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# Coupling of arylamine with coordinated arylazopyrimidine in platinum(II) complexes. Single crystal X-ray structure, spectra and electrochemistry

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#### Abstract

2-(Arylazo)pyrimidine (*p*-R-C<sub>6</sub>H<sub>4</sub>–N=N-C<sub>4</sub>H<sub>3</sub>N<sub>2</sub>, aapm, R = H (papm, **3a**), Me (tapm, **3b**), Cl (Clpapm, **3c**)) are *N*,*N*'-chelating ligands. Platinum(II) complexes, Pt(aapm)Cl<sub>2</sub> (**4**) have been synthesized by the reaction of K<sub>2</sub>PtCl<sub>4</sub> and aapm in MeCN-water under refluxing condition. The reaction of Pt(aapm)Cl<sub>2</sub> with ArNH<sub>2</sub> in MeCN has synthesized C–N coupled product, Pt(aapm-N–Ar)Cl (**5–10**). The single crystal X-ray structure determination of one of the compounds has suggested the coupling of ArNH<sub>2</sub> at *ortho*-C-H of the pendant aryl part of aapm in the chelated complex. The stereochemistry and the bonding are described by <sup>1</sup>H NMR data. The solution electronic spectra of Pt(aapm-N–Ar)Cl exhibit multiple transition at Vis–NIR region (500–1250 nm) which are absent in Pt(aapm)Cl<sub>2</sub>. Cyclic voltammograms show two quasireversible azo reductions of Pt(aapm)Cl<sub>2</sub>; Pt(aapm-N–Ar)Cl exhibit four successive redox couples, one of them (positive to SCE) is oxidative in nature and other (negative to SCE) are ligand reductions. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Arylazopyrimidine; Platinum(II); C-N coupling reaction; Crystal structure; Electrochemistry

## 1. Introduction

The coordination of ligand to metal center changes the electronic property of them and the ligand itself may undergo reaction with nucleophiles at enhanced rate on comparing with free ligand case. This is a growing field in the metal assisted organic transformation [1,2]. The  $\pi$ -acidity of the coordinating ligand plays a vital role in regulating the reaction. Arylazoheterocycles are potent  $\pi$ -acidic ligands and undergo varieties of metal assisted organic transformation [3–7]. We have been designing different series of azoheterocycles such as azoimidazoles [8], azopyridines, [9] and azopyrimidines [10]. Being a strongest  $\pi$ -acidic *N*-heterocycle, pyrimidine in the series of imidazole, pyridine and pyrimidine, the

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arylazopyrimidines are most efficient.  $\pi$ -acidic azoimine chelating substance. This property has been utilized to stabilize low valent metal oxidation state [10]. Besides, we have been able to use Pd(aapm)Cl<sub>2</sub> to bring the C–N coupling reaction with ArNH<sub>2</sub> [5] at ambient condition. In this work, we will report hitherto unknown platinum(II) complexes of aapm (3) and their coupling reaction with ArNH<sub>2</sub>. The complexes have been characterized by the spectral and electrochemical data. The structure of the coupled product has been characterized in one case by single crystal X-ray diffraction study.

# 2. Experimental

#### 2.1. Measurements

Microanalytical data (C, H, N) were collected on Perkin– Elmer 2400 CHNS/O elemental analyzer. Spectroscopic

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data were obtained using the following instruments: UV– Vis spectra, JASCO UV–Vis–NIR model V 570; IR spectra (KBr disk, 4000–200 cm<sup>-1</sup>), FTIR JASCO model 420; <sup>1</sup>H NMR spectra, Bruker (AC) 300 MHz FTNMR spectrometer. Electrochemical measurements were performed using computer-controlled PAR model 270 VERSASTAT electrochemical instruments with Pt-disk electrodes. All measurements were carried out under a nitrogen environment at 298 K with reference to saturated calomel electrode (SCE) in acetonitrile using [ $nBu_4N$ ][ClO<sub>4</sub>] as supporting electrolyte. The reported potentials are uncorrected for junction potential.

#### 2.2. Materials

2-(Arylazo)pyrimidines were prepared by the reported procedure [10].  $H_2PtCl_6 \cdot xH_2O$  was purchased from Arrora Matthey, Kolkata, India.  $K_2PtCl_4$  was prepared from the reported method [8]. Aniline, *o*-toluidine, *m*-toluidine, *p*-toluidine, *p*-chloroaniline were received from Sisco Research Lab (SRL). The purification of acetonitrile and preparation of *n*-tetra butylammonium perchlorate [*n*Bu<sub>4</sub>N][ClO<sub>4</sub>] for electrochemical work were done as before [10]. Dinitrogen was purified by bubbling through an alkaline pyrogallol solution. All other chemicals and solvents were of reagent grade and were used without further purification. Commercially available SRL silica gel (60–120 mesh) was used for column chromatography.

### 2.3. Preparation of complexes

## 2.3.1. Dichloro[2-(phenylazo)pyrimidine]platinum(II), Pt(papm)Cl<sub>2</sub> (4a)

2-(Phenylazo)pyrimidine (papm) (0.2 g, 1.09 mmol) in MeCN-H<sub>2</sub>O (15 ml) was added to an MeCN-H<sub>2</sub>O (1:1, v/v, 40 ml) solution of K<sub>2</sub>PtCl<sub>4</sub> (0.4 g, 0.96 mmol) and the mixture was refluxed for 24 h. On slow evaporation, a brown precipitate gradually appeared; it was filtered and washed with cold MeCN-H<sub>2</sub>O (1:1, v/v,  $3 \times 5$  ml). The dried mass was dissolved in a minimum volume of CH<sub>2</sub>Cl<sub>2</sub> and chromatographed over a silica gel column. The desired compound was eluted by  $C_7H_9$ -MeCN (2:1, v/v) as an orange-red band; yield, 0.3 g (50%). Other complexes were prepared under identical conditions and yield varied in the range 45–50%. Calc. for  $C_{10}H_8N_4Cl_2Pt$  (4a): C, 26.66; H, 1.77; N, 12.44. Found: C, 26.55; H, 1.69; N, 12.35%. Calc. for C<sub>11</sub>H<sub>10</sub>N<sub>4</sub>Cl<sub>2</sub>Pt (4b): C, 28.44; H, 2.15; N, 12.07. Found: C, 28.55; H, 2.08; N, 11.99%. Calc. for C<sub>10</sub>H<sub>7</sub>N<sub>4</sub>Cl<sub>2</sub>Pt (4c): C, 24.76; H, 1.44; N, 11.56. Found: C, 24.62; H, 1.37; N, 11.42%.

## 2.3.2. Chloro[(2-(8-imidophenyl)phenylazo)pyrimidine-N,N',N"]platinum(II), Pt(papm-N- $C_6H_5$ )Cl, (5a)

To an acetonitrile solution (15 ml) of  $Pt(papm)Cl_2$  (90.3 mg, 0.67 mmol) was added slowly aniline (0.1 g, 1.08 mmol) in the same solvent (10 ml). The reaction mixture was stirred and refluxed continuously for 4 h. The col-

our of the solution changed gradually from orange-red to brown. The solution was evaporated in air, and the residue was washed thoroughly first with water  $(2 \times 5 \text{ ml})$  and then with 50% aqueous-ethanol  $(3 \times 5 \text{ ml})$ . The residue was dissolved in dichloromethane (10 ml) and the solution was chromatographed over silica gel column (60–120 mesh). An orange-brown band was eluted by C<sub>7</sub>H<sub>9</sub>–MeCN (9:1) mixture. The eluted solution on evaporation in vacuo gave pure compound. Orange-brown compound was isolated in 45% yield.

The greenish-brown product is the coupled product,  $Pt(papm-N-C_6H_5)Cl$ . All other complexes were prepared similarly; yield, 40–55%. Calc. for  $C_{16}H_{12}N_5ClPt$  (5a): C, 38.05; H, 2.38; N, 13.87. Found: C, 38.12; H, 2.31; N, 13.73%. Calc. for C<sub>17</sub>H<sub>14</sub>N<sub>5</sub>ClPt (6a): C, 39.34; H, 2.70; N, 13.50. Found: C, 39.23; H, 2.61; N, 13.41%. Calc. for C<sub>17</sub>H<sub>14</sub>N<sub>5</sub>ClPt (7a): C, 39.34; H, 2.70; N, 13.50. Found: C, 39.24; H, 2.62; N, 13.40%. Calc. for C<sub>17</sub>H<sub>14</sub>N<sub>5</sub>ClPt (8a): C, 39.34; H, 2.70; N, 13.50. Found: C, 39.20; H, 2.60; N, 13.39%. Calc. for C<sub>17</sub>H<sub>14</sub>N<sub>5</sub>OClPt (9a): C, 38.16; H, 2.62; N, 13.09. Found: C, 38.00; H, 2.56; N, 13.20%. Calc. for C<sub>16</sub>H<sub>11</sub>N<sub>5</sub>Cl<sub>2</sub>Pt (**10a**): C, 35.62; H, 2.04; N, 12.98. Found: C, 35.48; H, 2.11; N, 12.86%. Calc. for C<sub>17</sub>H<sub>14</sub>N<sub>5</sub>ClPt (**5b**): C, 39.34; H, 2.70; N, 13.50. Found: C, 39.22; H, 2.66; N, 13.42%. Calc. for C<sub>18</sub>H<sub>16</sub>N<sub>5</sub>ClPt (6b): C, 40.56; H, 3.00; N, 13.14. Found: C, 40.43; H, 2.94; N, 13.02%. Calc. for C<sub>18</sub>H<sub>16</sub>N<sub>5</sub>ClPt (7b): C, 40.56; H, 3.00; N, 13.14. Found: C, 40.37; H, 2.84; N, 13.05%. Calc. for C<sub>18</sub>H<sub>16</sub>N<sub>5</sub>ClPt (**8b**): C, 40.56; H, 3.00; N, 13.14. Found: C, 40.41; H, 2.89; N, 13.00%. Calc. for C<sub>18</sub>H<sub>16</sub>N<sub>5</sub>OClPt (**9b**): C, 39.38; H, 2.91; N, 12.76. Found: C, 39.15; H, 2.82; N, 12.64%. Calc. for C<sub>17</sub>H<sub>13</sub>N<sub>5</sub>Cl<sub>2</sub>Pt (10b): C, 36.88; H, 2.35; N, 12.65. Found: C, 36.74; H, 2.28; N, 12.54%. Calc. for  $C_{16}H_{11}N_5Cl_2Pt$  (5c): C, 35.62; H, 2.04; N, 12.98. Found: C, 35.53; H, 2.10; N, 12.77%. Calc. for C<sub>17</sub>H<sub>13</sub>N<sub>5</sub>Cl<sub>2</sub>Pt (6c): C, 36.88; H, 2.35; N, 12.65. Found: C, 36.75; H, 2.31; N, 12.53%. Calc. for C<sub>17</sub>H<sub>13</sub>N<sub>5</sub>Cl<sub>2</sub>Pt (**7c**): C, 36.88; H, 2.35; N, 12.65. Found: C, 36.69; H, 2.28; N, 12.54%. Calc. for C<sub>17</sub>H<sub>13</sub>N<sub>5</sub>Cl<sub>2</sub>Pt (8c): C, 36.88; H, 2.35; N, 12.65. Found: C, 36.74; H, 2.29; N, 12.52%. Calc. for C<sub>17</sub>H<sub>13</sub>N<sub>5</sub>OCl<sub>2</sub>Pt (9c): C, 35.85; H, 2.28; N, 12.30. Found: C, 35.71; H, 2.20; N, 12.19%. Calc. for C<sub>16</sub>H<sub>10</sub>N<sub>5</sub>Cl<sub>3</sub>Pt (10c): C, 36.47; H, 1.74; N, 12.20. Found: C, 36.55; H, 1.81; N, 12.23%.

#### 2.4. X-ray structure determination

The X-ray quality single crystal of Pt(papm-N–C<sub>6</sub>H<sub>4</sub>– Me-*m*)Cl (**7a**) was grown by slow diffusion of hexane into dichloromethane solution of the complex at 298 K. The crystal size was  $0.25 \times 0.11 \times 0.08 \text{ mm}^3$ . X-ray diffraction data were collected at 293(2) K with the Siemens SMART CCD using graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Unit cell parameters were determined from least-squares refinement of setting angles with 2 $\theta$  in the range 4–57°. A summary of the crystallographic data and structure refinement parameters are given in Table 1.

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Table 1 Crystallographic data of Pt(papm-N-C<sub>4</sub>H<sub>4</sub>-Me-m)Cl (7a)

C <sub>17</sub> H <sub>14</sub> ClN <sub>5</sub> Pt
517.88
$0.25 \times 0.11 \times 0.08$
monoclinic
$P2_{1/n}$
7.459(1)
16.899(2)
13.117(18)
92.497(3)
1652.0(4)
4
295(2)
0.71073
4–57
9981
2522
$-9 \leq h \leq 9, -21 \leq k \leq 20, 20 \leq l \leq -15$
2.082
8.662
0.0303
0.0569
0.904

 $I > 2\sigma(I)\%$ .

 $R = \sum |F_{\rm o} - F_{\rm c}| / \sum F_{\rm o}$ 

 $\sum w(F_o^4) \Big]^{1/2}, w = 1/[\sigma^2(F_o)^2 + (0.0283P)^2],$  where  $wR = \left| \sum (F_{\rm o}^2 - F_{\rm c}^2)^2 \right|$  $=(F_{\rm o}+^{\rm L}2F_{\rm c}^2)/3.$ 

Goodness-of-fit is defined as  $[w|F_0 - F_c|/(n_0 - n_y)]^{1/2}$ , where  $n_0$  and  $n_y$ denotes the numbers of data and variables, respectively.

Of 9981 collected reflections 2522 unique reflections were recorded using  $\omega$ -scan technique. Data were corrected for L<sub>p</sub> effects and for linear decay. Semi-empirical absorption corrections based on  $\psi$ -scans were applied. The structure was solved by direct method using SHELX-97 and successive difference Fourier syntheses [11]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using riding model. In the final difference Fourier maps the residual maximum and minimum were 1.312 and  $-0.627 \text{ e} \text{ Å}^{-3}$ . All calculations were carried out using the shelx-97.

## 2.5. Molecular orbital calculations

Extended Huckel molecular orbital calculation [12,13] was performed using the ICON software package originally developed by Hoffmann. The atomic parameters were taken from the crystallographic data (Table 1). For drawing figures and graphic package 'cacao' was used.

# 3. Results and discussion

## 3.1. Synthesis and formulation

2-(Arylazo)pyrimidines (aapm, 3) are N,N'-chelators. The reaction of aapm with  $K_2PtCl_4$  in MeCN-H<sub>2</sub>O (1:1, v/v) has yielded orange-red crystalline product,  $Pt(aapm)Cl_2$  (4), in the yield of 45–50%.

The reaction between Pt(aapm)Cl<sub>2</sub> and ArNH<sub>2</sub> in 1:1 ratio in MeCN suspension under refluxing condition has yielded greenish brown product (Eq. (1)). This has been identified as amine coupled product abbreviated Pt(aapm-N-C<sub>6</sub>H<sub>4</sub>-R'Cl) [where, R' = H (5), o-Me (6) m-Me (7), p-Me (8), p-OMe (9), p-Cl (10)].



The arylamination takes place at the *ortho* position (at the C(8)-H bond) to azo function in the pendant aryl ring (Bring) of aapm and forms platinum(II) complex of tridentate N, N', N''-chelating ligand (N, N', N'') refer to N(pyrimidine), N(azo) and N(arylamine), respectively). Microanalytical data support the composition of the complexes (see Section 2).

# 3.2. Molecular structure of $Pt(papm-N-C_6H_4-Me-m)Cl$ (7a)

A molecular view of Pt(papm-N-C<sub>6</sub>H<sub>4</sub>-Me-m)Cl is shown in Fig. 1 and the selected bond parameters are listed in Table 2. The crystallographic asymmetry unit contains 24 non-hydrogen atoms of which 17 lie in a plane nearly perpendicular to crystallographic *c*-axis. These atoms comprise the two chelate rings, the aromatic groups fused to them and the Pt and Cl-atoms. The atomic groups Pt, N(1), C(4), N(3), N(4), and Pt, N(4), C(5), C(10), N(5) constitute two chelate planes (mean deviation <0.04 Å) and they are nearly planar (dihedral angle 1.8°). The chelate bite angles are N(1)-Pt-N(4), N(4)-Pt-N(5), 79.3°(4) and  $81.8^{\circ}(8)$ . The Pt atom lies within the square plane defined by N<sub>3</sub>Cl donor centers (deviation, <0.01). The pendant *m*-tolyl ring is inclined at an angles of 64.35° with the principal plane of 17 atoms. There are three types of Pt-N bonds: Pt–N(pyrimidine) [Pt–N(1)], 2.013(3) A; Pt–N(azo) [Pt-N(4)], 1.919(9) Å and longest Pt-N(arylamine) [Pt-N(5)], 2.014(9) Å. The shortest Pt-N bond length is Pt-N(1) and longest Pt-N distance is Pt-N(5). The N=N bond length is 1.312(1) Å. The free ligand value of N=N bond is not available but the literature data available in some free arylazoheterocycles suggest that it is nearly 1.25(1) Å [14]. The elongation of N=N azo distance is consistent with electron delocalization from metal to ligand fragment [5,6]. A significant back-bone conjugation is also observed in the coordinated anionic ligand. This is viewed from the difference in N(azo)-C(phenyl-B/pyrimidine-C), distances. The N(azo)–C(pyrimidine-C) (N(3)–C(4)), 1.381(4) Å;



Fig. 1. Molecular structure of [Pt(papm-N-C<sub>6</sub>H<sub>4</sub>-Me-*o*)Cl] (7a).

Table 2									
Selected	bond	lengths (Å)	and	angles (°)	of l	Pt(papm	-N-C <sub>6</sub> I	H <sub>4</sub> –Me- <i>n</i>	n)Cl
( <b>7</b> a)									

Bonds	Distances (Å)	Angles	Value (°)
Pt-N(1)	2.013(3)	N(1)-Pt-N(4)	79.3(4)
Pt-N(4)	1.919(9)	N(4)-Pt-N(5)	81.8(8)
Pt-N(5)	2.014(9)	N(1)– $Pt$ – $Cl(1)$	97.0(4)
N(3)–N(4)	1.381(6)	N(5)-Pt-Cl(1)	101.7(4)
C(4) - N(1)	1.381(6)	N(1) - Pt - N(5)	161.1(8)
C(4)–N(3)	1.381(6)	N(4)-Pt-Cl(1)	176.3(8)
Pt–Cl(1)	2.291(2)	Pt-N(1)-C(4)	110.2(6)
C(5)–N(4)	1.346(6)	Pt-N(5)-C(10)	111.3(50)
C(10)–N(5)	1.332(8)	Pt-N(4)-C(5)	116.4(1)
C(11)–N(5)	1.441(1)		
N(1)-C(1)	1.332(8)		
N(2) - C(4)	1.322(1)		
N(2)-C(3)	1.333(3)		
C(2) - C(3)	1.361(9)		
C(1) - C(2)	1.353(8)		
C(5)–C(6)	1.411(7)		
C(6) - C(7)	1.350(8)		
C(7)–C(8)	1.419(9)		
C(8)–C(9)	1.367(6)		
C(9)-C(10)	1.435(1)		

N(azo)–C(phenyl-B) (N(4)–C(5)), 1.346(6) Å are noticeably shorter than that of N(imino)–C(phenyl-A) (N(5)–C(11)), 1.441(1) Å. More interesting feature is the ring C–C distance in B-ring C(5)–C(10); they have been elongated by 0.02–0.1 Å from that of ring-A and ring-C parameters. This leads us to conclude that the ring-B is more efficiently involve in back bone conjugation than that of other rings (A and C) with the coordinated Pt(II). This is also supported by the shortening of Pt–N(4) distance (1.919(9) Å) with reference to Pt–N(1), 2.013(3) and Pt–N(5), 2.014(9) Å. The bond parameters and backbone conjugation are also comparable with the literature data [5,6]. A hydrogen bonded cyclic dimmer is observed through  $C(12)-H(12)\cdots N(3)$  C(12)-H, 0.93 Å;  $H(12)\cdots N(3)$ , 2.598(7) Å;  $C(12)\cdots N(3)$ , 2.598(7) Å and  $\angle C(12)-H(12)-N(3)$ , 165.53°. Dimers are then arranged compactly to provide a platform for  $\pi-\pi$  interaction between pyrimidine (acceptor) of one unit with azophenyl ring (donor) of adjacent unit (distance between Cg(4) of pyrimidine  $\cdots$ Cg(3) of azophenyl equals to 3.735(5) Å) and a supramolecular ladder is formed (Fig. 2).



Fig. 2. Supramolecular ladder constituted via  $\pi \cdots \pi$  interaction between pyrimidine and azoaryl in hydrogen-bonded cyclic dimers.

## 3.3. Spectra and bonding

The presence of two v(Pt-Cl) stretches at 340 and  $300 \text{ cm}^{-1}$  in Pt(aapm)Cl<sub>2</sub> is in agreement with *cis*-PtCl<sub>2</sub> configuration [15] while a single transmission at 300- $320 \text{ cm}^{-1}$  is observed in the amine coupled products (5– 10). The sharp single band at  $1400-1415 \text{ cm}^{-1}$  in free ligand is referred to v(N=N) [5]. This has been shifted to lower frequency, 1360–1375 cm<sup>-1</sup> in Pt(aapm)Cl<sub>2</sub> and supports the coordination of azo-N to Pt(II). In Pt(aapm-N-Ar)Cl (5–10) the v(N=N) appears at 1260–1290 cm<sup>-1</sup>; this significant reduction in azo frequency may be due to charge delocalization from N-Ar fragment (ring A) to the azo function intramolecularly (vide infra).

In chloroform solution of Pt(aapm)Cl<sub>2</sub> the absorption bands are observed at 250-550 nm. On comparison with free ligand data we may conclude that the transitions <400 nm are intraligand charge transfer transitions [10]. The spectral pattern have changed abruptly in Pt(aapm-N-Ar)Cl (5-10) and exhibit multiple transitions in the visible to NIR region (500-1250 nm). The spectral data are collected in Table 3 and a representative figure is shown in Fig. 3. The low energy spectral band in Pt(aapm-N-Ar)Cl, is associated with HOMO  $\rightarrow$  LUMO (62a  $\rightarrow$  63a) charge transfer [5,6]. The MOs are calculated by EHMO approximation using X-ray crystallographic parameter of  $Pt(papm-N-C_6H_4-Me-m)Cl$  (7a). The HOMO (62a) receives 68% azoaryl group and 26% metal orbitals and

Table 3

Solution spectral <sup>a</sup> and cyclic voltammetric <sup>b</sup> data

Compounds	UV–Vis–NIR spectra $\lambda_{max}/nm(10^{-3}\epsilon/dm^3 mol^{-1} cm^{-1})$	Cyclic voltammetric data <sup>b</sup> $E_{1/2}/V (\Delta E_p/mV)$					
		$E_{1/2}^{1}$	$-E_{1/2}^2$	$-E_{1/2}^3$	$-E_{1/2}^4$		
$Pt(papm)Cl_2$ (4a)	541(1.10), 408(4.40), 324(2.97)		0.12(100)	1.14(180)			
$Pt(p-tapm)Cl_2$ (4b)	528(1.42), 405(4.82), 328(3.08)		0.17(120)	1.20(200)			
$Pt(p-Clpapm)Cl_2$ (4c)	546(0.97), 415(3.82), 335(4.52)		0.09(100)	1.05(200)			
$Pt(papm-N-C_6H_5)Cl (5a)$	1222(0.86) <sup>c</sup> , 1046(1.93), 902(2.11) 806(1.58) <sup>c</sup> , 736(0.88) <sup>c</sup> , 550(1.18) <sup>c</sup> , 472(4.39), 412(6.03), 358(8.91)	1.113(100)	0.314(70)	0.778(170)	1.085(180)		
$Pt(papm-N-C_6H_4-Me-o)Cl (6a)$	1216(1.08) <sup>c</sup> , 1038(2.46), 900(2.74), 804(2.66), 758(2.06) <sup>c</sup> , 688(1.15) <sup>c</sup> , 474(5.02) <sup>c</sup> , 418(7.46), 358(11.66)	1.047(150)	0.375(105)	0.898(140)	1.264(190)		
Pt(papm-N-C <sub>6</sub> H <sub>4</sub> -Me-m)Cl (7a)	1224(1.40) <sup>c</sup> , 1050(2.90), 906(3.44), 808(2.50) <sup>c</sup> , 738(1.25) <sup>c</sup> , 470(6.16) <sup>c</sup> , 414(8.68), 356(13.15)	1.018(100)	0.388(95)	0.935(160)	1.269(160)		
$Pt(papm-N-C_6H_4-Me-p)Cl (8a)$	1220(1.55), 1052(3.49), 918(3.84), 807(2.79), 740(1.45), 474(6.99) <sup>c</sup> , 420(10.06), 358(15.05)	1.052(76)	0.325(140)	0.870(100)	1.294(170)		
Pt(papm-N-C <sub>6</sub> H <sub>4</sub> -OMe- <i>p</i> )Cl (9a)	1216(1.08) <sup>c</sup> , 1054(3.18), 914(3.47), 811(2.55) <sup>c</sup> , 734(1.24) <sup>c</sup> , 510(3.80) <sup>c</sup> , 456(7.98), 428(8.38), 356(12.85)	1.009(95)	0.413(100)	0.945(170)	1.448 <sup>d</sup>		
$Pt(papm-N-C_6H_4-Cl-p)Cl (10a)$	$1220(1.08)^{\circ}, 1060(3.05), 892(3.29), 800(2.50)^{\circ}, 732(1.20)^{\circ}, 540(1.10)^{\circ}, 470(4.21), 410(5.96), 356(10.43)$	1.127(100)	0.304(120)	0.746(160)	1.018(180)		
$Pt(p-tapm-N-C_6H_5)Cl$ (5b)	1160(0.92) <sup>c</sup> , 1050(2.05), 928(1.23) <sup>c</sup> , 840(2.60) <sup>c</sup> , 738(1.89), 556(1.23) <sup>c</sup>	1.018(90)	0.409(110)	0.904(140)	1.236(175)		
$Pt(p-tapm-N-C_6H_4-Me-o)Cl~(\mathbf{6b})$	1164(1.07) <sup>c</sup> , 1020(2.15), 920(1.35) <sup>c</sup> , 830(2.22), 730(1.42), 520(5.62)	1.011(90)	0.438(100)	0.930(120)	1.227(190)		
$Pt(p-tapm-N-C_6H_4-Me-m)Cl (7b)$	1156(1.22), 1018(2.24), 906(1.56), 828(2.19) <sup>c</sup> , 732(1.40), 518(5.08) <sup>c</sup>	1.010(95)	0.430(100)	0.925(130)	1.240(190)		
$Pt(p-tapm-N-C_6H_4-Me-p)Cl (8b)$	$1166(0.97), 1055(1.88), 933(2.39)^{\circ}, 852(1.70), 746(0.91), 560(1.50), 485(4.61)$	1.007(80)	0.450(100)	0.923(120)	1.253(170)		
$Pt(p-tapm-N-C_6H_4-OMe-p)Cl (9b)$	1154(0.94)°, 1016(1.53), 912(1.69)°, 872(2.45)°, 736(1.09), 442(6 39)	0.968(90)	0.474(110)	0.938(140)	1.532 <sup>d</sup>		
$Pt(p-tapm-N-C_6H_4-Cl-p)Cl (10b)$	1174(1.08), 1032(2.10), 910(1.45) <sup>c</sup> , 830(2.45), 755(1.57), 530(5.36).	1.086(100)	0.383(100)	0.801(95)	1.208(160)		
$Pt(p-Clpapm-N-C_6H_5)Cl (5c)$	$1198(0.62)^{\circ}, 1028(1.32)^{\circ}, 908(1.46), 729(1.40), 740(1.51), 768(1.99)^{\circ}, 482(4.53)^{\circ}$	1.117(85)	0.405(100)	0.749(120)	1.159(150)		
$Pt(p-Clpapm-N-C_6H_4-Me-o)Cl (\mathbf{6c})$	1198(0.64), 1044(1.19), 930(1.45), 745(1.40), 568(1.95), 500(3.64), 445(8.95)	1.026(90)	0.375(110)	1.040(100)	1.136(190)		
$Pt(p-Clpapm-N-C_6H_4-Me-m)Cl (7c)$	1200(0.79), 1048(1.35), 935(1.55), 740(1.50), 570(2.00), 500(3.50), 440(9.05)	1.031(80)	0.368(120)	1.048(90)	1.127(170)		
Pt( <i>p</i> -Clpapm-N-C <sub>6</sub> H <sub>4</sub> -Me- <i>p</i> )Cl (8c)	1208(0.71) <sup>c</sup> , 1040(1.40), 920(1.66), 740(1.50), 572(2.03), 490(4.85)	1.026(100)	0.375(100)	1.040(130)	1.136(160)		
$Pt(p-Clpapm-N-C_6H_4-OMe-p)Cl (9c)$	1200(0.68), 1060(2.04), 950(2.89), 805(2.83), 745(1.65°), 565(1.34), 475(5.32)	0.938(90)	0.394(110)	0.823(130)	1.359 <sup>d</sup>		
$Pt(p-Clpapm-N-C_6H_4-Cl-o)Cl (10c)$	1224(1.06), 1066(2.10), 910(3.05), 810(2.42), 740(1.22) <sup>c</sup> , 560(1.26), 480(5.42)	1.122(90)	0.300(100)	0.728(110)	1.048(140)		

Solvent CHCl<sub>3</sub>.

b Solvent MeCN, supporting electrolyte [nBu<sub>4</sub>N][ClO<sub>4</sub>], Pt-disk milli working electrode, Pt-wire auxiliary electrode, reference electrode SCE, at 298 K.

Shoulder. <sup>d</sup>  $E_{\rm pc}$ .



Fig. 3. Electronic spectra of  $Pt(p-tapm)Cl_2$  (4b) (....) and  $Pt(p-tapm-N-C_6H_4-Me-m)$  (7b) (—) in CHCl<sub>3</sub>.

the LUMO (63a) shares 33% azo and 31% azoaryl character. Other transitions may be characterized to HOMO – 1 (61a)  $\rightarrow$  LUMO (63a), HOMO – 2 (60a)  $\rightarrow$  LUMO (63a), HOMO (62a)  $\rightarrow$  LUMO + 1 (64a) etc. The effect of substituent R (at B-ring of arylazopyrimidine) and R' (at A-ring of N–Ar) are also observed. Both steric and electronic effects of X influence the energy of HOMOs. The electron donating substituents destabilize the MOs and thus energy of HOMO is increased. The *o*-Me provides greater steric effect compared to other and influences the HOMO. The

Table 4  $^1\rm H$  NMR spectral data of Pt(aapm)Cl\_2 (4) and Pt(aapm-N–Ar)Cl (5–10) in CDCl\_3

substituent R (at B-ring) influences more prominently to the LUMOs and the band maxima ( $\lambda_{max}$ ) follow the sequence *p*-Clpapm < papm < *p*-tapm. This is expected in view of the electronic property of *p*-Me and *p*-Cl groups.

In the <sup>1</sup>H NMR spectra the signals were assigned on the basis of chemical shifts, spin–spin interaction and their effect on substitution and on comparison with the spectra of Pd(aapm)Cl<sub>2</sub> [5]. The spectral data are given in Table 4. The downfield portion of the spectra corresponds to pyrimidine-H (4-H–6-H, C-ring) [10] and upperfield portion refers to azo–aryl-protons, 8-H–12-H (B-ring). The binding of aapm with Pt(II) is supported by the appearance of spin–spin coupling [16] of <sup>1</sup>H (4-H) and <sup>195</sup>Pt (33.1%) and the coupling constant is <sup>3</sup>J<sub>Pt–H</sub> is 20–24 Hz.

The NMR spectra of 5-10 resemble those of their Pdcontaining analogues, Pd(aapm-N-Ar)Cl, [5] and are consistent with their proposed structures. A strong <sup>195</sup>Pt-<sup>1</sup>H (J = 21-27 Hz) was observed to the pyrimidine 4H resonance (Fig. 4). The effect of substituents  $R' (R'-C_6H_4-N-)$ on the signal movement is in accordance with the electronic effect of the group [16,17]. A significant observation is that azo-aryl protons (B-ring) (9-H-12-H) in Pt(aapm-N- $C_6H_4$ -R'Cl) are up field shifted by 0.5–1.2 ppm relative to Pt(aapm)Cl<sub>2</sub> while pyrimidine protons (C-ring protons, 4-H-6-H) are shifted to up field side by 0.2-0.5 ppm compared to the parent complex, Pt(aapm)Cl<sub>2</sub>. Azopyrimidine function is electron deficient while N-aryl ring (ring A) is  $\sigma$ -donor and may support intramolecular charge transfer transition. This may be reason for up field shifting of arylazopyrimidine protons (4-H-12-H) in the fused compound.

Compound	δ/ppm (J/Hz)														
	4-H <sup>a</sup>	5-H <sup>b</sup>	6-H <sup>a</sup>	8-H <sup>a</sup>	9-H	10-H	11-H	12-H <sup>a</sup>	14-H <sup>a</sup>	15-H	16-H	17 <b>-</b> H	18-H <sup>a</sup>	R	$\mathbf{R}^{\prime}$
4a	8.41(6.0)	7.63(7.0)	8.19(7.0)	7.26(7.0)	7.12 <sup>c</sup>	7.12 <sup>c</sup>	7.12 <sup>c</sup>	7.26 <sup>°</sup>							
4b	8.36(6.0)	7.60(7.0)	8.17(7.0)	7.11(7.0)	$6.86^{a}(7.0)$		$6.86^{a}(7.0)$	7.11(7.0)						2.44	
4c	8.44(6.0)	7.60(7.0)	8.28(7.0)	7.34(7.0)	$7.44^{a}(8.0)$		$7.44^{a}(8.0)$	7.34(7.0)							
5a	8.04(6.0)	6.80(7.0)	8.29(6.0)		$6.21^{a}(7.0)$	6.99 <sup>c</sup>	6.99°	6.69(8.0)	7.28(8.0)	6.62 <sup>c</sup>	6.62 <sup>c</sup>	6.62 <sup>c</sup>	7.28(8.0)		
6a	8.02(6.0)	6.74(7.0)	8.26(6.0)		$6.18^{a}(7.0)$	6.93°	6.93°	6.67(8.0)		$6.40^{a}(7.0)$	6.58 <sup>°</sup>	6.58°	7.22(8.0)		2.67
7a	8.04(6.0)	6.74(7.0)	8.27(6.0)		$6.19^{a}(7.0)$	6.90 <sup>°</sup>	6.90°	6.67(8.0)	6.92 <sup>d</sup>		6.39 <sup>c</sup>	6.39 <sup>c</sup>	7.20(7.0)		2.56
8a	8.00(6.0)	6.72(7.0)	8.25(6.0)		$6.17^{a}(7.0)$	6.88 <sup>c</sup>	6.88°	6.65(8.0)	7.20(9.0)	$6.39^{a}(8.0)$		$6.39^{a}(8.0)$	7.20(9.0)		2.31
9a	8.00(6.0)	6.73(6.0)	8.24(6.0)		$6.14^{a}(7.0)$	6.86 <sup>c</sup>	6.86 <sup>c</sup>	6.63(8.0)	7.15(9.0)	$6.34^{a}(9.0)$		$6.34^{a}(9.0)$	7.15(9.0)		3.81
10a	8.07(6.0)	6.81(7.0)	8.33(6.0)		$6.30^{a}(7.0)$	7.06 <sup>c</sup>	7.06 <sup>c</sup>	6.77(7.0)	7.38(8.0)	$6.82^{a}(7.0)$		$6.82^{a}(7.0)$	7.38(8.0)		
5b	8.03(6.0)	6.77(7.0)	8.20(6.0)		6.04 <sup>a</sup>		6.71 <sup>a</sup> (9.0)	6.60(7.0)	7.35(8.0)	6.60 <sup>c</sup>	6.60 <sup>c</sup>	6.60 <sup>c</sup>	7.35(8.0)	2.42	
6b	8.04(6.0)	6.76(7.0)	8.18(6.0)		6.02 <sup>d</sup>		$6.69^{a}(7.0)$	6.58(7.0)		$6.37^{a}(7.0)$	6.60 <sup>c</sup>	6.60 <sup>c</sup>	7.20(8.0)	2.44	2.60
7b	8.05(6.0)	6.75(7.0)	8.16(6.0)		6.04 <sup>d</sup>		$6.70^{a}(7.0)$	6.60(7.0)	6.90 <sup>d</sup>		6.38 <sup>c</sup>	6.38 <sup>c</sup>	7.18(7.0)	2.42	2.50
8b	8.04(6.0)	6.70(7.0)	8.22(7.0)		$6.00^{d}$		$6.68^{a}(7.0)$	6.60(7.0)	7.24(7.0)	$6.42^{a}(7.0)$		$6.42^{a}(7.0)$	7.24(7.0)	2.42	2.33
9b	8.00(6.0)	6.71(7.0)	8.20(7.0)		6.03 <sup>d</sup>		$6.70^{a}(7.0)$	6.62(7.0)	7.19(8.0)	$6.35^{a}(9.0)$		$6.35^{a}(9.0)$	$7.19^{a}(8.0)$	2.44	3.84
10b	8.05(6.0)	6.80(6.0)	8.35(6.0)		6.08 <sup>d</sup>		$6.66^{a}(7.0)$	6.60(7.0)	7.42(8.0)	$6.35^{a}(9.0)$		$6.78^{a}(7.0)$	$7.42^{a}(8.0)$	2.45	
5c	8.08(6.0)	6.88(7.0)	8.35(6.0)		6.42 <sup>d</sup>		$7.20^{a}(8.0)$	7.07(7.0)	6.88(7.0)	6.54°	6.54	6.54°	6.88(7.0)		
6c	8.06(6.0)	6.86(7.0)	8.33(6.0)		6.40 <sup>d</sup>		$7.17^{a}(8.0)$	7.09(7.0)		$6.44^{a}(7.0)$	6.60	6.60 <sup>c</sup>	7.38(8.0)		2.69
7c	8.06(6.0)	6.87(7.0)	8.32(6.0)		6.40 <sup>d</sup>		$7.79^{a}(7.0)$	7.06(7.0)	7.23 <sup>d</sup>	. ,	6.46	6.46 <sup>c</sup>	7.34(8.0)		2.58
8c	8.09(6.0)	6.82(6.0)	8.31(6.0)		6.39 <sup>d</sup>		$7.16^{a}(7.0)$	7.09(7.0)	6.69(7.0)	$6.17^{a}(7.0)$		$6.17^{a}(7.0)$	6.69(7.0)		2.33
9c	8.05(6.0)	6.80(7.0)	8.36(6.0)		6.33 <sup>d</sup>		$7.13^{a}(7.0)$	7.01(7.0)	6.65(7.0)	$6.12^{a}(7.0)$		$6.12^{a}(7.0)$	6.65(7.0)		3.82
10c	8.10(6.0)	6.84(7.0)	8.35(6.0)		6.37 <sup>d</sup>		7.16(7.0)	7.05(7.0)	7.22(7.0)	6.80 <sup>a</sup> (7.0)		6.80 <sup>a</sup> (7.0)	7.22(7.0)		

<sup>a</sup> Doublet.

<sup>b</sup> Triplet.

<sup>c</sup> Multiplet.



Fig. 4. <sup>1</sup>H NMR spectrum of Pt(*p*-Clpapm–N–C<sub>6</sub>H<sub>4</sub>–Me-*p*)Cl (8c) in CDCl<sub>3</sub> at 298 K.

### 3.4. Electrochemistry

The electrochemical properties of Pt(aapm)Cl<sub>2</sub> (4) and Pt(aapm-N–Ar)Cl (5–10) have been investigated by cyclic voltammetry. The results are given in Table 3 and a representative voltammogram is shown in Fig. 5. Pt(aapm)Cl<sub>2</sub> exhibit two quasireversible ( $\Delta E_p > 100 \text{ mV}$ ) reduction couples at negative to SCE and have assigned to reduction of azo group [13,18,19]. Pt(aapm-N–Ar)Cl show four successive redox couples. One redox couple appears at positive side to SCE in the potential range 0.8–1.1 V and oxidative in nature. This redox response is quasireversible in nature which is supported from  $\Delta E_p \ge 80 \text{ mV}$  ( $\Delta E_p = [E_{pa} - E_{pc}]$ , peak-to-peak separation). One electron nature of the redox couple is supported from  $i_{pa}/i_{pc}$  ( $\approx 1.0$ ) and differential pulse voltammetry (DPV). Platinum(II) unlike palladium



Fig. 5. Cyclic voltammogram of  $Pt(p-tapm-N-C_6H_4-Me-m)Cl$  (7b) in MeCN.

is irreversibly oxidized to platinum(IV) by 2e stoichiometry [6,18]. The redox responses at positive potential to SCE may be corresponding to electron extraction from HOMO (62a), which has major share from N–Ar group (68%). Thus Eq. (2) is justified.

Three redox responses at negative to SCE are reductive in nature. The reductions correspond to sequential electron feeding at LUMOs. There are four successive redox accessible levels in -N=N-C=N- group (Eqs. (3)–(6)). The LUMO (63a) shares 33% azo (-N=N-) contribution and thus electron may be localized at azo center. So the reductions may be ascribed by Eqs. (3)–(6).



$$[-N=N-C=N-] \xrightarrow{+e} [-N=N-C=N-]^{-}$$
(3)

$$[-N = N - C = N - N^{2-} \xrightarrow{+e} [-N - N - C = N^{3-}]^{3-}$$
(5)

$$\left[-N-N-C-N-\right]^{3-1} \xrightarrow{+e} \left[-N-N-C-N-\right]^{4-} \tag{6}$$

#### 4. Conclusion

 $Pt(arylazopyrimidinie)Cl_2$  have been reacted with arylamine (ArNH<sub>2</sub>). The coupled products have been characterized by spectroscopic and electrochemical studies. In one case the structural confirmation has been carried out by X-ray diffraction study. Crystallographic parameters have been used to EHMO calculation. The spectral and electrochemical results have been correlated with MO calculation and compared with the results of palladium complexes.

#### 5. Supplementary materials

Crystallographic data for the structure  $Pt(papm-N-C_6H_4-Me-m)Cl$  (7a) have been deposited with the Cam-

bridge Crystallographic Data center, CCDC No. 184679. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk or www: htpp://www.ccdc.cam.ac.uk.

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