



Synthesis, Structural Characterization, and Catalytic Properties of Cu (II), Ru (II) and Pd (II) Complexes with Nitrogen & Oxygen Donor Tetradentate Schiff Base Ligands

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ABSTRACT

Cu (II), Pd (II) and Ru (II) metal complexes of N_4 and N_2O_2 based tetradentate Schiff base ligands were prepared via non-template method by the condensation of 3,5-diaminobenzoic acid with *o*-salicylaldehyde (HL) and *o*-phthalaldehyde (OPA)(HL¹) respectively. The synthesized ligands and metal complexes were well characterized by a variety of techniques such as elemental analysis, FTIR, ¹H NMR, MS, electronic spectroscopy, and conductance measurements. The catalytic activity of Schiff base metal complexes were screened in the reduction of dabigatrin which is an intermediate in the morphine synthesis and C-N cross coupling reactions resulting nilutamide is an anticancer drug, abacavir which is antiviral drug. The Schiff base metal complexes can catalyze selectively and shows moderate to high yields.

Keywords: Schiff bases ligands, Metal complexes, Characterization, Catalysis

INTRODUCTION

Schiff bases were versatile compounds synthesized from the condensation of a variety of readily available aldehydes and primary amines and regarded as privileged ligands due to their capability to form complexes with different transition metals [1-26]. Schiff base metal complexes have wide range of applications in many fields including analytical [27,28], medicinal [29,30], organic [31], inorganic chemistry. These complexes can act as catalysts in several reactions such as polymerization [32], oxidation [33,34], hydrolysis [14,35] reduction [36], epoxidation [37], hydrosilylation [38] Henry reaction [39], C-N [40], C-S, Kumada Corriu cross coupling [41] reactions, and C-H activation of various substrates. Schiff base metal complexes have great importance in industrial applications and in various biological processes including photosynthesis, dioxygen transport, and potential applications as metal extractants, radiotherapeutic, medical imaging agents and anti-tumour therapeutic agents [42]. For the past few years, several investigations have been done on the coordination chemistry of Schiff base coordinated transition metal complexes and supramolecules in order to mimic the physical and chemical properties and applied in biological processes. Macrocyclic Schiff base metal complexes derived from *o*-phthalaldehyde (OPA) were recently reported by Shakir and co-workers via template method [43]. To the best of our knowledge, there are very few reports on the synthesis and catalytic applications of Schiff base ligated transition metal (II) compounds derived from *o*-phthalaldehyde. In the present work, in continuation to earlier studies towards the synthesis of novel coordination compounds and their catalytic activities, we have synthesized N_4 and N_2O_2 tetradentate ligands from *o*-phthalaldehyde by non-template method, and their complexes with copper, palladium and ruthenium. Catalytic activities of metal complexes were investigated in reduction of dabigatrin which is an intermediate in the synthesis of morphine and C-N cross coupling reactions resulting nilutamide and abacavir. Dabigatrin is a new oral anti-coagulant which inhibits factor thrombin and an alternative to warfarin in patients requiring cardioversion [44]. Nilutamide is a non-steroidal prostate anticancer drug and pneumotoxic, hepatotoxic nitro aromatic anti androgen and used in the treatment of prostate carcinoma in man [45]. Abacavir is a nucleoside analogue reverse-transcriptase inhibitor of HIV type 1 replication and deoxy-guanosine base. Abacavir shows similar *in vitro* potency to other nucleoside analogues and an antiretroviral drug. Abacavir is associated with hypersensitivity in patients [46].

MATERIAL AND MEASUREMENTS

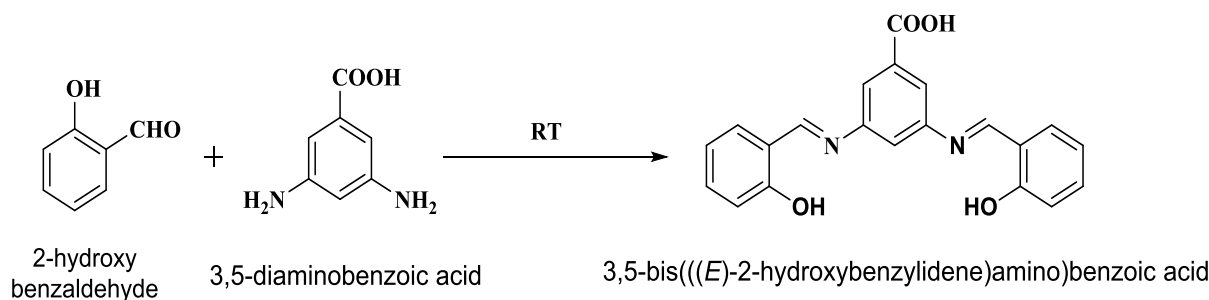
Materials

All the solvents, amines, aldehydes, and metal salts used in this study were of analar grade. The solvents were distilled by standard procedures before use. The ligands used in this work were prepared and characterized by IR, UV-Visible and ¹H-NMR spectral data. The water used in the study was essentially double distilled water. The solvents were distilled and stored over molecular sieves. The purity of the compounds was checked by TLC using Merck 60F254 silica gel plates

Physical measurements

The MPs of all the ligands were determined on a Buchi- 510 melting point apparatus. The MPs of the complexes could not be determined as the complexes were found to decompose before melting. UV-Visible spectra were recorded with Shimadzu UV-2140 A, a UV-Visible double beam spectrophotometer with matched quartz cells of path length 1 cm at Osmania University, Hyderabad. The IR spectra were recorded in KBr pellets on Perkin Elmer-283 spectrophotometer at Osmania University, Hyderabad. The scanning rate was 6 min in the range of 4000-200 cm^{-1} . $^1\text{H-NMR}$ spectra were recorded in CDCl_3 or DMSO-d_6 on a Bruker AVAVCE III 400 MHz-NMR spectrometer using TMS as the internal standard at ICT Hyderabad. NMR spectral data provide valuable information regarding the structure of Schiff bases. The NMR spectra of the Metal (II) complexes were also recorded to know the nature of binding of metal ion.

Synthesis of HBAB Schiff base ligand: 2 ml of salicylaldehyde dissolved in minimum quantity of methanol and added drop by drop to methanolic solution of 3,5 diamino benzoic acid (1.52 g, 0.1 mol) with continuous stirring and refluxed on water bath for about 1 h. Yellow colored precipitate was separated out. It was filtered off and washed with hot methanol and glacial acetic acid and dried.



HBAB(S): $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_4$; ESI-MS m/z $[\text{M}+1]$ 361; IR: HBAB(S): 3070, 1719, 1687, 1620, 1569, 1305, 751; $^1\text{H-NMR}$: 6.97-7.02 (3H), 7.41-7.46 (5H), 7.69-7.72 (3H, t), 7.76-7.77 (3H, t), 7.84-7.86 (2H, d).

Preparation of metal complexes

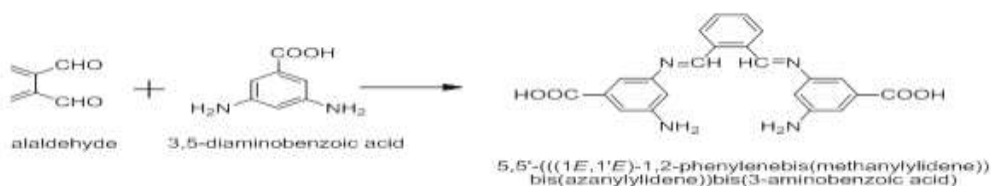
Preparation of Cu (II) complex with HBAB: 0.0025 mol HBAB dissolved in 50:50 of chloroform and methanol. To this 0.0025 mol methanolic solution of copper (II) chloride added drop wise with continuous stirring on magnetic stirrer for about 30 min. A pista green coloured precipitate was separated out. It was filtered off and washed with hot methanol and 50:50 chloroform and methanol solution and dried.

Preparation of Pd (II) complex with HBAB: 0.0025 mol HBAB dissolved in 50:50 of chloroform and methanol. To this hot solution add 0.0025 mmol of methanolic solution of Palladium (II) chloride with continuous stirring on magnetic stirrer for about 1 h. Orange red, Black coloured precipitate respectively was separated out. It was filtered off and washed with hot methanol and 50:50 of chloroform and methanol and dried.

Preparation of Ru (II) complex With HBAB: 0.0025 mol HBAB dissolved in 50:50 of chloroform and methanol. 0.0025 mol Ruthenium tri chloride hydrate was dissolved in methanol. This solution was added to hot solution of HBAB with continuous stirring on magnetic stirrer. Black colored precipitate was separated off which was filtered and dried.

Synthesis of PMAA Schiff base ligand

The methanolic solution of ortho phthalaldehyde (1.34 g, 0.1 mol) is mixed with methanolic solution of 3,5-diamino benzoic acid (1.52 g, 0.1 mol) with continuous stirring. A yellow coloured solution was refluxed for about 2 h and cooled to room temperature, which yielded a yellow coloured precipitate. It was filtered off and washed with hot methanol and dried.



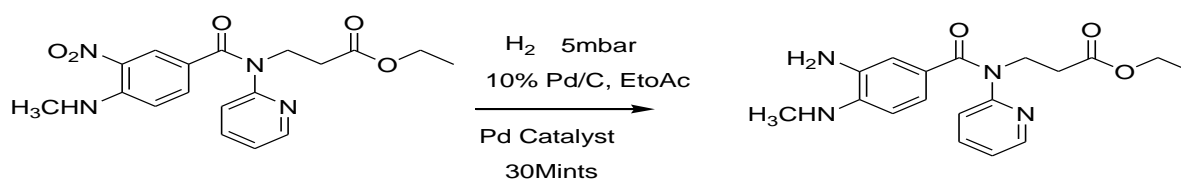
PMAA(A): $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_4$; FTIR: 3360, 3221, 3076, 2919, 1685, 1635, 1384, 776, 726; $^1\text{H-NMR}$: 4.96-5.07 (3H, q), 6.33-6.40 (1H, q), 6.59-6.67 (1H, q), 6.92-6.94 (1H, d), 7.16 (2H, s), 7.46-7.77 (6H, m), 8.51 (1H, s); ESI-MS m/z $[\text{M}+1]$ 403.

Preparation of Cu (II) complex with PMAA: 0.0025 mol of Cu^{2+} was dissolved in methanol and added to hot DMSO solution of 0.0025 mol PMAA with continuous stirring on magnetic stirrer. Bluish green colored was formed and refluxed on water bath about ½ hour. Bluish green precipitate was separated off this was filtered and dried.

Preparation of Pd (II) complex with PMMA: 0.0025 mol of palladium (II) chloride was dissolved in chloroform and added drop wise in to hot DMSO solution of 0.0025 mol PMMA with continuous stirring on water bath. After 1 h yellow colored precipitate was separated off this was filtered and dried.

Preparation of Ru (II) complex with PMMA: 0.0025 mol of PMMA were dissolved in DMSO. To this methanolic solution of 0.0025 mol ruthenium tri chloride was added drop wise with continuous stirring on hot plate. A black colored compound separated. This was filtered and dried Scheme 1.

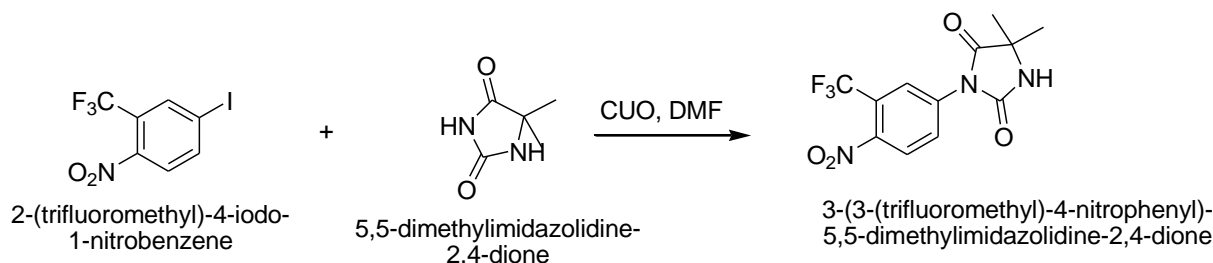
Catalysis



Scheme 1: Reduction of dabigatrin using Pd-Schiff's base metal complexes

Dissolve Ethyl 3-(4-(methylamino)-3-nitro-N-(pyridin-2-yl)benzamido)propanoate (2.5 g) in ethyl acetate (25 ml) in an autoclave. Add 250 mg of Pd/C at 25°C to 35°C and Pd Catalyst (Pd-HBAB & Pd-PMAA complex, 50 mg) stirred for 20 min. Heat the reaction mixture at 50- 55°C under 5 Kg hydrogen pressure for 5 h. The reaction mixture was filtered and washed with ethyl acetate and distil the filtrate to get residue. Add 30 mL isopropanol to the residue and heat for 5-10 min at 70-75°C. The reaction mixture was cooled to 0-5°C and filtered. The wet-cake is washed with isopropanol and dried to afford 850 mg ethyl 3-(3-amino-4-(methylamino)-N-(pyridin-2-yl)benzamido) propanoate as a solid. Yield%-58 to 65

Mol Formula: C₁₈H₂₂N₄O₃; IR: 3271, 3160, 2925, 2210, 1753, 1728, 1637, 1182, 1023, 894, 826; ¹H-NMR (DMSO-d₆, 300 Hz's): 1.09 (3H, t), 2.65-2.70 (2H, t), 3.75 (3H, s), 3.93-4.0 (2H, Q), 4.19-4.24 (2H, t), 4.24-4.61 (2H, d), 7.09-7.17 (2H, m), 7.26-7.29 (1H, t), 7.39-7.57 (5H, m); ESI-MS m/z [M+1] 343 (Scheme 2).



Scheme 2: C-N cross coupling reactions using Cu-Schiff's base metal complexes

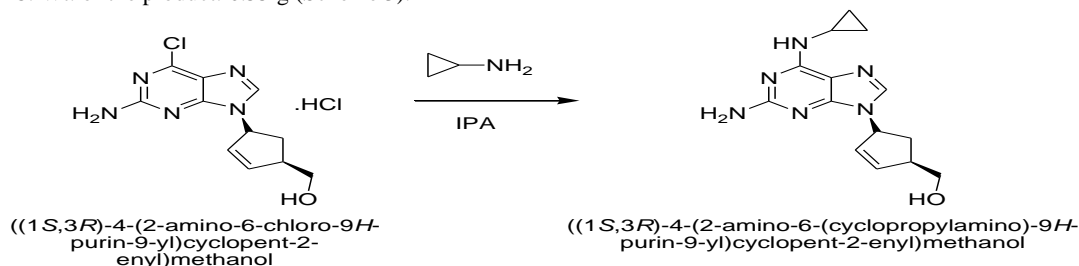
Procedure with Copper Catalyst-PMAA complex

Dissolve 2-(trifluoromethyl)-4-iodo-1-nitrobenzene (2 g) in N,N-dimethylformamide (5 ml) at 25-30°C, add 5,5-dimethylimidazolidine-2,4-dione (1.3 g) and CuO (250 mg), Copper catalyst-1 (40 mg) in to the mixture. Heat the mixture to 100-110°C and maintained at 100-110°C till 2-(trifluoromethyl)-4-iodo-1-nitrobenzene should be absent completely by TLC (30% EtOAc in Hexane), it takes 10 h for completion of the reaction. Filter the reaction mass over hyflo bed and washed with DMF (1 ml), quench the filtrate in to the water and stir for 30 min to get precipitate. Filter the solid and wash with water. Dissolve the solid in tert-butyl methyl ether and wash the organic layer with 10% EDTA solute on and dry the organic layer over sodium sulfate. Distill the solvent up to ¼ of volume and crystallize the product at 0-5°C. Filter the solid and dry at 60-65°C. Wt. of the product: 1.2 g

Mol Formula: C₁₂H₁₀F₃N₃O₄; IR: 3283, 2988, 1778, 1722, 1540, 1318, 1138; ¹H-NMR (DMSO-d₆, 300 Hz's): 1.44 (6H, s), 8.07-8.09 (1H, Q), 8.20-8.21 (1H, d), 8.30-8.32 (1H, d), 8.84 (1H, s); ESI-MS m/z [M+1] 317.

Procedure with Copper Catalyst- HBAB complex

Dissolve 2-(trifluoromethyl)-4-iodo-1-nitrobenzene (1 g) in N,N-dimethylformamide (5 ml) at 25-30°C, add 5,5-dimethylimidazolidine-2,4-dione (0.65 g) and CuO (125 mg), Copper catalyst-1 (20 mg) in to the mixture. Heat the mixture to 100-110°C and maintained at 100-110°C till 2-(trifluoromethyl)-4-iodo-1-nitrobenzene should be absent completely by TLC (30% EtOAc in Hexane), it takes 10 h for completion of the reaction. Filter the reaction mass over hyflo bed and washed with DMF (1 ml), quench the filtrate in to the water and stir for 30 min to get precipitate. Filter the the solid and wash with water. Dissolve the solid in tert-butyl methyl ether and wash the organic layer with 10% EDTA solute on and dry the organic layer over sodium sulfate. Distill the solvent up to ¼ of volume and crystallize the product at 0-5°C. Filter the solid and dry at 60-65°C. Wt. of the product: 0.55 g (Scheme 3).



Scheme 3: Copper Catalyst- HBAB complex

Procedure

Add ((1S,3R)-4-(2-amino-6-chloro-9H-purin-9-yl)cyclopent-2-enyl)methanol (2 g), NaHCO₃ (475 mg, 5.65 mmol), cyclopropylamine (2 ml, 28.3 mmol) and Copper Catalyst (Cu-HBAB & Cu-PMAA complex, 45 mg) in to Isopropanol (15 ml). Stir the mixture for 30-35 min at 80-82 °C. Filter the salts. Distill off the filtrate, isopropanol (10 ml) was added and concentrated twice to dryness. The syrup was dissolved in hot isopropanol (15 ml). This mixture is cooled to 0-2 °C and filters the resulting slurry. Dry the solid under vacuum at 30-35 °C. Wt. of compound: 1.25-1.3 g

Mol Formula: C₁₄H₁₈N₆O IR; ¹H-NMR (DMSO-d₆, 300 Hz's): 0.6 (2H,), 0.7 (2H,), 1.55 (1H,), 2.0 (1H,), 2.6-2.7 (1H,), 2.8 (1H,), 3.1 (1H,), 3.40 (1H,), 3.45 (2H,), 4.10 (1H,), 5.4 (1H,), 5.85 (3H,), 6.15 (1H,), 7.3 (1H,), 7.7 (1H,); ESI-MS m/z [M+1] 287.

RESULTS AND DISCUSSION

In the present investigations, six new Schiff base Cu (II), Ru (II), Pd (II), complexes were synthesized by treating Metal chlorides with two Schiff base ligands separately using non template method and all the complexes are stable in air and soluble in various organic solvents. The purity of the Schiff base ligands were monitored by TLC. The percentages of carbon, hydrogen and nitrogen were determined experimentally using CHN analyzer. The physical and analytical data for the newly synthesized compounds is in good agreement with the proposed molecular formulae Table 1.

Table 1: Analytical data of Schiff base ligands and their Cu (II), Ru (II), and Pd (II) metal complexes

Schiff base complex	Λ_M^a ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	Found (Cald (%))			
		C	H	N	M
1. HBAB	-	69.95 (69.99)	4.49 (4.48)	7.78 (7.77)	-
2. PMAA	-	65.67 (65.66)	4.50 (4.51)	13.90 (13.92)	-
3. [Cu(HBAB)Cl ₂]	14.0	50.98 (50.97)	3.27 (3.26)	5.67 (5.66)	12.82 (12.84)
4. [Cu(PMAA)Cl ₂]	15.2	49.23 (49.22)	3.39 (3.38)	10.45 (10.44)	11.83 (11.84)
5. [Ru(HBAB)Cl ₂]	16.0	47.39 (47.38)	3.05 (3.03)	5.27 (5.26)	18.98 (18.99)
6. [Ru(PMAA)Cl ₂]	15.5	46.03 (46.00)	3.16 (3.16)	9.74 (9.75)	17.61 (17.60)
7. [Pd(HBAB)] Cl ₂	59.0	46.90 (46.91)	3.01 (3.00)	5.20 (5.21)	19.78 (19.79)
8. [Pd(PMAA)] Cl ₂	63.0	45.59 (45.58)	3.14 (3.13)	9.67 (9.66)	18.37 (18.36)

Infrared spectral analysis

In the IR spectra of the both ligands, a medium intensity band in the range of 1630-1660 cm⁻¹ is assigned to azomethine (C=N) and disappearance of the bands characteristic of the (-NH₂) amine group at 3250 cm⁻¹ of 3,5-diaminobenzoic acid and carbonyl group (-C=O) at 1680 cm⁻¹ of o-phthalaldehyde suggests the formation of Schiff bases. Bands appearing in the region of 1492-1455, 1144-1033 and 799-751 cm⁻¹ were assigned to aromatic ring vibrations. A broad medium intensity band at 3274-3349 in PMMA ligand ascribed to (O-H) stretching frequency of aromatic carboxylic acid. The coordination of azomethine nitrogen was suggested by the negative shift of 20-50 cm⁻¹ of (C=N) stretch. This was further supported by a medium intensity band in the region of 430-450 cm⁻¹ which is ascribed to metal to nitrogen (M-N) stretching vibration. A band in the region of 530-570 cm⁻¹ assigned to (M-O) stretching vibration and band around 340 cm⁻¹ is due to (M-Cl) vibrational frequency. The selected spectral bands of ligands and metal complexes were presented in Table 2.

Table 2: Important infrared frequencies

S. No.	Compound	(C=N)	(M-N)	(M-O)	(M-Cl)
1.	HL(HBAB)	1620	-	-	-
2.	HL ¹ (PMMA)	1635	-	-	-
3.	[Cu(HBAB)Cl ₂]	1590	430	550	320
4.	[Cu(PMAA)Cl ₂]	1605	432	-	340
5.	[Ru(HBAB)Cl ₂]	1580	440	530	338
6.	[Ru(PMAA)Cl ₂]	1610	445	-	345
7.	[Pd(HBAB)] Cl ₂	1599	450	570	-
8.	[Pd(PMAA)] Cl ₂	1590	448	-	-

NMR spectral analysis

In ¹H-NMR spectra of the ligand PMMA a signal due to four equivalent CH=N [4H] protons appeared at 8.5 ppm. A broad peak in the range of 4.96-5.07 ppm is assigned to four equivalent aromatic (C-NH) protons and all the peaks in the range of 6.33-7.77 ppm are corresponding to [10H] aromatic protons. ¹H-NMR spectra of N₂O₂ ligand (HBAB) shows a signal at 7.84-7.86 is due to azomethine (CH=N) protons [2H] appeared in the range 7.84-7.87 ppm suggests the formation of Schiff base ligands. Additionally, in the spectra of Ru (II), and Pd (II) complexes the signal was moved down-field, this suggests the coordination of imino nitrogen to metal ion. No appreciable change is seen in the peak positions corresponding to aromatic protons and NH protons and hydroxy protons in the complexes.

Electronic spectral analysis

The electronic spectra of Cu (II) complexes reported here show two characteristic bands in the range 660–870 (${}^2B_{1g} \rightarrow {}^2A_{1g}$) and 430–515 nm (${}^2B_{1g} \rightarrow {}^2E_g$) transitions, respectively. Because of the low intensity of ${}^2B_{1g} \rightarrow {}^2B_{2g}$, this band is usually not observed separately in the tetragonally distorted complexes [9]. Electronic spectral data suggesting that an appreciable distortion from octahedral geometry in Cu (II) complexes [9] Figure 1. All the Ru (II) complexes exhibit four transitions corresponding to ${}^1A_{1g} \rightarrow {}^3T_{1g}$; ${}^1A_{1g} \rightarrow {}^3T_{2g}$; ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$. Two bands are observed in the 200–530 nm region at the longer wavelength (460–520 nm) have been assigned to the spin allowed ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition based on molar extinction coefficients. The other high intensity band, at 260–300 nm region has been assigned to the charge-transfer transition arising from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbital derived from the Π^* level of the ligands, in accordance with the assignments confirms octahedral geometry for Ru (II) complexes [25] Figure 1. The electronic spectra of Pd (II) complexes show a broad d–d transition band in the region of 495–450 nm assignable to ${}^1B_{1g} \leftarrow {}^1A_{1g}$ transition [23]. Further a relatively strong charge transfer band has been observed in the spectra of all the Pd (II) complexes in the range of 320–280 nm. From the electronic spectroscopic data and the diamagnetic behavior of the complexes the square planar geometry has been proposed to all the Pd (II) complexes Figure 1.

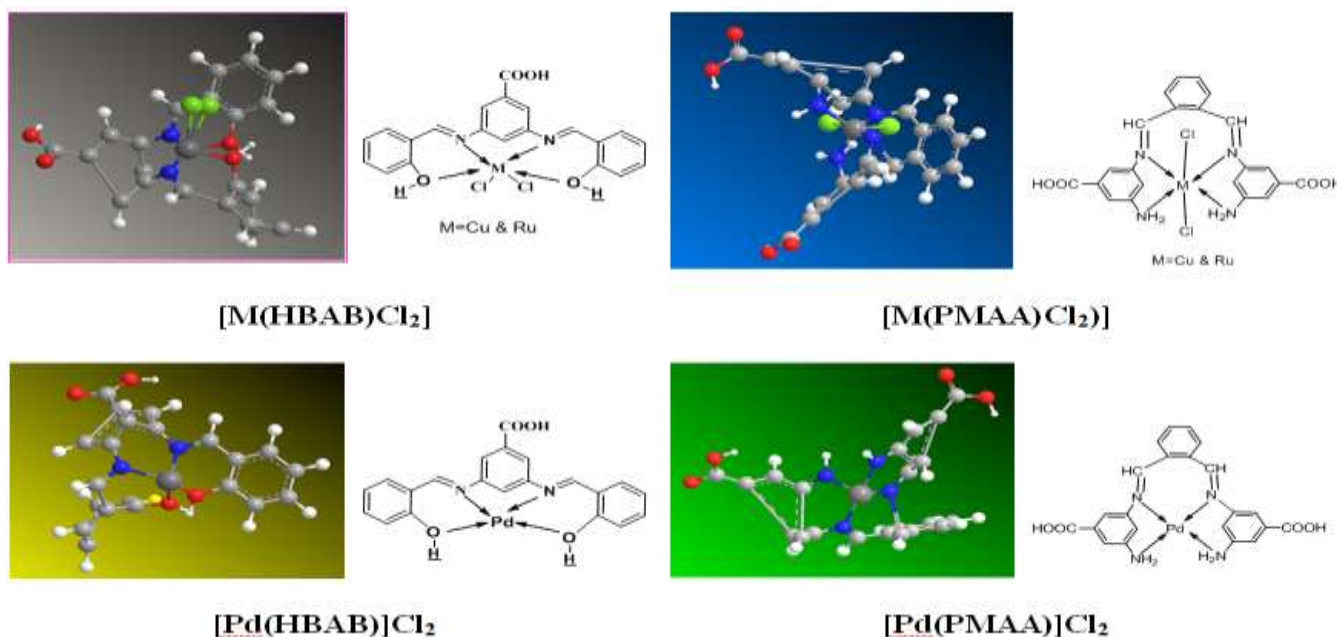


Figure 1: Proposed structures of all Schiff base metal complexes

Conductance measurements

The molar conductance values for the Cu (II) and Ru (II) complexes are determined in dichloromethane and these values are found to be low ($14\text{--}16 \text{ ohm}^{-1}\text{cm}^2 \text{ mol}^{-1}$) indicating non-electrolytic nature. Two Pd (II) complexes were determined in dimethyl formamide. The conductance values were found 59 and 63 $\text{ohm}^{-1}\text{cm}^2 \text{ mol}^{-1}$ indicating 1:2 electrolytic nature. The electrolytic nature of these Pd (II) complexes is due to the presence of two chloride ions outside the coordination sphere. The presence of chloride ions Pd (II) complexes is detected by the addition of silver nitrate reagent leading to the formation of white precipitate of silver chloride [4,23–25].

Mass spectral analysis

In the mass spectra of PMMA ligand molecular ion peak was observed at m/z $[M+1]$ 403 and HBAB ligand gives molecular ion peak at m/z $[M+1]$ 361. The proposed molecular formula of all the metal complexes was confirmed by comparing their molecular formula weights with m/z values. The molecular ion peaks at m/z (M+) 494 ($[\text{Cu}(\text{HBAB})\text{Cl}_2]$), 536 ($[\text{Cu}(\text{PMAA})\text{Cl}_2]$), 532 ($[\text{Ru}(\text{HBAB})\text{Cl}_2]$), 574 ($[\text{Ru}(\text{PMAA})\text{Cl}_2]$), 537 ($[\text{Pd}(\text{HBAB})]\text{Cl}_2$), 579 ($[\text{Pd}(\text{PMAA})]\text{Cl}_2$). This data is in good agreement with the respective molecular formulae of metal complexes.

CONCLUSION

In this report the non-template synthesis of six new Schiff base metal complexes. The analytical data show the presence of one metal ion per molecule and suggest a mononuclear structure for all the complexes. In Cu (II) and Ru (II) complexes, two ligands coordinate through four nitrogen (N_4) atoms/ or two nitrogen and two oxygen (N_2O_2) atoms and two chloride ions. These compounds were found to have non-electrolytic nature and distorted octahedral structures were assigned to these complexes. The electronic spectral data are in the favor of square planar structure for Pd (II) metal complexes. Cu (II) and Pd (II) metal complexes showed excellent catalytic activity in different types of organic reactions such as reduction of dabigatin and C–N cross coupling reactions. These Schiff base metal complexes can catalyze selectively and shows moderate to high yields.

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