

Arylazopyridines–mercury(II) coordination and organometallic compounds: Theoretical support

K BAG^a, N K DE^a, B R DE^a and C SINHA^{*b}

^aDepartment of Chemistry and Chemical Technology, Vidyasagar University, Midnapore 721 102, India

^bDepartment of Chemistry, University of Burdwan, Burdwan 713 104, India

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Abstract. Arylazopyridines (Haap, 1) are mercurated by Hg(OAc)₂ in methanol followed by LiCl addition. Two classes of compounds are identified: Hg(Haap)Cl₂ (2), a simple coordination compound of tetrahedral geometry, and organomercury compounds, Hg(aap)Cl (3). The compounds are characterised by elemental analyses, IR and ¹H NMR spectra. The NMR results suggest that mercury is directed to the C-5 position (meta to pyridine-N) in the pyridine fragment of the ligand. This assumption is supported by net atomic charge calculation using the MNDO method.

Keywords. Mercury; arylazopyridines; coordination compounds; organomercury; MNDO; site selection.

1. Introduction

The activation of the C–H bonds by a metal-catalyzed route is a topic of current interest (Wardel 1982; Cauty and van Koten 1995) that could lead to new functionalisation at the carbon centre. The heteroatom metal bond formation followed by the M–C bond, leading to chelate structures known as cyclometallates is stabler than the non-chelated system (Omae 1986; Dunina *et al* 1988; Basuli *et al* 1996) and the process is widely used in transition metal complexes. Non-transition organometallics are less familiar than transition metal organometallics. Mercury is one of the non-transition elements whose organic chemistry has attracted great attention (Wardel 1982; Ding *et al* 1992; Chattopadhyay and Sinha 1994). Mercuration is electron population controlled and the stability of the product arises from the conformation of the substrate (Ding *et al* 1992; Chattopadhyay and Sinha 1994). Mercury(II) forms varieties of complexes of different coordination numbers and geometries (Lobana 1985; Blower and Dilworth 1987) as well as organometallic compounds (Wardel 1982; Ding *et al* 1992; Chattopadhyay and Sinha 1994). The coordination chemistry of arylazopyridines (Haap, 1) has been extensively studied for transition metals (Pal *et al* 1994; Chakravarty and Bhattacharya 1995; Roy *et al* 1996) and to some extent for mercury(II) chloride (Rolling *et al* 1976; Basubaul and Dey 1990). The structure of Hg(Haap)Cl₂ was partially characterized (Basubaul and Dey 1990), while the synthesis of organometallic mercury(II) compounds of Haap by Rolling *et al* (1976) failed. We describe here the complete structural characterization of Hg(Haap)

*For correspondence

Cl_2 (**2**) and organometallic compounds (**3**) by spectroscopic techniques. The site of mercuration in **3** is corroborated by theoretical electron density calculation by the MNDO method.

2. Experimental

2.1 Materials

$\text{Hg}(\text{OAc})_2$ was purchased from Lancaster, UK; $\text{LiCl}\cdot\text{H}_2\text{O}$ was from SRL. Purification of solvents were performed as reported (Vogel 1959). 2-(Arylazo) pyridines were prepared following known procedures (Chakravarty and Bhattacharya 1995).

2.2 Preparation of complexes

$\text{Hg}(\text{Hpap})\text{Cl}_2$ (**2a**) and $\text{Hg}(\text{Pap})\text{Cl}$ (**3a**): A solution of $\text{Hg}(\text{OAc})_2$ (0.30 g, 0.94 mmol) in dry MeOH was added dropwise to a solution of 2-(phenylazo) pyridine (**1a**) (0.18 g, 0.98 mmol) in the same solvent (10 ml) and a drop of HClO_4 . The mixture was stirred and refluxed for 6h. A grey-brown deposition was found on the container wall. The solution was filtered while it was hot, LiCl (0.18 g, 4.24 mmol) in MeOH (10 ml) was added and the resultant thick mixture was stirred with warming for about 0.5 h. The solution was then cooled to room temperature. The orange needle-shaped crystals were separated, filtered and washed with MeOH (3×5 ml) and dried. The dry crystals were then dissolved in CHCl_3 (20 ml) and filtered. The filtrate was diffused through a hexane layer for a week and needle-shaped crystals of $\text{Hg}(\text{HPap})\text{Cl}_2$ (**2a**) were collected. Yield: 40%. The brown residue on repeated washing with chloroform, dissolving in DMSO and recrystallising from the MeOH layer, gave $\text{Hg}(\text{Pap})\text{Cl}$ (**3a**), in 20% yield. Other complexes were also similarly prepared with yields varying in the range 30–45% for **2** and 20–25% for **3**. Micro-analytical data are given in table 1.

2.3 Electron density calculation

Net atomic charges of the ligands **1** were calculated by the MNDO method. Calculations, were made from the optimized geometries of the molecules. The molecules are planar and the bond parameters are within experimental limits. The physical data, viz. heats of formation, ionisation potential dipole moments and minimum electron transition energies are listed in table 2.

2.4 Physical measurements

Microanalyses were performed using a Perkin–Elmer 240C elemental analyser. Infrared spectra were obtained on a Perkin–Elmer 783 spectrometer using KBr discs. Electronic spectra were obtained using a Shimadzu UV-160A spectrophotometer. ^1H NMR data were collected for **1** and **2** in CDCl_3 and for **3** in d_6 -DMSO by using Varian Gemini 300 MHz FT NMR spectrometers. Conductances were measured using a Systronics digital 304 conductivity meter.

3. Results and discussion

The ligands 2-arylazopyridines (Haap **1**) are α -diimine type N, N chelating agent (Roy *et al* 1996). Two types of mercury(II) complexes are isolated on refluxing methanolic

Table 1. Microanalytical^a, infrared and ¹H NMR spectral data.

Compound	Elemental analysis (%)			IR data ^b (cm ⁻¹)		¹ H NMR data ^c δ (ppm)									
	C	H	N	γ(N=N)	γ(Hg-Cl)	3-H ^e	4-H	5-H ^f	6-H	8,12-H ^g	9,11-H	10-H			
1a^d	73.3	5.4	21.4	1425		7.78	7.87 ^f	7.39	8.70 ^e	7.95	7.50 ^f	7.50 ^f			
1b^d	(73.1)	(5.6)	(21.3)	1428		7.77	7.85 ^f	7.37	8.70 ^e	7.94	7.45 ^e	—			
1c	60.5	3.5	19.4	1420		7.80	7.90 ^f	7.39	8.73 ^e	7.98	7.49 ^e	—			
	(60.7)	(3.7)	(19.3)		322	8.13	8.13 ^f	7.68	8.67 ^e	7.99	7.52 ^f	7.52 ^f			
2a	29.2	2.1	9.3	1400		8.14	8.14 ^f	7.66	8.66 ^e	7.96	7.47 ^e	—			
	(29.0)	(2.0)	(9.2)		330	8.14	8.14 ^f	7.70	8.73 ^e	8.04	7.60 ^e	—			
2b^d	30.5	2.5	8.9	1405		8.17	8.17 ^f	—	9.24 ^g	8.05	7.54 ^f	—			
	(30.7)	(2.4)	(9.0)		320	8.18	8.23 ^e	—	9.24 ^g	8.03	7.41 ^e	—			
2c	26.8	1.5	8.4	1400		8.16	8.22 ^e	—	9.30 ^g	8.05	7.62 ^e	—			
	(27.0)	(1.6)	(8.6)		325	8.22	8.26 ^e	—	—	—	—	—			
3a	31.7	2.0	9.8	1420		8.16	8.22 ^e	—	—	—	—	—			
	(31.6)	(1.9)	(10.0)		330	8.22	8.26 ^e	—	—	—	—	—			
3b^d	33.4	2.2	9.8	1425		8.22	8.26 ^e	—	—	—	—	—			
	(33.3)	(2.3)	(9.7)		320	8.22	8.26 ^e	—	—	—	—	—			
3c	29.1	1.7	9.1	1420		8.22	8.26 ^e	—	—	—	—	—			
	(29.2)	(1.6)	(9.3)		320	8.22	8.26 ^e	—	—	—	—	—			

^a Calculated values are in parentheses; ^b as KBr discs; ^c in CDCl₃ for **1** and **2**, in DMSO-d₆ for **3**; ^d δ (Me): **1b** 2.49, **2b** 2.50 and **3b** 2.52 ppm; ^e doublet; ^f triplet; ^g singlet

Table 2. Physical parameters and electron densities of **1** by MNDO method

Compound	1a	1b	1c
<i>Physical parameters</i>			
Heat of formation (kcal/mole)	87.025	79.516	79.770
Ionisation potential (eV)	9.180	9.192	9.396
Dipole moments, $\pi \rightarrow \pi^*$ (eV)	1.496	1.422	2.795
	8.416	8.427	8.652
Number of filled MOs	34	37	37
<i>Net atomic charges (in e units)</i>			
C3	-0.08263	-0.08718	-0.08532
C4	-0.01190	-0.01098	-0.01015
C5	-0.12180	-0.12531	-0.12171
C6	0.05952	0.06695	0.06614
C8	0.00358	0.00474	0.00601
C9	-0.08105	-0.06479	-0.06288
C10	-0.03088	-0.06963	0.02571
C11	-0.07815	-0.06378	-0.05922
C12	-0.01129	-0.01507	-0.01004
N1	-0.21411	-0.22543	-0.22532
N2	-0.09651	-0.09141	-0.08764
N3	-0.03275	-0.03765	-0.03469

solution of ligands and $\text{Hg}(\text{OAc})_2$ for several hours in the presence of a few drops of HClO_4 at a concentration limit of 0.1 (M) with respect to $\text{Hg}(\text{II})$, followed by metathesis using LiCl . The compounds so isolated are dissolved in chloroform and filtered. The filtrate on slow diffusion in hexane layer separates out orange-coloured crystalline compounds of composition $\text{Hg}(\text{Haap})\text{Cl}_2$ (**2**). The residue so left is characterised as the organomercury complex, $\text{Hg}(\text{aap})\text{Cl}$ (**3**). The reactions are shown in scheme 1.

The composition of these two classes of compounds are supported by elemental analyses (table 1). The coordination complexes (**2**) are fairly soluble in common organic solvents and, unlike organomercury compounds (**3**), are soluble only in DMSO and DMF. The molar conductance measurements show that the complexes are nonelectrolytes. The solution electronic spectra of complexes (**2**) support the literature report (Basubaul and Dey 1990). The spectra of (**3**) in DMSO exhibit bands at 310–320 and 400–420 nm, corresponding to $\pi - \pi^*$ and $n - \pi^*$ transitions.

Infrared spectral data of complexes **2** also support literature information (Basubaul and Dey 1990). The complexes **3** do not exhibit any informative shift of the $\text{N}=\text{N}$ bond frequency from the free ligand value. This indicates that the azo group remains uncoordinated. The medium intense band around $320\text{--}330\text{ cm}^{-1}$ is assigned to $\nu(\text{Hg} - \text{Cl})$.

The structure and site of mercuration is confirmed by ^1H NMR spectra. All aromatic protons are unambiguously assigned on the basis of spin-spin structure and changes therein on substitution. The spectral data are listed in table 1. There are two well-defined doublets of AA' BB' systems which are highly sensitive to the substituents at the 10th position and are characterized as 8, 12 and 9, 11 protons. A doublet at the most downfield position is assigned as 6-H. In complexes **2**, 3-H is a doublet while 4- and 5-H resonate at two different frequencies in triplet-splitting patterns. All these

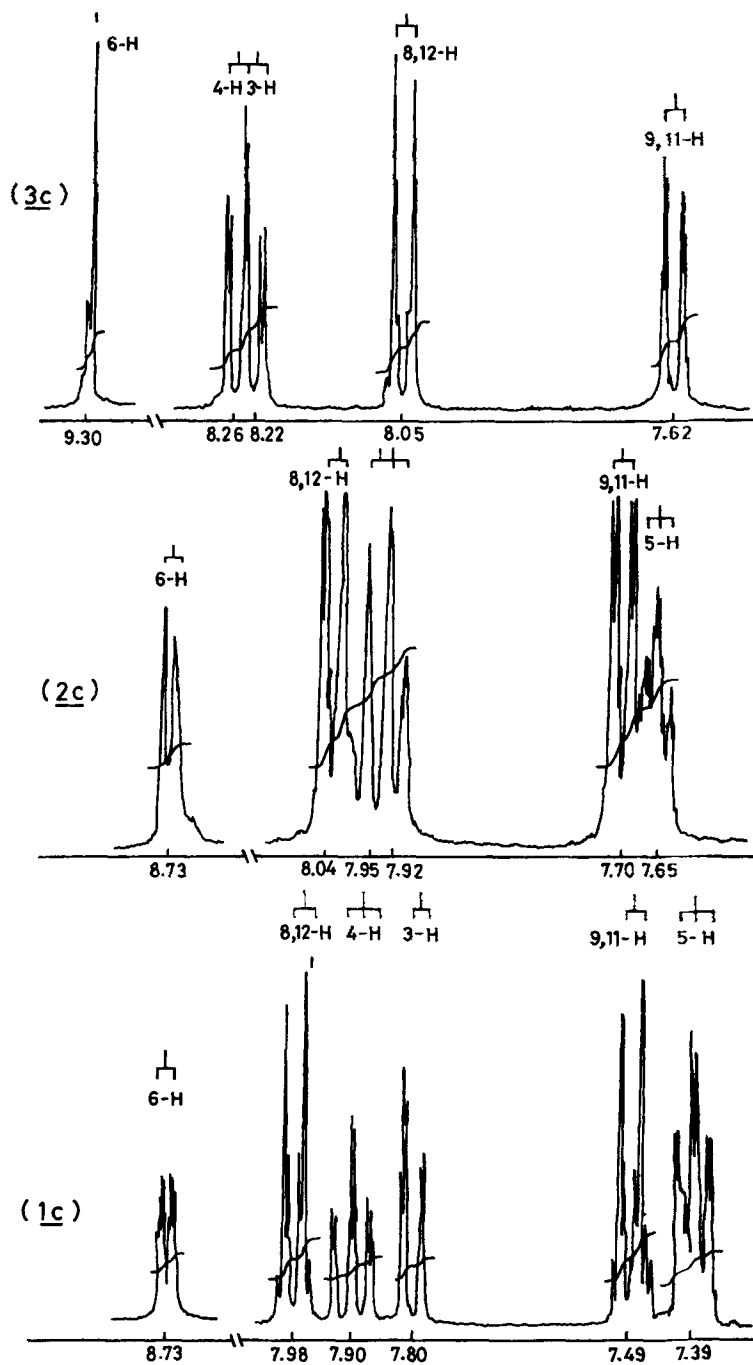
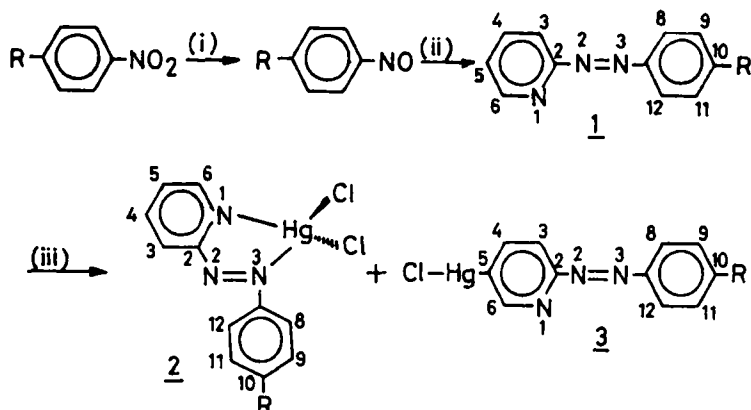


Figure 1. ^1H NMR spectra of (1c), (2c) in CDCl_3 and (3c) in $\text{DMSO}-d_6$.



- (i) Zn/NH₄Cl, Na₂Cr₂O₇ / H₂SO₄ ;
 (ii) 2-Aminopyridine / Na in benzene ;
 (iii) Hg(OAc)₂ in MeOH, reflux followed by LiCl.

Scheme 1.

protons show downfield shifting on mercuriation. In complexes **3**, the most important feature is the loss of resonance due to 5-H from the NMR spectra. 6-H appears as a singlet at a more downfield position (~ 9.3 ppm) compared to complexes **2** (~ 8.7 ppm). 8-/12-H signals remain almost insensitive in complexes **3** and suggest remote bonding of mercury(II). Thus, mercuriation at the 5th carbon centre is established. Representative spectra of ligand and complexes are shown in figure 1.

The position of mercuriation is supported by theoretical calculations. The MNDO method was employed to calculate the net atomic charges from the optimized geometry of the molecules **1**. The molecules are planar and their bond parameters are accurate within experimental limits. The physical data, and the net charges of the aromatic carbon and nitrogen centres are listed in table 2. The calculation indicates that the pyridinic-N has the highest atomic charge followed by the meta position of the pyridinic-N, i.e. the carbon-5 centre. Therefore electrophilic addition should occur at the pyridinic-N centre followed by chelation via azo-N to maintain the five-membered chelate ring structure, thus forming the coordination compounds, Hg(Haap)Cl₂. If electrophilic substitution is considered, it should be directed to C-5. Mercuriation is an electrophilic-substitution process carried out by Hg(OAc)⁺. In pyridine the substitution is directed to the meta position (Wardel 1982) by Hg(OAc)⁺ which is shown by MO calculation to have the highest electron population (Acheson 1976). Pyrroles are mercurated at all four positions (Wardel 1982). N-phenylpyrazine directs Hg(OAc)⁺ at the C-4 centre to participate in resonance and has the highest charge density (Begtrup 1973). Azophenols are mercurated at the phenolic ring ortho to the phenolic-OH (Patai 1975). It has the highest electron density due to the electron releasing effect of the -OH group. Aniline is mercurated at positions ortho and para (Wardel 1982) to the -NH₂ group, being directly influenced by its electron-releasing ability. Thus mercuriation at C-5 is supported by theoretical calculation and is also evident from the available literature.

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