds will be published later. For the present we can make the following observations: (a) 2,6-DMP–Pt(II)Cl_2 showed mass peaks at 500 and 555 mass regions which are probably the hydrated species of the said complex. No other peak at higher mass region was found. (b) For both 2,3- and 2,5-DMP–Pt(II) complexes besides the peaks in the 500–555 mass range, peaks up to 1000 mass region were also found reinforcing the idea that 2,3- and 2,5-DMP–Pt(II) complexes have polymeric units.

I.R. Spectra

No attempt was made to carry out any theoretical interpretation of the I.R. spectra. It is known that the Pt–Cl bond usually has an ir peak in the 300–333 cm^{-1} range [13]. Nyholm and coworkers [6–8] have postulated an empirical rule for the metal–pyrazine complexes: complexes that have terminal pyrazines only have an extra peak at *ca.* 1250 cm^{-1} and this is totally absent in those complexes which contain only bridged pyrazines. Goldstein [14] has shown that metal–pyrazine bonds have an absorption band between 230–270 cm^{-1} range. In our set of complexes an ir peak is found at 325 cm^{-1} which is assigned to the Pt–Cl bond. The 2,6-DMP–Pt(II) complex shows an ir absorption at 260 cm^{-1}, for the 2,5 complex at 265 cm^{-1} while for the 2,3-DMP–Pt(II) a peak at 275 cm^{-1} is found, all due to the Pt–N stretching mode. Assuming Nyholm's empirical rule is applicable to our set of complexes also, we find that the 1250 cm^{-1} ir peak is present for the 2,6-DMP complex; with the 2,5-DMP complex it is at 1240 cm^{-1} and broad; for the 2,3-DMP complex, the 1250 cm^{-1} band is totally absent. This would indicate that the 2,3-DMP complex has a polymeric unit which contains only bridging pyrazines.

In addition the 2,6-DMP–Pt(II) complex has two additional ir bands at 560 and 520 cm^{-1} which are not found with 2,5- and 2,3-DMP complexes, another distinguishing feature of a simple 2:1 complex as opposed to a polymeric complex unit. We must point out that we did not find any evidence of polymerization with other azine systems like dimethyl pyrimidine complexation with Pt(II) chloride [10]. Also, complexation of 2,6-DMP with

Au(III) halides has resulted only in a simple 1:1 complex [19].

Platinum(II) complexes are generally square planar. $PtCl_4^{-2}$ reactions with pyridines have always resulted in the formation of *cis*-dichloro dipyridine Pt(II) complexes. For such Pt complexes several tests are available [11] for confirming if the complex formed in a *cis* or *trans* isomer. The Kurnakov [12] test was positive for the 2,6-DMP–Pt(II) complex, indicating a *cis* entity. The same test for the other two complexes was inconclusive.

In summary, ^{13}C, ir and mass spectral studies show that the isomers have formed a variety of complexes with the same metal Pt(II) halide.

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