Novel Alkyl Pyrazine Complexes of Less Common Metals-II

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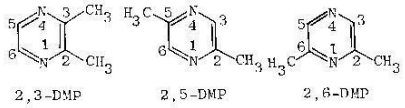
Summary: Alkyl pyrazines are found in plants and certain glands of some insects where they appear to behave as pheromones. We have initiated a project on the metal complexation of these alkyl pyrazines. We report the synthesis, elemental analysis, i.r., ^{1}H and ^{13}C studies of gold (III) halide complexes with 2,6-DMP (2,6-dimethyl pyrazine). A brief comparison is made with the corresponding 2,6-DMP-Pt(II) halide complex. Here, as in the case of 2,6-DMP-Pt(II) complex, metal-pyrazine bonding is evidenced through N-1 rather than N-4.

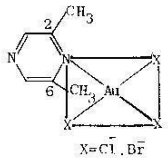
Introduction

Alkyl pyrazines are an important constituent of certain plants and the insect world [1-3]. We have reported elsewhere [4] the synthesis and characterization of Pt-complexes with alkyl pyrazines. Metal complexation of alkyl pyrazines is not a new field. Numerous workers have reported the characterization of metal-pyrazine complexes, [5-6] specially with the first transition series metals. In the present study, we investigate the complexation of the less common metal-gold (III) halides with 2,6-DMP (Fig. 1).



2,3-DMP 2,5-DMP 2,6-DMP

ISOMERS OF DIMETHYL PYRAZINE



X=Cl, Br

POSSIBLE STRUCTURE OF 2,6-DMP-Au(III) X_3 COMPLEX

Experimental

2,6-DMP was purchased from Aldrich Chemical Co. and used without further purification, $HAuCl_4$, $KAuCl_4.2H_2O$, normal and deuterated DMSO were also purchased from the Aldrich Chemical Co. and were used as such. ^{1}H and ^{13}C nmr spectra were recorded on a Nicolet 200 MHz spectrometer. TMS was used as an internal reference for the proton nmr while deuterated DMSO was used as a reference solvent for ^{13}C nmr. All chemical shifts are reported in parts per million (ppm) with respect to TMS for ^{1}H spectra and with respect to DMSO-d_6 for ^{13}C spectra. Infra-red spectra was recorded on a Perkin-Elmer model 621 in the 4000-200 cm^{-1} range as KBr (Aldrich Chemical Co.) pellets. Elemental analysis was performed by Mid-Atlantic Micro Lab. Inc., Atlanta, Georgia and Mic-Anal, Tucson, Arizona. Melting points were determined by using Melt-Kemp apparatus and are reported uncorrected.

Analysis

$Au(2,6\text{-DMP})Cl_3$ (m.p. 145°C decomposed) Calc. C, 17.51 H, 1.95 N, 6.85. Found: C, 17.47 H, 1.92 N, 6.77 Au $(2,6(DMP)Br_3$ (m.p. 135°C decomposed) Calc. C, 13.27 H, 1.45 N, 5.16 Found: C, 13.141 H, 1.47 N, 5.25.

Synthesis

The method of synthesis has been described earlier [4]. The red product Au (2,6-DMP) Br_3 and the yelllow product Au (2,6-DMP)Cl_3 were washed with acetone (the bromide complex was slightly soluble in acetone) and then with ether. These were then air dried at room temperature for twenty-four hours.

Results and Discussion

Table 1A and 1B summarizes the proton and ^{13}C nmr data for the present complexes as well as 2,6-DMP -Pt (II) chloride complex for comparison. Table 2 enlists the i.r. data and it includes data for 2,6-DMP-Pt (II) chloride complex. Earlier workers have shown convincingly [5,6] that pyrazine and alkyl pyrazines have a tendency to form polymeric complexes, having bridged pyrazines, with the first transition series metals. A similar trend was found with pyridine to metal complexation reactions.

In our previous study, we have found that 2,6 DMP-did not show any tendency to polymerize with Pt(II) halide while 2,5-DMP and 2,3-DMP isomers increasingly formed polymeric complexes. In our present study, 2, 6-DMP complexed with gold (III) chloride and bromide and formed a 1:1 complex. Some interesting and additional aspects emerge from the present study vis-a-vis metal-pyrazine bonding and we discuss briefly what each technique contributes to understanding the metal-pyrazine bonding.

For the chloro complex, the proton spectra shows an upfield shift for both C_3 and C_5 protons and for the methyl protons. In the bromo complex, however, the chemical shifts for all protons involved show little change, although the metal protons appear as a doublet instead of a singlet as in the free ligand (Table 1A).

Table-1-A

Proton NMR Spectra

Compound	C_2-CH_3, C_6CH_3 Protons	C_3,C_5 Protons
2,6-DMP	2.55(s)	8.3(s)
$Au(2,6\text{-DMP})Cl_3$	1.5(s)	7.5(s)
$Au(2,6\text{-DMP})Br_3$	2.5(d)	8.45(s)

Table-1-B

^{13}C NMR Spectra

Compound	C_2,C_6	C_3,C_5	C_2-CH_3,C_6-CH_3
2,6-DMP	152.353(s)	141.209(s)	20.866(s)
$Au(2,6\text{-DMP})Cl_3$	151.255(s)	140.337(s)	19.749,18.119 (doublet)
$Au(2,6\text{-DMP})Br_3$	151.0(s)	140.487(s)	19.846,18.114 (doublet)

Table 2[a]

IR Data (in cm^{-1})

2,6 DMP[b]	$Pt(2,6\text{-DMP})_2Cl_2$	$Au(2,6\text{-DMP})Cl_3$	$Au(2,6\text{-DMP})Br_3$
300(sh)	3030(bd)	3015(bd)	3035(w)
1550(sh)	1590(sh)	1585(w)	1585(w)
1480(w)	1406(bd)	1525(sh)	1527(sh)
1450(w)	1370(bd)	1365(w)	1420(w)
1433(sh)	1290(sh)	1286(sh)	1365(w)
1380(sh)	1250(sh)	1247(bd)	1286(sh)
1315(w)	1173(sh)	1175(sh)	1250(bd)
1280(sh)	1155(sh)	1155(sh)	1180(sh)
1190(w)	1015(bd)	1020(w)	1155(sh)
1160(sh)	947(sh)	847(sh)	945(w)
1020(sh)	875(sh)	847(sh)	945(w)
970(w)	730(sh)	780(w)	847(sh)
865(sh)	520(w)	555(w)	715(w)
935(sh)	520(w)	555(w)	715(w)
845(sh)	440(w)	505(w)	560(sh)
710(w)	325(bd)	440(w)	505(sh)
	260(w)	365(sh)	280(w)

Abbrevations: sh = sharp; bd = broad; w = weak
a = as KBr pellets
b, = c = reference (4)
d = this work

The ^{13}C spectra are more revealing. In both the chloro and the bromo complexes, all C-atoms show an upfield shift (1 ppm) - more in the chloro complex than in the bromo one. Moreover, in the complexes, again, the methyl carbons appear as a doublet in contrast to the free ligand methyl carbon atoms. In the corresponding 2,6 DMP-Pt (II) chloride complex, the proton spectra showed no change in the chemical shifts while the ^{13}C showed downfield shift for all carbon atoms. Also no doublet is observed for the methyl carbon atoms.

It is known that N_1 is more basic (and hence a better candidate for bonding) than N_4 [7]. In the 2,6 DMP complex, we postulated that platinum binds through N_1 and not N_4 despite the steric hinderance created by the close proximity of the methyl groups with N_1. In the present study also a number of factors point to the similar complexation of gold (III) halides through N_1.

The appearances of methyl groups as a doublet in both the chloro and the bromo complex in ^{13}C spectra strongly indicate that the two methyl groups are no longer identical. Presumably, the pyrazine ring is twisted away (stagggered) from the plane of Au(III) halide making the two methyl groups to be in different chemical environments. Same arguments can be forwarded for the proton spectra for the bromo complex where the two methyl groups appear as a doublet. It is not clear why the proton spectra would not differentiate between the two methyl group signals in the chloro complex. Possibly the 2,6-DMP is more staggered in the bromo complex than in the chloro complex. Hence, the spectrometer is able to pick up the signals for the bromo complex only.

The upfield shift in the ^{13}C for both the complexes indicate an increased shielding. Based on the fact that gold is more electronegative than platinum (on Pauling Scale) [8] plus the higher electronegativities of the halogens, the overall electron density should be shifted more toward metal halides which in effect would make the pyrazine ring slightly electron deficient compared to the free ligand and should result in less shielding of the atoms in the ring system and a downfield shift could possibly be observed. However, the appearance of upfield shift in the ^{13}C spectra for both the complexes indicate an increased shielding. One can advance the following argument for the increased shielding (and the upfield shifts) in both the complexes: as the metal halide complexes with the N_1 of the pyrazine ring, because of the proximity of the bulky methyl and halide groups, a staggered configuration of the pyrazine ring ensues, making the methyl/halide groups move away from one another to minimize the steric hinderance. This facilities the non-bonding 5d-electrons in the gold (III) ion. (Au(III) is d^8 system and assuming a square planar geometry is retained in the complex) to back-bond to the molecular orbital of the aromatic ring, thereby increasing the electron density on the azine system, which in turn increases the shielding of the atoms on the aromatic system and hence the upfield shifts in the ^{13}C spectra. In addition, the ^{13}C (table 1B) spectra indicates (qualitatively) that the ring staggering is greater in the bromo complex than in the chloro complex. Back-bonding due to staggering of the aromatic ring system has been observed in a number of cases [9,10].

I.R. Spectra

Nyholm et.al. [5,6] have postulated that if the alkyl pyrazine complexes through one nitrogen only and does not form any bridged or polymeric compounds by bonding through both nitrogens than a 1250 cm^{-1} ir. peak is present. In our series of complexes we did find a peak at 1250±3 cm^{-1} strongly pointing to the fact that 2,6-DMP has complexed with the gold (III) halide through one nitrogen only (N_1). It should be mentioned that a 1250±3 cm^{-1} absorption peak is completely absent in the 2,3-DMP-Pt halide complex [4] which has been shown to be polymeric.

For the $AuCl_4^-$ and $AuBr_4^-$ square planar ions the Au-Cl and Au-Br i.r. absorption peaks are at 356 cm^{-1} and 252 cm^{-1} respectively (11). We observed two peaks one at 365 cm^{-1} and 280 cm^{-1} probably due to the chloro and bromo ions complexation with the aromatic ring.

Gold (I) compounds have been in use for treatment of arthritis [12] for quite some time. It has been shown [13] that $AuCl_4^-$ forms a complex with DNA - probably through nitrogens of purines and pyrimidines. This makes the ion a potential anti-tumour drug as it would hinder the cell division and it would be as effective or more effective than the cis $Pt(NH_3)_2Cl_2$ complex. Some reports on the chloro complex of gold diazouracil point in th same direction [14].

In summary, the gold (III) halide complexes with 2,6-DMP are in 1:1 ratio; back-bonding from the non-bonding 5d electrons to the aromatic molecular orbital is strongly indicated. We must observe that only x-ray crystallographic studies can resolve the issue whether the gold (III) halide-2,6-DMP complexes have a staggered or an eclipsed aromatic system and that if it is a staggered system, it is either due to crystal forces or due to metal-ligand back-bonding.

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