Asian Journal of Chemistry; *Vol. 31, No. 2 (2019), 287-292*

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2019.21584

Hydrolysis of -N=CH- Bond in 2-Salicylidene-4-aminophenyl benzimidazole by Palladium(II)

M. CHANDRAKALA[1,2,*]

[1]Department of Chemistry, Bangalore Institute of Technology, Bengaluru-560004, India
[2]Department of Chemistry, V.V. Pura College of Science, K.R. Road, Bengaluru-560004, India

*Corresponding author: E-mail: mchandrakala.kum@gmail.com

Received: 16 July 2018; *Accepted*: 31 August 2018; *Published online*: 31 December 2018; AJC-19196

The Schiff base, 2-salicylidene-4-aminophenyl benzimidazole (**I**, SAPbzlH) in ethanolic medium reacts with palladium(II) in acidic medium (HCl/HBr) and coordinated SAPbzlH undergoes hydrolysis at -N=CH- bond to yield salicylaldehyde and square planar complexes having composition $[Pd(C_{13}H_{11}N_3)_2X_2]·2HX$ (**II**) (X = Cl, Br). The obtained complexes have been characterized by elemental analysis, atomic absorption spectra, infrared, electronic and extensive utility of NMR. Possible mechanism for the hydrolysis of coordinated 2-salicylidene-4-aminophenyl benzimidazole (SAPbzlH) has been proposed.

Keywords: Schiff base, Divalent palladium, Correlation spectroscopy, Hydrolysis.

INTRODUCTION

Transition metal complexes containing N-heterocycles have attracted considerable attention over several years, in view of their catalytic activity, biological importance, interesting spectral, magnetic and structural aspects [1-13]. Rosenberg *et al*. [14] have demonstrated a remarkable chemotherapeutic potential of *cis*-$Pt(NH_3)Cl_2$ (cisplatin) in a large variety of human cancers [15,16]. The replacement of ammonia by other amines, such as, cyclopentylamine and cyclohexylamine in cisplatin have shown higher therapeutic indices [17,18]. Nevertheless these drugs suffer from drawbacks of low water solubility, high nephrotoxicity and low activity against gastrointestinal tumors [19]. Coordination geometry and complex formation processes of palladium(II) are very similar to those of platinum(II). As a consequence palladium(II) ions are frequently employed to mimic the binding properties of various platinum(II) species.

Based on this, Gill *et al*. [19] have reported several palladium complexes with coordinated bidentate amine ligands that have exhibited anticancer activities comparable to or greater than cisplatin. Large amount of work has been performed on the equilibrium constant studies of palladium(II) complexes with aliphatic amines [20-22]. *N*-heterocycles act as σ-donors and can also function as effective π-acceptors. This will enhance mechanism of complex formation with DNA subunits that are the principal targets in chemotherapy of tumors [23,24]. Such enormous importance of palladium complexes, prompted us to initiate study on other palladium complexes with *N*-heterocycles, such as 2-salicylidene-4-aminophenyl benzimidazole (SAPbzlH).

The Schiff base, 2-salicylidene-4-aminophenyl benzimidazole (SAPbzlH) in ethanolic medium undergoes hydrolysis at -N=CH- bond in acid medium (HCl/HBr) in the presence of Pd^{2+} ions to yield 4-aminophenyl benzimidazole (4-APbzlH) and salicylaldehyde. 4-Aminophenyl benzimidazole will coordinate with Pd^{2+} ions yielding square planar complexes of the composition $[Pd(C_{13}H_{11}N_3)_2X_2]·2HX$ (X = Cl, Br). These complexes have been characterized by elemental analysis, atomic absorption spectra, conductivity measurements, infrared, electronic and extensive NMR studies. The possible mechanism for hydrolysis of 2-salicylidene-4-aminophenyl benzimidazole (SAPbzlH) has also been proposed.

EXPERIMENTAL

Elemental analyses were carried out using Elementer Vario EI 111 and Carlo Erba-1108 instruments. The IR spectra of the complexes (KBr) were recorded on a Nicolet-impact-400D spectrometer in the range 4000-400 cm^{-1}. The metal content was determined by Atomic Absorption spectrometer ECIL model-

4139. Electronic spectra of SAPbzlH, 4-APbzlH and Pd(II) complexes were recorded in the range 200-600 nm on a Elico SL 159 UV-Visible spectrophotometer in DMSO.

The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of Schiff base and palladium complexes were recorded in DMSO-d_6 on Bruker DRX-500 MHz and Avance-III 400.13 MHz NMR spectrometers equipped with 5 mm inverse detection probe and Z-gradient coil, at ambient temperature with TMS as internal reference. The operating frequencies for ^{1}H and ^{13}C are 500.13, 400.13 for ^{1}H and 125.76 and 100.61 MHz, respectively. The experimental parameters for one-dimensional $^{1}H/^{13}C$ NMR spectra used were spectral width: 17.2/238.0 ppm, data points: 65K/32K, spectral resolution: 0.83/0.17 Hz, number of accumulations: 16/4k, acquisition time: 2.9/0.59 s, relaxation delay: 2/1.5 s and pulse length: 14.1/9.62 μs.

The spectral assignments have been carried out by extensive utilization of 2D TOCSY, ^{1}H-^{13}C HSQC, HMBC, DEPT-135 experiments using standard pulse sequences [25]. For TOCSY the spectral widths of 17.35 ppm were used in both incremented and detected dimensions and the acquisition data size was 320 × 4 K, respectively. Eight transients were accumulated for each of 256 t_1 increments with 2 s relaxation delay. For HSQC experiment, the spectral width of 17.36 ppm in F_2 dimension and 200 ppm in the F_1 dimension were used. The optimized τ delay for efficient transfer of magnetization was set to one bond J_{CH} of 145 Hz. The size of the time domain data was 320 × 5554 points and the number of accumulations was 8 for each t_1 data point with a relaxation delay of 1.5 s between transients. The gradient ratio was maintained at 80:20. In the case of HMBC experiment, the spectral widths used were 2.88 ppm in F_2 dimension and 54.85 ppm in F_1 dimension. The delay responsible for polarization transfer was optimized for ^{13}C-^{1}H coupling of 8 Hz. The size of 2D data was 256 × 2048 points. The number of scans for each increment was 32 and a relaxation delay of 2 s was used between the transients. Gradient ratio was 50:30:40. For DEPT-135 experiments the time domain data size was maintained at 32 K and the number of scans was 500, with a relaxation delay of 2s between each transient.

For 4Q-SQ correlation experiments, indirect dimension pertains to non-selective excitation and detection of 4^{th} quantum and the direct dimension corresponds to single quantum detection. The spectral widths of 3.20 and 12.00 ppm were employed in F_2 and F_1 dimensions, respectively. Eight scans were accumulated for each t_1 increment with a recycle delay of 2 s. The optimized τ delay was 10.6 μs. The 4^{th} quantum signal was detected using the appropriate gradient ratio of 4:1.

The chemicals used for the synthesis of Schiff base and metal complexes were of Merck make. The solvents were distilled prior to their use. The products: *bis*(4-aminophenyl benzimidazole)-dichloropalladium(II) dihydrochloride $[Pd(C_{13}H_{11}N_3)_2Cl_2]\cdot 2HCl$ (**1**); *bis*(4-aminophenyl benzimidazole)dibromopalladium(II) dihydrobromide, $[Pd(C_{13}H_{11}N_3)_2Br_2]\cdot 2HBr$ (**2**).

Synthesis: To an ethanolic solution (10 mL) of palladium(II) chloride (0.11 g; 0.60 mmol) in conc. HCl /conc. HBr (0.5 mL) was added 2-salicylidene-4-aminophenyl benzimidazole (0.38 g; 1.20 mmol) dissolved in ethanol (10 mL). The mixture was refluxed on a steam-bath for about 6 h, during which an orange coloured solid precipitated. The solid was separated from the solution by filtration and washed with ethanol and dried in vacuum (yield: 0.39/0.42 g; 95.0/83.0 %). The filtrate was subjected to Schiff reagent test, which showed the presence of salicyladehyde after work up (solid, m.p. 250 ºC). The solids were analyzed for the formula $Pd(C_{13}H_{11}N_3)_2X_2\cdot 2HX$; X = Cl (**1**), Br (**2**); m.p. > 250 ºC. The test indicated the formation of salicylaldehyde during the reaction; m.p. > 250 ºC. Analytical analysis calcd. (found) % for $C_{26}H_{24}N_6Cl_4Pd$ (**1**): C, 46.65 (46.65); H, 3.58 (4.11); N, 12.55 (11.66); Pd, 15.99 (15.60). IR (KBr, ν_{max}, cm^{-1}): 3419, 3334, 1629, 1604, 1503.

Analytical analysis calcd. (found) % for $C_{26}H_{24}N_6Br_4Pd$ (**2**): C, 36.85 (37.71); H, 2.83 (3.65); N, 9.92 (9.87); Pd, 12.63 (12.10). IR (KBr, ν_{max}, cm^{-1}): 3479, 3280, 1612, 1604, 1502.

RESULTS AND DISCUSSION

Palladium(II) salts in ethanol react with SAPBz1H in molar ratio (1 : 2) in presence of conc. HCl/conc. HBr at refluxing temperature to produce complexes having composition $[Pd(C_{13}H_{11}N_3)_2X_2]\cdot 2HX$ (**II**). The complexes are non-hygroscopic orange coloured crystalline solids. They are soluble in DMF and DMSO and insoluble in other organic solvents. The IR spectrum of Schiff base, SAPbzlH showed a band in the range 3450-3300 cm^{-1} and due to ν(OH) and ν(NH). The spectrum also displayed multiple peaks in the range 3050-2660 cm^{-1} and these are assigned to ν(CH) of phenyl and methine groups. Two bands at 1600 and 1618 cm^{-1} are respectively ascribed to ν(N=CH) and ν(C=C) of C_6H_4 rings. A peak at 1572 cm^{-1} is assigned to ν(N=C) of imidazole ring. A band at 1276 cm^{-1} is attributed to ν(C-O) of phenolic group. The IR spectrum of 4-aminophenyl benzimidazole (4-APbzlH) showed bands at 3439 and 3356 cm^{-1} which are assigned to ν($NH_{2)}$ and ν(NH), respectively. A single and broad band at 1608 cm^{-1} is assigned to both ν(N=C) and ν(C=C). The appearance of a peak at 1502 cm^{-1} is ascribed to bending mode of NH_2.

The IR spectra of palladium complexes displayed minor shifts in the positions of the bands as compared to those of 4-APbzlH. Bands observed at 3419 and 3379 cm^{-1} are assigned to ν(NH_2). The ν(NH) band observed at 3334 and 3280 cm^{-1} has shifted by nearly 160 cm^{-1}. The band around 1620 cm^{-1} is assi-gned to ν(C=N) of benzimidazole moiety and the same is split on coordination to metal ion. These observations have indicated that 4-APbzlH acts as a monodentate ligand bonding through tertiary nitrogen of benzimidazole. The band at 1502 cm^{-1} observed in the spectrum of 4-APbzlH is assigned to NH_2 bending mode and this has not undergone any observable shift in the spectra of the complexes implying that the amino group is not involved in the coordination to the metal ion [25-28]. A band around 1572 cm^{-1} due to νN=C present in the spectrum of Schiff base-2-salicylidene-4-aminophenyl benzimidazole is absent in the spectra of the complexes implying the cleavage of -N=CH- bond.

Electronic spectral studies: The electronic spectrum of SAPbzlH in DMSO exhibits three bands and they are observed at 297 (33,670 cm^{-1}) to 379 (26,385 cm^{-1}) and at 414 (24,154 cm^{-1}) nm. These are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The electronic spectrum of 4-APbzlH in DMSO exhibits three bands and observed at 36832, 26350, 26075 cm^{-1}. These are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

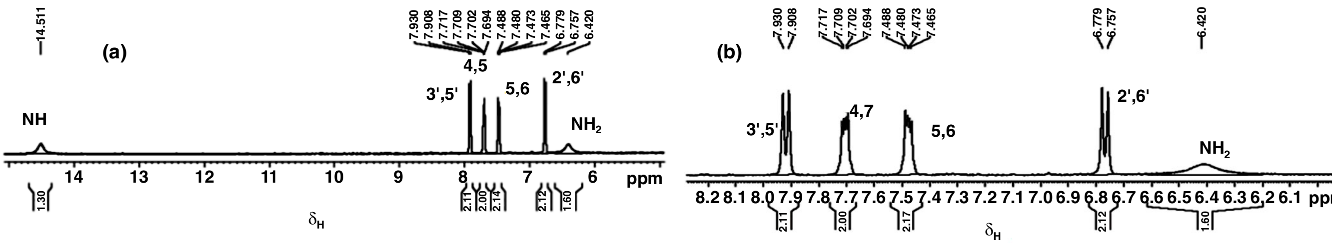


Fig. 1. [1]H NMR spectrum of $[Pd(C_{13}H_{11}N_3)_2Cl_2]·2HCl$ complex and expanded region of pmr spectrum of $[Pd(C_{13}H_{11}N_3)_2Cl_2]·2HCl$ (between 8.2-6.1 ppm)

The spectra of palladium complexes (**II**, Table-1) displayed multiple absorption bands at 23,148 and 23,255 cm^{-1} and these are ascribed to $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively of square planar palladium(II) complexes [29-33].

TABLE-1
ELECTRONIC SPECTRAL DATA OF 4-APbzlH AND PALLADIUM(II) COMPLEXES

Compound	λ, nm ($\bar{\nu}$, cm^{-1})	Transitions
4-APbzlH	271.5 (36, 832) - 379.5 (26, 350) 383.5 (26, 075)	n → π* and π → π*
$[Pd(C_{13}H_{11}N_3)_2Cl_2]·2HCl$	432 (23, 148)	d-d $^1A_{1g} \rightarrow {}^1B_{1g}$
$[Pd(C_{13}H_{11}N_3)_2Br_2]·2HBr$	430 (23, 255)	d-d $^1A_{1g} \rightarrow {}^1B_{1g}$

NMR spectral studies: A detailed study of [1]H and [13]C NMR spectra of SAPbzlH and 4-APbzlH involving various 2D correlation experiments such as, COSY, TOSCY, HSQC, HMBC and 4Q-SQ have been reported earlier [34-36]. In the present investigation, NMR analysis of 4-APbzlH coordinated to palladium ion has been carried out using TOSCY, HSQC, HMBC, DEPT-135 and 4Q-SQ correlated spectra.

The [1]H NMR spectrum (Fig. 1; Table-2) of $[Pd(C_{13}H_{11}N_3)_2Cl_2]·2HCl$ in DMSO displayed two singlets one at δ 14.51 and the other at 6.42 ppm and these are assigned to protons of NH and NH_2, respectively. Two doublets observed at 7.93 ppm (J_{HH}, 8.60 Hz) are assigned to sets to two sets of protons 3′, 5′ and 2′,6′ respectively. Another two multiplets observed at δ 7.70 and 7.47 ppm are assigned to two sets of protons 4, 7 and 5, 6 respectively. Assignments were obaserved based on TOCSY experiment (Fig. 2).

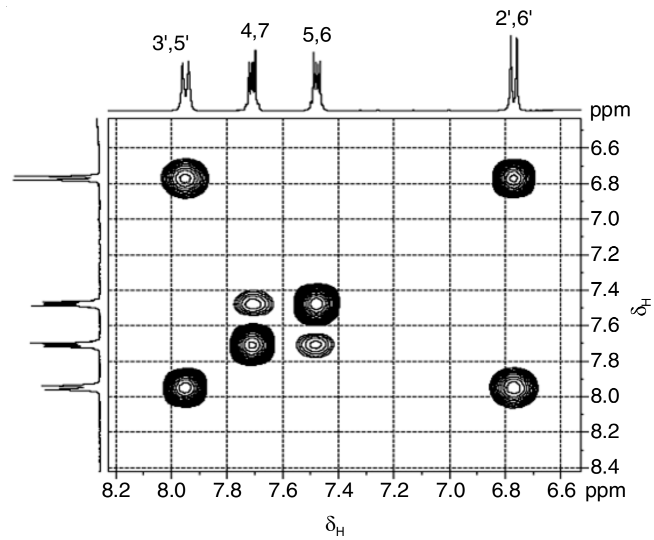


Fig. 2. TOCSY spectrum of $[Pd(C_{13}H_{11}N_3)_2Cl_2]·2HCl$ complex

The [1]H NMR spectrum (Fig. 3) of $[Pd(C_{13}H_{11}N_3)_2Br_2]·2HBr$ in DMSO displayed two singlets one at δ 14.41 ppm

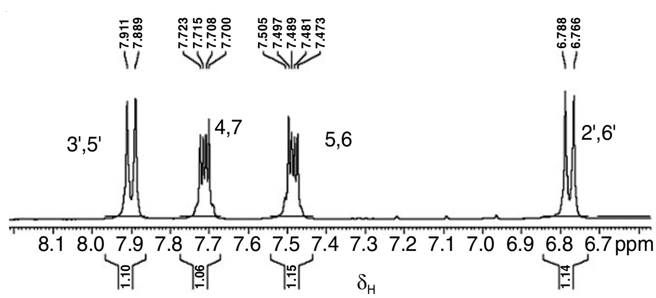


Fig. 3. [1]H NMR spectrum of $[Pd(C_{13}H_{11}N_3)_2Br_2]·2HBr$ complex

and the other at δ 6.41 ppm and are assigned to protons of NH and NH_2, respectively. Two doublets observed at 7.89 ppm (J_{HH}, 8.61 Hz) and the other at 6.77 ppm (J_{HH}, 8.61 Hz) are assigned to two sets of protons 3′,5′ and 2′,6′ respectively.

TABLE-2
[1]H NMR SPECTRAL DATA OF SAPbzlH, 4-APbzlH AND PALLADIUM(II) COMPLEXES[a]

Compound	Benzimidazole ring				Aminophenyl ring				Salicylidene ring				
	NH	H_4	H_7	$H_{5,6}$	$H_{2',6'}$	$H_{3',5'}$	NH_2	N=CH	OH	$H_{3''}$	$H_{4''}$	$H_{5''}$	$H_{6''}$
SAPbzlH	12.95s	7.53d (7.40)	7.68t (8.40)	7.20q (6.70, 8.60)	7.60d (8.30)	8.25d (8.30)	–	9.06s	12.97s	7.00t (8.10, 8.80)	7.44t (7.30)	7.00t (8.10, 8.00)	7.68t (8.4)
4-APbzlH	12.40s	7.48 (7.90)	7.46s (7.90)	7.11m (–)	6.70d (8.60)	7.84d (8.60)	5.60s	–	–	–	–	–	–
$[Pd(C_{13}H_{11}N_3)_2Cl_2]·2HCl$	14.51s	7.70m (–)	7.70m (–)	7.47m (–)	6.76d (8.60)	7.93d (8.60)	6.42s	–	–	–	–	–	–
$[Pd(C_{13}H_{11}N_3)_2Br_2]·2HBr$	14.41s	7.71m (–)	7.71m (–)	7.48m (–)	6.77d (8.61)	7.89d (8.61)	6.41s	–	–	–	–	–	–

[a]Spectra have been recorded in DMSO-d_6; δ in ppm and coupling constant in Hz are given in parentheses.

Another two multiplets observed at δ 7.71 and other at δ 7.48 ppm are assigned to another two sets of protons 4, 7 and 5, 6 respectively.

The off-resonance ^{13}C NMR spectrum of $[Pd(C_{13}H_{11}N_3)_2Cl_2]\cdot 2HCl$ (Fig. 4; Table-3) in DMSO displayed eight resonances (four of them being doublets) for the carbons and four of them at 129.73d, 125.16d, 113.58d and 113.05d ppm are assigned respectively to the sets of protonated carbons (3′,5′), (5,6), (2′,6′) and (4,7). The other four resonances each as a singlet observed at 154.05, 149.84, 131.34 and 107.77 ppm are assigned respectively to quaternary carbons 2, 4′, (8, 9) and 1′, respectively. These assignments have been made by the combined utility of HSQC (Fig. 5), HMBC (Fig. 6) and DEPT-135 (Fig. 7) experiments.

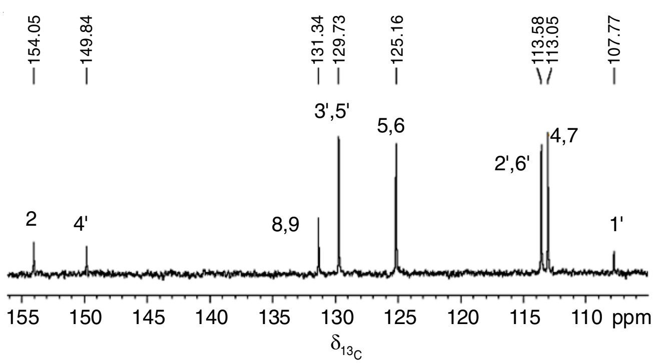


Fig. 4. ^{13}C NMR spectrum of $[Pd(C_{13}H_{11}N_3)_2Cl_2]\cdot 2HCl$ complex

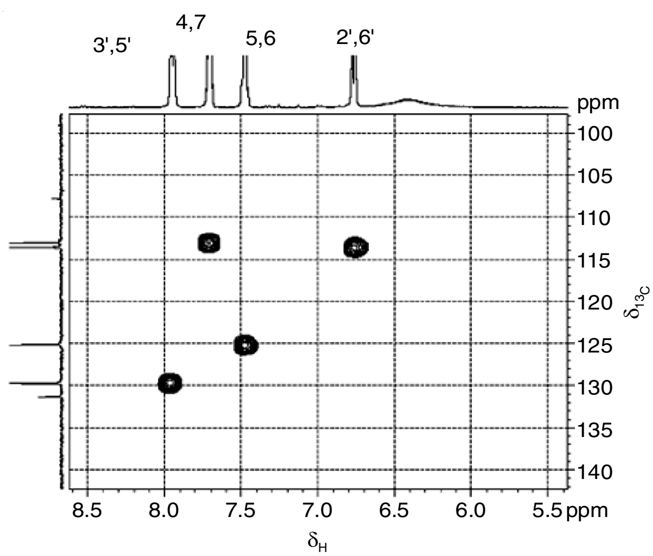


Fig. 5. ^1H-^{13}C HSQC spectrum of $[Pd(C_{13}H_{11}N_3)_2Cl_2]\cdot 2HCl$ complex

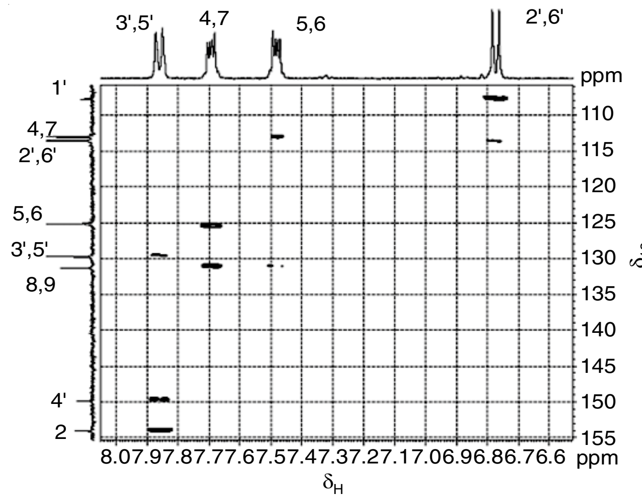


Fig. 6. HMBC spectrum of $[Pd(C_{13}H_{11}N_3)_2Cl_2]\cdot 2HCl$ complex

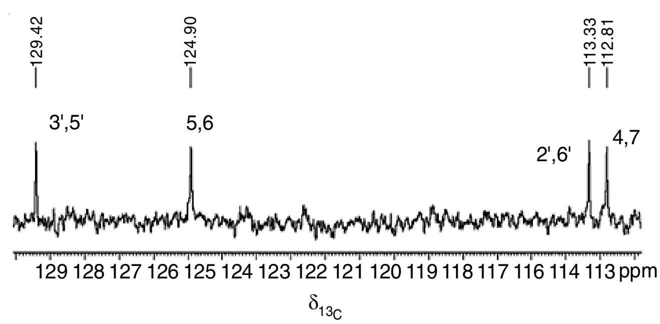


Fig. 7. DEPT-135 spectrum of $[Pd(C_{13}H_{11}N_3)_2Cl_2]\cdot 2HCl$ complex

The off-resonance ^{13}C NMR spectrum of $[Pd(C_{13}H_{11}N_3)_2Br_2]\cdot 2HBr$ (Fig. 8) in DMSO displayed eight resonances (four of them being doublets) for the carbons and four of them observed at 129.67d, 125.25d, 113.62d and 113.05 d ppm are assigned respectively to four sets of protonated carbons (3′,5′), (5,6), (2′,6′) and (4,7). The other four resonances observed at 154.07, 149.92, 131.26 and 107.66 ppm are assigned respectively to quaternary carbons 2, 4′, (8, 9) and 1′, respectively.

The ^1H 4Q-SQ correlated spectra of the complexes (Figs. 9 and 10) were recorded using appropriate pulse sequence [37-39]. The 4Q-SQ spectrum for palladium(II) chloro complex distinctly differentiated the overlapped sub-spectra of two coupled groups of protons, arising from benzimidazole and aminophenyl rings. Thus, 4Q dimension showed only two peaks at the cumulative additive values of the chemical shifts of coupled protons. The 4Q chemical shifts pertaining to each cross section are marked in the spectrum. The cross section taken along F_2

TABLE-3
^{13}C NMR SPECTRAL DATA OF SAPbzlH, 4-APbzlH AND PALLADIUM(II) COMPLEXES[a]

Compound	2	4	5	6	7	8	9	1'	2', 6'	4'	3', 5'
SAPbzlH	150.7t	111.2br	122.5br	121.7br	116.6d (161.0)	143.9s	135.0s	149.1s	122.0d (162.0)	128.6s	127.5d (162.0)
4-APbzlH	151.0s	114.0d (160.0)	121.7d (160.0)	121.7d (160.0)	114.0d (160.0)	138.3s	138.3s	152.1s	113.5d (157.9)	115.8s	128.0d (158.0)
$[Pd(C_{13}H_{11}N_3)_2Cl_2]\cdot 2HCl$	154.0s	113.0d (167.0)	125.1d (162.0)	125.1d (162.0)	113.0d (167.0)	131.3s	131.3s	1074.7s	113.5d (165.0)	149.8s	129.7d (158.9)
$[Pd(C_{13}H_{11}N_3)_2Br_2]\cdot 2HBr$	154.0s	113.0d (–)	125.2d (–)	125.2d (–)	113.0d (–)	131.2s	131.2s	107.6s	113.6d (–)	149.9s	129.6d (–)

[a]Spectra have been recorded in DMSO-d_6; coupling constant in Hz are given in parentheses.

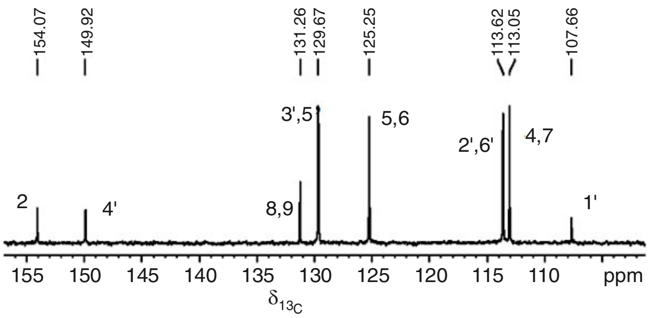


Fig. 8. ^{13}C NMR spectrum of $[Pd(C_{13}H_{11}N_3)_2Br_2]\cdot 2HBr$ complex

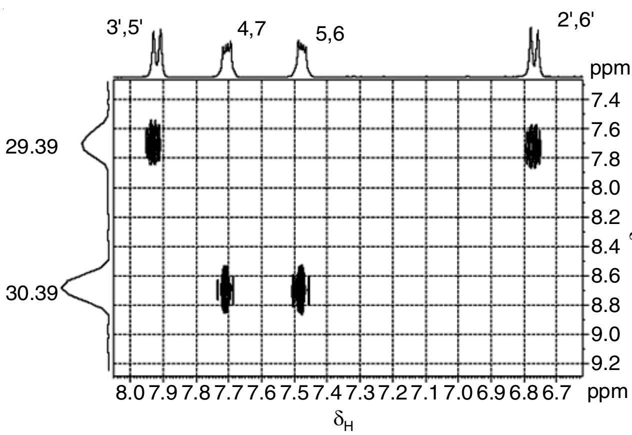


Fig. 9. 4Q-SQ spectrum of $[Pd(C_{13}H_{11}N_3)_2Cl_2]\cdot 2HCl$ complex

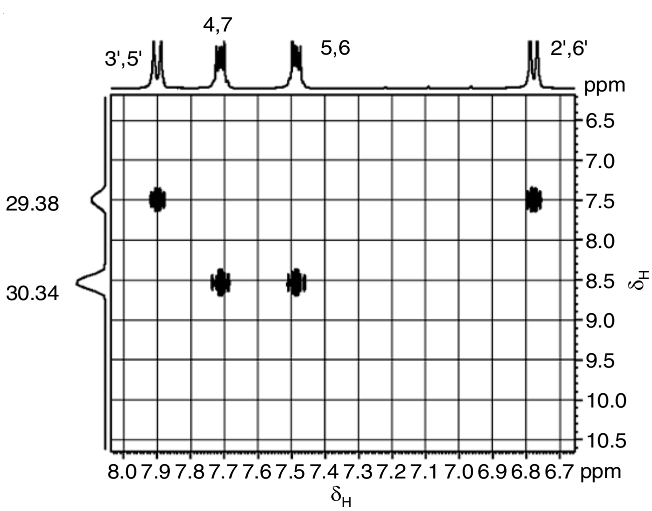
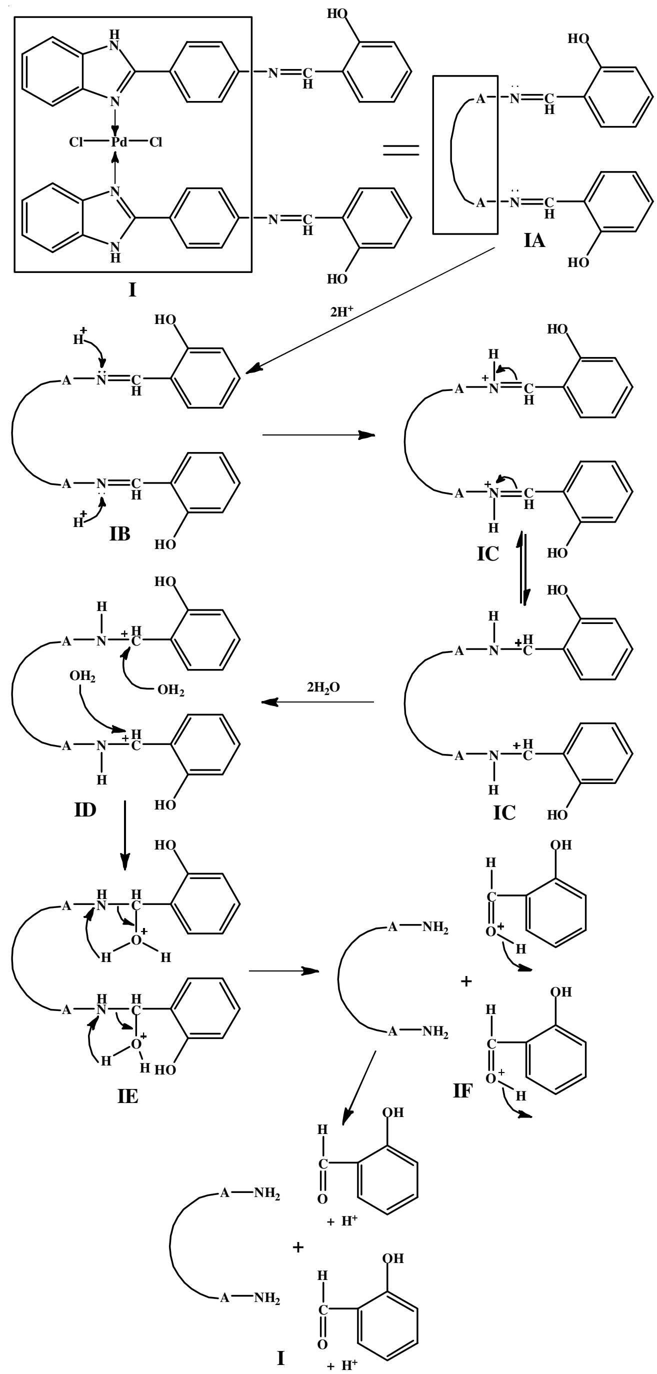


Fig. 10. 4Q-SQ spectrum of $[Pd(C_{13}H_{11}N_3)_2Br_2]\cdot 2HBr$ complex

dimension for each peak in the F_1 dimension pertains to single quantum spectrum of a particular spin system. The assignment of single quantum spectrum was carried out on the basis of multiplet structure, that arises due to spin topology of the coupled protons. The F_2 cross section taken at 4Q chemical shift of 29.39 ppm in F_1 dimension resembles the spectrum of an AA′ BB′ type spin system and is assigned to the aminophenyl ring. The multiplicity patterns expected for the spin topologies, the cross section taken at 30.39 ppm in the F_1 dimension is assigned to benzimidazole ring with protons numbered (4,7), (5,6). In each group of the coupled spin system, the assignment to different protons has been made using both the multiplicity pattern and the chemical intuition. Thus, 4Q-SQ spectrum unambiguously confirmed the assignment of peaks. A similar NMR experiment was carried out on palladium bromo complex and the spectral data is compiled in Table-2.

Mechanistic studies: Palladium(II) chloride in ethanol in the presence of dilute HCl reacts with Schiff base in 1:2 molar ratio to produce $PdCl_2(SAPbzlH)_2$ (**IA**; **Scheme-I**) [40] in which SAPbzlH molecules are bound to Pd(II) ion through tertiary nitrogens of imidazole ring. The coordinated SAPbzlH molecules undergo hydrolysis at uncoordinated nitrogens of -N=CH- bonds. The electrophilic attack of protons on N atoms makes the latter electrophilic (**IB**, **IC**) and this gets transferred to the carbon atoms (**IC**). Nucleophilic attack of H_2O molecules (**ID**) on carbo cations react in the cleavage of N-C bond (**IE**). Thus, aldehyde (**IF**) is formed by acid hydrolysis of each of the coordinated SAPbzlH, latter being converted into an amine.



Scheme-I

Conclusion

The present studies suggest that the hydrolysis at -N=CH- of 2-salicylidene-4-aminophenyl benzimidazole (SAPbzlH) takes place only in the presence of Pd^{2+} ions. The formation of amine has been conclusively proved by detailed ^{1}H and ^{13}C NMR studies. The amine formed coordinates to palladium through imidazole nitrogen. The complexes have been assigned a square planar structure.

ACKNOWLEDGEMENTS

The author sincerely thank Bangalore Institute of Technology and V.V. Pura College of Science, Bengaluru, India for providing all the research facilities.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. U.A. Çevik, B.N. Saglik, Y. Özkay, Z. Cantürk, J. Bueno, F. Demirci and A.S. Koparal, *Curr. Pharm. Des.*, **23**, 2276 (2017); https://doi.org/10.2174/1381612822666161201150131.
2. S. Bellemin-Laponnaz and S. Dagorne, *Chem. Rev.*, **114**, 8747 (2014); https://doi.org/10.1021/cr500227y.
3. P.-H. Lanoë, B. Najjari, F. Hallez, G. Gontard and H. Amouri, *Inorganics*, **5**, 58 (2017); https://doi.org/10.3390/inorganics5030058.
4. J.C. Ruble, and G.C. Fu, *J. Org. Chem.*, **61**, 7230 (1996); https://doi.org/10.1021/jo961433g.
5. L. Pan, N. Hang, C. Zhang, Y. Chen, S. Li, Y. Sun, Z. Li and X. Meng, *Molecules*, **22**, 213 (2017); https://doi.org/10.3390/molecules22020213.
6. M. Selvaganapathy and N. Raman, *J. Chem. Biol. Ther.*, **1**, 108 (2016); https://doi.org/10.4172/2572-0406.1000108.
7. R.E. Harmon, S.K. Gupta and D.J. Brown, *Chem. Rev.*, **73**, 21 (1973); https://doi.org/10.1021/cr60281a003.
8. S.S. Kukalenko, B.A. Bovykin, S.I. Shestakova and A.M. Omel'chenko, *Russ. Chem. Rev.*, **54**, 676 (1985); https://doi.org/10.1070/RC1985v054n07ABEH003103.
9. R.J. Sundberg and R.B. Martin, *Chem. Rev.*, **74**, 471 (1974); https://doi.org/10.1021/cr60290a003.
10. P.N. Preston, *Chem. Rev.*, **74**, 279 (1974); https://doi.org/10.1021/cr60289a001.
11. R.C. Van Landschoot, J.A.M. Van Hest and J. Reedijk, *J. Inorg. Nucl. Chem.*, **38**, 185 (1976); https://doi.org/10.1016/0022-1902(76)80081-4.
12. L.K. Thompson, B.S. Ramaswamy and R.D. Dawe, *Can. J. Chem.*, **56**, 1311 (1978); https://doi.org/10.1139/v78-218.
13. G.K.N. Reddy and B.R. Ramesh, *Indian J. Chem.*, **15A**, 621 (1977).
14. B. Rosenberg, L. Vancamp, J. Trosko and V.H. Mansour, *Nature*, **222**, 385 (1969); https://doi.org/10.1038/222385a0.
15. E. Wong and C.M. Giandomenico, *Chem. Rev.*, **99**, 2451 (1999); https://doi.org/10.1021/cr980420v.
16. Z. Guo and P.J. Sadler, *Adv. Inorg. Chem.*, **49**, 183 (1999); https://doi.org/10.1016/S0898-8838(08)60271-8.
17. B. Rosenberg, ed.: H. Sigel, Metal Ions in Biological Systems, Dekker: New York, vol. 11, p. 127 (1980).
18. J.J. Roberts, eds.: G.L. Eichhorn and L.G. Marzilli, Metal Ions in Genetic Information Transfer, Elsevier: Amsterdam, p. 273 (1981).
19. D.S. Gill, eds: M.P. Hacker, E.B. Douple and I.H. Krakoff, Platinum Coordination Complexes in Cancer Chemotherapy, Nijhoff: Boston, pp. 267–278 (1984).
20. M.M. Shoukry, M.R. Shehata, A. Abdel-Razik and A.T. Abdel-Karim, *Monatsh. Chem.*, **130**, 409 (1999); https://doi.org/10.1007/PL00010222.
21. A.A. El-Sherif, M.M. Shoukry and R. van Eldik, *J. Chem. Soc., Dalton Trans.*, 1425 (2003); https://doi.org/10.1039/b212104b.
22. T. Rau, M.M. Shoukry and R. van Eldik, *Inorg. Chem.*, **36**, 1454 (1997); https://doi.org/10.1021/ic961192v.
23. M.M.A. Mohamed and M.M. Shoukry, *Polyhedron*, **20**, 343 (2001); https://doi.org/10.1016/S0277-5387(00)00612-4.
24. A.A. El-Sherif, *J. Solution Chem.*, **35**, 1287 (2006); https://doi.org/10.1007/s10953-006-9062-9.
25. P. Tamayo, M.A. Mendiola, J.R. Masaguer and C. Molleda, *Transition Met. Chem.*, **14**, 283 (1989); https://doi.org/10.1007/BF01098230.
26. N. Shashikala, N.M. Nanje Gowda and G.K.N. Reddy, *J. Indian Chem. Soc.*, **62**, 928 (1985).
27. S. Santra, G. Krishnamoorthy and S.K. Dogra, *J. Mol. Struct.*, **559**, 25 (2001); https://doi.org/10.1016/S0022-2860(00)00684-0.
28. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compound, Part B, Wiley: Chichester, edn 5 (1997).
29. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier: Amsterdam (1968).
30. D.N. Sathyanarayana, Electronic Absorption Spectroscopy and Related Techniques, Universities Press India (2001).
31. M. Biddau, M. Massacesi, G. Ponticelli, G. Devoto and I.A. Zakharova, *Polyhedron*, **2**, 1261 (1983); https://doi.org/10.1016/S0277-5387(00)84384-3.
32. M. Massacesi, R. Pinna, M. Biddau, G. Ponticelli and I.A. Zakharova, *Inorg. Chim. Acta*, **80**, 151 (1983); https://doi.org/10.1016/S0020-1693(00)91276-3.
33. T.N. Hazarika and T. Bora *J. Indian Chem.*, **22A**, 439 (1983).
34. M. Chandrakala, B.S. Sheshadri, N.M. Nanje Gowda, K.G.S. Murthy and K.R. Nagasundara, *J. Chem. Res.*, **34**, 576 (2010); https://doi.org/10.3184/030823410X12864689639476.
35. M. Chandrakala, N.M. Nanje Gowda, K.G.S. Murthy and K.R. Nagasundara, *Magn. Reson. Chem.*, **50**, 335 (2012); https://doi.org/10.1002/mrc.2857.
36. N. Chandrashekhar, B. Thomas, V. Gayathri, K.V. Ramanathan and N.M.N. Gowda, *Magn. Reson. Chem.*, **46**, 769 (2008); https://doi.org/10.1002/mrc.2239.
37. B. Baishya, G.N.M. Reddy, U.R. Prabhu, T.N.G. Row and N. Suryaprakash, *J. Phys. Chem. A*, **112**, 10526 (2008); https://doi.org/10.1021/jp8055174.
38. G.N. Manjunatha Reddy, T.N. Guru Row and N. Suryaprakash, *J. Magn. Reson.*, **196**, 119 (2009); https://doi.org/10.1016/j.jmr.2008.10.018.
39. G.N. Manjunatha Reddy, S.K. Nayak, T.N. Guru Row and N. Suryaprakash, *Magn. Reson. Chem.*, **47**, 684 (2009); https://doi.org/10.1002/mrc.2449.
40. N. Kumari, V.K. Yadav, S. Zalis and L. Mishra, *Indian J. Chem.*, **51A**, 554 (2012).