



Synthesis of Novel Pyridyl-Based Schiff Base and Its Coordination Behaviour with Ruthenium(II) and Zinc(II)

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High reactivity of the Schiff base product of *p*-toluidine with pyridine-2-carboxaldehyde was observed, leading to methyl group isomerization (immigration) to *ortho*-position followed by the dimerization reaction to form biphenyl system. This compound was identified and characterized using IR, ESI MS and NMR spectroscopic methods and its structure confirmed by XRD single crystal. The coordination behaviour of the Schiff base was examined using ruthenium(II) and zinc(II). Two metal complexes were only isolated and identified by X-ray crystallography for ruthenium(II) and zinc(II). The coordination behaviour of both metals differs significantly, although both of them promote the oxidation reaction on one of the azomethine bond.

Keywords: Pyridyl Schiff base, Biphenyl formation, Ruthenium(II), Zinc(II).

INTRODUCTION

Schiff Bases are organic class of compounds characterized with the azomethine ($-\text{CH}=\text{N}-$) bond. Due to the lone pair of the sp^2 nitrogen in the azomethine group, this organic class of compounds has a potential in coordination chemistry as ligands with high design flexibility and high functionality [1,2]. Transition metal complexes with Schiff bases have been of significant interest due to their antibacterial and antifungal activities [3-5]. Schiff base complexes can be tailored and designed as materials in many applications such as molecular sensing [6,7], optical switching [8], non-linear optics and photo-initiated processes [9]. Schiff bases are accessible by refluxing primary amines and aldehyde to form the carbinolamine moiety which undergoes a dehydration reaction to form the Schiff base. The dehydration step is reversible and hence the reaction sometimes is catalyzed by the addition of a weak acid or a weak base [10].

p-Toluidine has been used as a precursor in the synthesis of Schiff bases and showed good reactivity with aromatic aldehyde functionalized by a wide range of groups, ranging from strongly electron-withdrawing to strongly electron-releasing [11,12]. In this study, we are reporting our observations of the unusual reaction of pyridine-2-carboxaldehyde with *p*-toluidine. The resulted ligand was engaged with zinc(II) chloride in one experiment and with *cis*-bis(bipyridine)dichloro ruthenium(II) in another experiment to form two metal complexes.

EXPERIMENTAL

All the solvents were of HPLC grade and were used as received. Ammonium hexafluorophosphate, pyridine-2-carboxaldehyde (Alfa Asear), *p*-toluidine (Alfa asear) and zinc(II) chloride were purchased commercially and used as received. *cis*-Ru(bpy)₂Cl₂ was synthesized following the literature report [13].

Elemental analyses were conducted at King Abdulaziz University. Infrared spectra were recorded for powder samples of the complexes using a Bruker Alpha FT-IR; peaks are reported in cm^{-1} . ¹H NMR (600 MHz) spectra were recorded using a Bruker Avance III HD NMR spectrometer and ³¹P NMR spectra (121 MHz) were recorded using a Varian Mercury-300 FT NMR spectrometer. The spectra are referenced to residual chloroform (7.26, ¹H) or external H₃PO₄ (0.0 ppm, ³¹P). High-resolution electrospray ionization (ESI) mass spectra were recorded using an Agilent Q-TOF 6520 instrument; all mass spectrometry are reported as *m/z*.

Synthesis of pyridyl Schiff base (L): Pyridine-2-carboxaldehyde (0.50 g, 4.6 mmol) and *p*-toluidine (0.50 g, 4.6 mmol) were stirred in 17 mL methanol at room temperature under N₂ atmosphere for 30 min. A beige precipitation was formed and the mixture was left under stirring for further 2 h. The precipitation was collected by filtration and dried to afford a beige powder (0.55 g, 61 %).

HR ESI MS $[C_{26}H_{22}N_4]^+$: Calcd. 390.1844, found 390.1844. Anal. calcd. for $C_{26}H_{22}N_4$: C, 79.97; H, 5.68; N, 14.35 %, found: C, 80.31; H, 5.79; N, 13.92 %. IR (solid): 1625 and 1583 cm^{-1} ν (aromatic C=C and C=N), 1565 cm^{-1} ν (-HC=N). 1H NMR δ : 2.48 (s, 6H, CH_3), 7.11 (d, 2H, H_6), 7.38 (m, 2H, H_3), 7.49 (dd, 2H, H_7), 7.52 (s, 2H, H_8), 7.82 (t, 2H, H_2), 8.28 (d, 2H, H_4), 8.59 (s, 2H, H_5), 8.70 (d, 2H, H_1). ^{13}C NMR δ : 18.06 (CH_3), 117.95 (C_6), 121.69 (C_4), 125.03 and 125.30 (C_2 and C_7), 128.94 (C_8), 132.96 (C_3), 136.64 (C_{11}), 138.89 (C_{12}), 149.05 and 149.61 (C_1 and C_{10}), 154.90 (C_9), 159.57 (C_5).

Reaction of L with *cis*-Ru(bpy) $_2$ Cl $_2$ (Ru-L): *cis*-Ru(bpy) $_2$ Cl $_2$ (0.20 g, 0.38 mmol) and L (0.15 g, 0.38 mmol) were refluxed in a mixture of ethanol (16 mL) and water (4 mL) under nitrogen atmosphere for 8 h. The reaction mixture was cooled down and NH_4PF_6 (0.13 g, 0.77 mmol) was added with 15 mL water, leading to form a red precipitate. The precipitate was collected by filtration, washed several times with water and dried, affording the Ru-L as a dark red powder (0.20 g, 79 %). HR ESI MS $[C_{26}H_{20}N_5O_2Ru]^+$: calcd. 536.0660, found 536.0649. Anal. calcd. for $C_{26}H_{20}F_6N_5O_2PRu$: C, 45.89; H, 4.09; N, 11.62 %, found: C, 45.43; H, 4.32; N, 11.27 %. IR (solid): 1603 cm^{-1} ν (aromatic C=C and C=N), 1658 cm^{-1} ν (O=C=O).

Reaction of L with zinc(II) chloride (Zn-L): Zinc chloride (0.02 g, 0.15 mmol) and L (0.02 g, 0.05 mmol) were refluxed in methanol (10 mL) under normal conditions for 1 h. The reaction mixture was allowed to cool down and left to evaporate

over 2 days, affording red crystals. The crystals were washed with water several times to give Zn-L as a red crystals (0.01 g, 50 %). HR ESI MS $[C_{20}H_{19}Cl_2N_3Zn]^+$: calcd. 435.0247, found 435.0246. Anal. calcd. for $C_{20}H_{19}Cl_2N_3Zn$: C, 54.88; H, 4.38; N, 9.60 %, found: C, 54.69; H, 4.32; N, 9.74 %. IR (solid): 1606 cm^{-1} ν (aromatic C=C and C=N), 3312, 3129 cm^{-1} ν (NH $_2$).

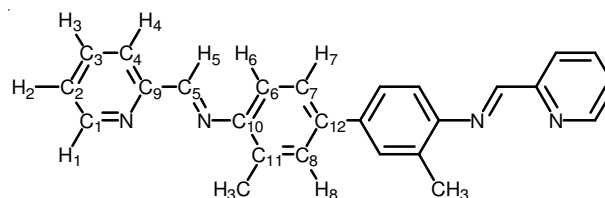


Fig. 1. NMR labeling for the ligand (L)

Crystallography of L, Ru-L and Zn-L: The crystals of L, Ru-L and Zn-L were crystallized from methanol by slow evaporation. D8 QUEST Bruker Diffractometer, equipped with graphite-monochromatic MoK $_{\alpha}$ radiation was used for data collection. The data collection was preceded using APEX3 software [15] at 293 K. The structure solution was performed using SHELXS-2014 [14-16] and refined by full-matrix least-squares methods on F^2 using SHELXL-2014 [15-17] in-built with APEX3 software [17]. All non-hydrogen atoms were refined anisotropically by full-matrix least squares methods.

TABLE-1
DATA COLLECTION AND STRUCTURE REFINEMENT FOR L, Ru-L AND Zn-L

Identification code	L	Ru-L	Zn-L
Chemical formula	$C_{26}H_{22}N_4$	$C_{26}H_{20}F_6N_5O_2PRu$	$C_{20}H_{19}Cl_2N_3Zn$
Formula weight	390.48 g/mol	680.51 g/mol	437.65 g/mol
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P 1 21/n 1	P-1
Unit cell dimensions	a = 10.57(2) Å, α = 110.77(3) $^\circ$ b = 11.59(2) Å, β = 91.61(4) $^\circ$ c = 13.23(3) Å, γ = 99.09(3) $^\circ$	a = 14.260(12) Å, α = 90 $^\circ$ b = 10.957(13) Å, β = 107.61(2) $^\circ$ c = 16.658(17) Å, γ = 90 $^\circ$	a = 7.43(2) Å, α = 93.20(3) $^\circ$ b = 8.81(2) Å, β = 91.67(4) $^\circ$ c = 16.37(4) Å, γ = 110.71(3) $^\circ$
Volume	1490.(5) Å 3	2481.(4) Å 3	999.(4) Å 3
Z	2	4	2
Density (calculated)	1.307 g/cm 3	1.822 g/cm 3	1.454 g/cm 3
Absorption coefficient	0.079 mm $^{-1}$	0.779 mm $^{-1}$	1.504 mm $^{-1}$
F(000)	618	1360	448
Theta range for data collection	2.48 to 25.41 $^\circ$	2.39 to 25.50 $^\circ$	2.48 to 25.30 $^\circ$
Index ranges	-12<= h <=12, -13<= k <=13, -15<= l <=15	-17<= h <=17, -13<= k <=13, -20<= l <=20	-8<= h <=8, -10<= k <=10, -19<= l <=19
Reflections collected	40718	77785	26959
Independent reflections	5467 [R(int) = 0.0515]	4608 [R(int) = 0.0372]	3622 [R(int) = 0.0898]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2014)	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$
Data/restraints/parameters	5467/0/409	4608/0/370	3622/0/245
Goodness-of-fit on F^2	1.017	1.030	1.081
Final R indices	3989 data; $I > 2\sigma(I)$ R1 = 0.0471, wR2 = 0.1061 All data R1 = 0.0744, wR2 = 0.1176	4048 data; $I > 2\sigma(I)$ R1 = 0.0327, wR2 = 0.0775 All data R1 = 0.0397, wR2 = 0.0812	2707 data; $I > 2\sigma(I)$ R1 = 0.0475, wR2 = 0.0863 All data R1 = 0.0770, wR2 = 0.0952
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.6848P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 6.5902P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0181P)^2 + 1.8431P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole	0.252 and -0.237 eÅ $^{-3}$	1.360 and -0.723 eÅ $^{-3}$	0.445 and -0.382 eÅ $^{-3}$
R.M.S. deviation from mean	0.051 eÅ $^{-3}$	0.080 eÅ $^{-3}$	0.068 eÅ $^{-3}$

APEX3 software [17] is used to draw figures. The molecules has only aromatic hydrogen atoms which were positioned geometrically and treated as riding atoms with C-H = 0.93 Å and Uiso (H) = 1.2 Ueq (C) carbon atoms. The crystal data (Table-1) and Data collection with structure refinement details for L, Ru-L and Zn-L listed in Table-1. The CIF files are obtainable free of charge from Cambridge crystallographic Data Center (CCDC) under CCDC number 1526413 for L, 1526414 for Ru-L and 1526415 for Zn-L.

RESULTS AND DISCUSSION

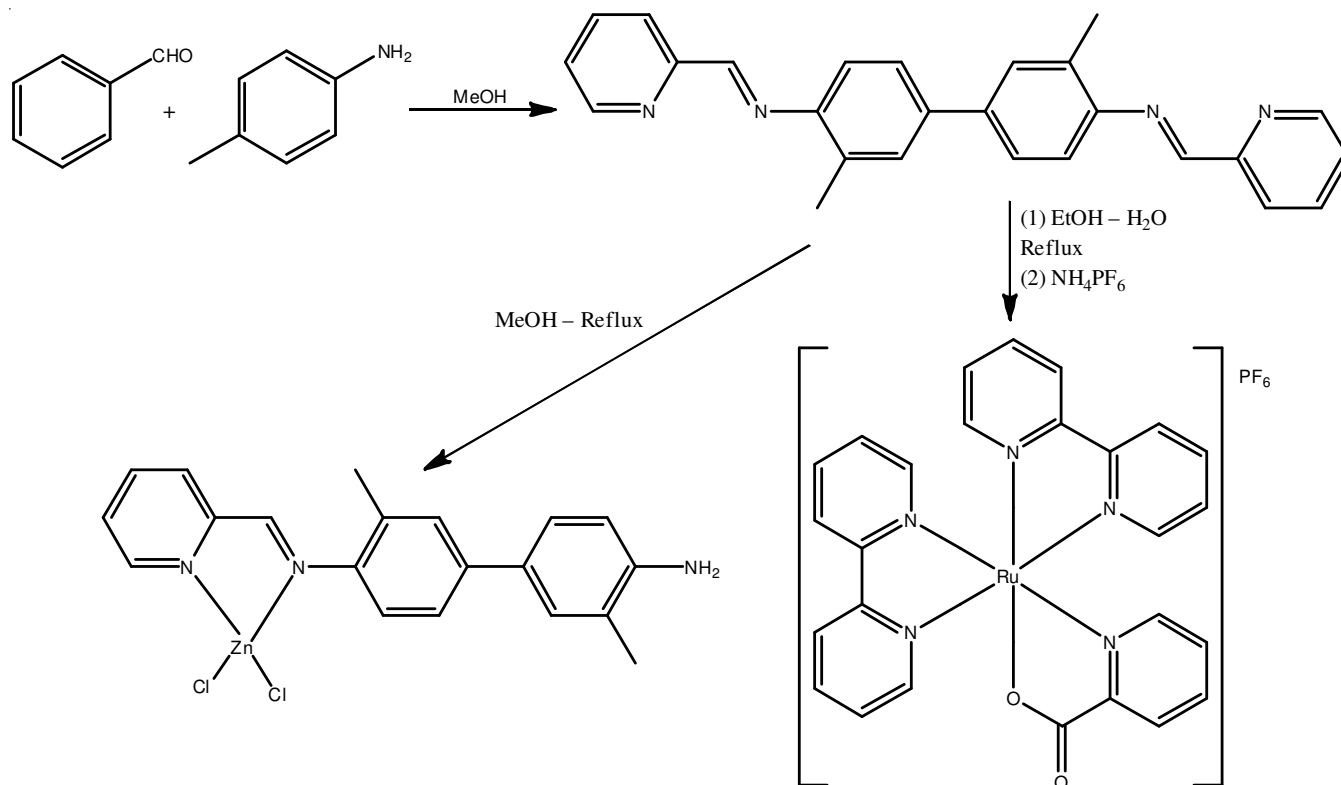
In our attempts to obtain a series of ligands derived from pyridine-2-carboxaldehyde, unusual reaction was encountered with *p*-toluidine. The methyl group isomerization and the dimerization (biphenyl formation) seems to proceed very fast after the Schiff base formation at room temperature in few minutes (**Scheme-I**). We tried to shorten the time, run the reaction in dark and in an ice bath, hoping to prevent the further reactions after the Schiff base formation. However, we could not observe any traces of the Schiff base (monomer).

Isomerization of alkyl and aryl groups in arene rings has been reported in literatures [18-21] and such reaction has been used in many industrial processes including the conversion of mixed xylene to *p*-xylene [22]. Many reports highlighted the importance of temperature and/or the presence of acid to catalyze the process [18-22]. In present case, the pyridine-2-carboxaldehyde (99 %) contains 0.5 % of the free acid and it is possibly the source of H⁺ that catalyze the isomerization of the methyl group (steps 1, 2 and 3 in **Scheme-II**).

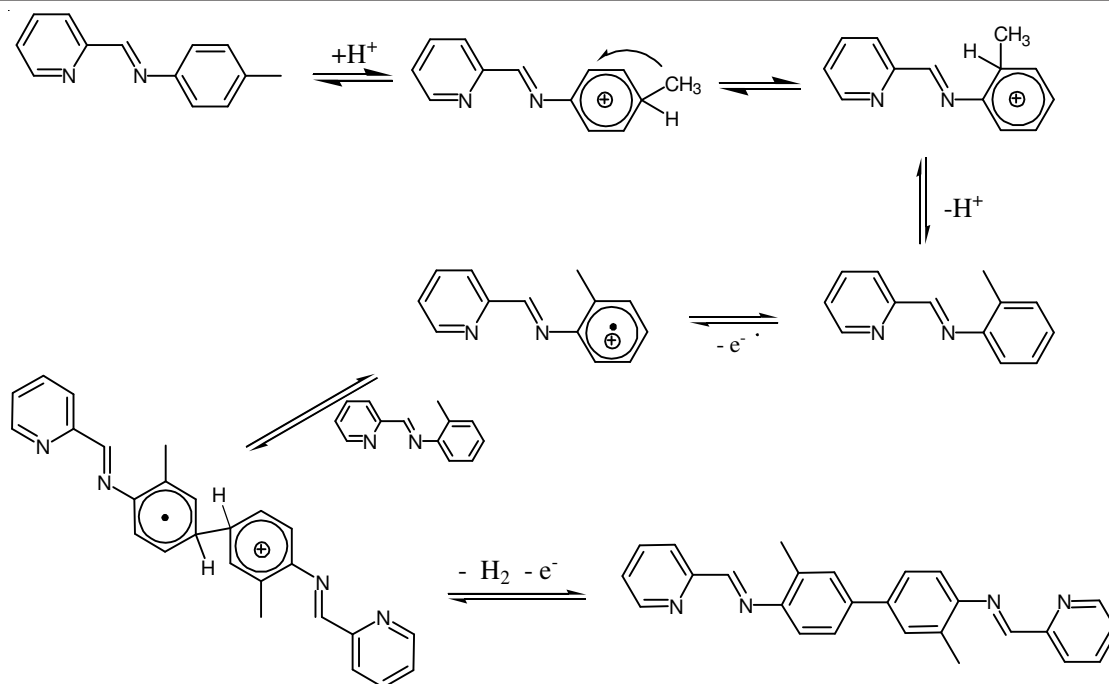
The dimerization process can only proceeds by the oxidative coupling to give the biphenyl system [23]. However, this

reaction requires a catalyst to promote the coupling unless the phenyl ring is reasonably electron rich (steps 4, 5 and 6 in **Scheme-II**) [24]. The methyl group on the ring is believed to be of huge importance in driving the biphenyl formation as the analogue Schiff base derived from the reaction of benzaldehyde and pyridine-2-carboxaldehyde does not proceed the dimerization [25]. More work is ongoing to gain a better understanding of the nature of the reaction of pyridine-2-carboxaldehyde with variant aromatic amine and the reactivity of the resulted Schiff bases.

The obtained dimerized Schiff base has two coordinating bidentate sites which encouraged us to try the preparation of bimetallic systems. Although, we tried many metal salts and some organometallic centers, but only two metal complexes were isolated and identified by X-ray crystallography (**Scheme-I**). The steric hindrance in the ligand slow down its coordination and the presence of metal ion with water seem to promote the oxidation of one of the azomethine bond [26]. The ruthenium(II) favours the coordination of the pyridine-2-carboxylic acid resulted from the azomethine oxidation due to the steric bulkiness of the pyridine-2-Schiff base. The ruthenium(II) complexes reported previously through the reaction of *cis*-[Ru(bpy)₂Cl₂] with (1-Methyl-1H-imidazol-2-yl)-pyridin-2-yl ketone as the ligand underwent an oxidation reaction before the coordination [27]. Ruthenium(II) complexes with carboxylate ligands are of interest because of their electrochemical and spectroscopic behaviour [28,29]. Zinc(II) can be coordinated to the pyridine-2-Schiff base moiety because of it is smaller ion radius compared to ruthenium and the absence of co-ligands which contributes to the steric-demand in the ruthenium center. The reaction of zinc(II) with



Scheme-I: Synthesis of the Schiff base ligand with their reaction with ruthenium(II) and zinc(II)



Scheme-II: Suggested mechanism for the ligand formation

multidentate N-based ligands provides coordination complexes with tetrahedral [30,31], trigonal bipyramidal [31,32] and octahedral geometries [32]. The zinc coordinates to one site of pyridyl-CH=N while the second CH=N undergoes an oxidation reaction to produce the amino group.

Crystallography of (E)-N-(3,3'-dimethyl-4'-((E)-(5-methylpyridin-2-yl)methylene)amino)-[1,1'-biphenyl]-4-yl)-1-(pyridin-2-yl)methanimine (L): The structure of (E)-N-(3,3'-dimethyl-4'-((E)-(5-methylpyridin-2-yl)methylene)amino)-[1,1'-biphenyl]-4-yl)-1-(pyridin-2-yl)methanimine, $C_{26}H_{22}N_6$, has triclinic (P-1) symmetry. The structure displays C—H...N intramolecular and intermolecular hydrogen bonds. The molecule consists of two (E)-1-(pyridin-2-yl)-N-(*o*-tolyl)-methanimine connected in *para*-position. The dihedral angles between the six-membered ring Pyridyl N1/C1-C5 and others six-membered rings C22-C26/N4, C7-C12 and C14-C20 are 37.04(9), 35.80(9) and 61.09(9), respectively. The torsion angles C7-N2-C6-C5 = 179.95(15) and C22-C21-N3-C17 = -177.82(15) which connected the pyridine and *N*-*o*-tolylmethanimine moieties. Fig. 2 displays the molecule structure of L and Table-2 displays some selected data for the compound.

Crystallography of Ru-L: The crystal structure of the complex is shown Fig. 3. The asymmetric unit of the title compound, $[Ru(C_{10}H_8N_2)_2(C_6H_4NO_2)]PF_6$, contains a monomeric $[Ru(bpy)2(py-COO)]$ cation {bpy is 2,2'-bipyridine and py-COO is pyridine-2-carboxylate and one hexafluorophosphate anion (Fig. 3). The ruthenium(II) ion is in a distorted octahedral environment coordinated by two bpy ligands and one py-COO ligand, the Ru—N and Ru—O bond lengths as follows: Ru1-N1 = 2.023(8) Å, Ru1-N2 = 2.011(8) Å, Ru1-N3 = 2.060(8) Å, Ru1-N4 = 2.043(8) Å, Ru1-N5 = 2.071(8) Å and Ru1-O1 = 2.094(7) Å. The ligands bite angles are N1-Ru1-N2 = 78.94(12)° to N3-Ru1-N4 = 79.00(10)° and N5-Ru1-O1 = 78.88(10)° to N2-Ru1-O1 = 170.7(3)°. Table-3 displays some selected data for ruthenium complex. The crystal structure data is in agreement with the data reported previously for the same complex synthesized *via* two different routes [27].

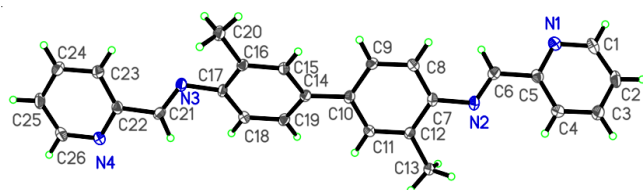


Fig. 2. Molecular structure of the L compound, shown with 50 % probability displacement ellipsoids and the atom-numbering scheme

Bond length (Å)		Bond angles and Torsion angles	
N2-C6	1.272(3)	C21-N3-C17	120.60(19)°
N3-C21	1.272(3)	C6-N2-C7	119.65(19)°
N2-C7	1.409(3)	C26-N4-C22	116.8(2)°
N3-C17	1.415(3)	C1-N1-C5	116.86(19)°
C10-C14	1.482(3)	N1-C5-C4	122.69(17)°
—	—	C11-C10-C14-C15	155.64(17)°

phate anion (Fig. 3). The ruthenium(II) ion is in a distorted octahedral environment coordinated by two bpy ligands and one py-COO ligand, the Ru—N and Ru—O bond lengths as follows: Ru1-N1 = 2.023(8) Å, Ru1-N2 = 2.011(8) Å, Ru1-N3 = 2.060(8) Å, Ru1-N4 = 2.043(8) Å, Ru1-N5 = 2.071(8) Å and Ru1-O1 = 2.094(7) Å. The ligands bite angles are N1-Ru1-N2 = 78.94(12)° to N3-Ru1-N4 = 79.00(10)° and N5-Ru1-O1 = 78.88(10)° to N2-Ru1-O1 = 170.7(3)°. Table-3 displays some selected data for ruthenium complex. The crystal structure data is in agreement with the data reported previously for the same complex synthesized *via* two different routes [27].

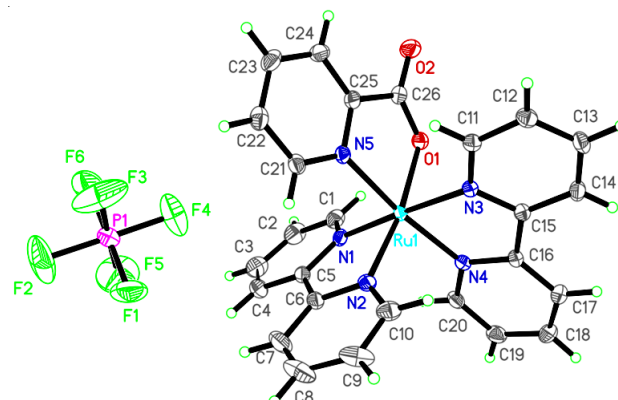


Fig. 3. Molecular structure of Ru-L complex, shown with 50 % probability displacement ellipsoids and the atom-numbering scheme

TABLE-3
SELECTED BOND LENGTHS AND ANGLES IN Ru-L COMPLEX

Bond length (Å)		Bond angles	
Ru1-N1	2.024(3)	N2-Ru1-O1	171.06(9)°
Ru1-N2	2.017(3)	N5-Ru1-O1	78.88(10)°
Ru1-N3	2.054(3)	N2-Ru1-N1	78.94(12)°
Ru1-N4	2.039(3)	N1-Ru1-N3	176.22(9)°
Ru-N5	2.051(3)	N4-Ru1-N3	79.00(10)°
Ru1-O1	2.092(2)	N4-Ru1-N5	173.08(9)°

Crystallography of Zn-L: A view of the molecular structure of the title compound is shown in Fig. 4. The Zn(II) ion is coordinated by two chloride ions and by the bidentate NN site of the ligand. The Zn—N2 bond is longer than that of Zn—N1 (2.059(5) and 2.096(5) Å, respectively), due to the strong steric effect of the methyl group while the Zn—Cl bonds are almost identical. The coordination environment of Zn(II) ion can be described as trigonal pyramidal, $\tau = 0.81$ (Extreme Forms: 0.00 for SQP and 1.00 for TET; 0.85 for TRP) [33]. Although, Zn(II) complexes normally adopt tetrahedral geometry [30,31] or less commonly trigonal bipyramidal [31,32] due to the lack of any ligand field stabilization energy of the d^{10} metal, the bulkiness of the methyl group forces the unusual geometry of the complex. The bond angles around the Zn(II) ion are N1-Zn1-N2 = 81.3(2), N1-Zn1-Cl2 = 116.87(16), N2-Zn1-Cl2 = 105.57(11), N1-Zn1-Cl1 = 108.68(19), N2-Zn1-Cl1 = 123.16(16) and Cl2-Zn1-Cl1 = 116.74(9)°. Table-4 illustrates some selected bond lengths and angles for the zinc compound.

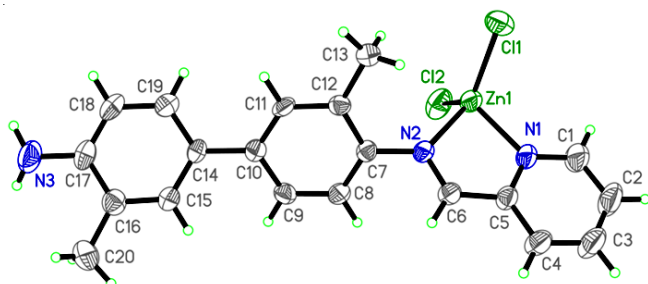


Fig. 4. Molecular structure of Zn-L complex shown with 50 % probability displacement ellipsoids and atom-numbering scheme

TABLE-4
SELECTED BOND LENGTHS AND ANGLES IN Zn-1 COMPLEX

Bond length (Å)		Bond angles	
Zn1-Cl1	2.212(5)	Cl2-Zn1-Cl1	116.74(9)°
Zn1-Cl2	2.208(5)	N2-Zn1-Cl1	123.16(16)°
Zn1-N1	2.059(5)	N1-Zn1-Cl1	108.67(19)°
Zn1-N2	2.096(5)	N2-Zn1-Cl2	105.57(11)°
N2-C6	1.275(5)	N1-Zn1-Cl2	116.87(16)°
C5-C6	1.467(6)	N1-Zn1-N2	81.3(2)°

Conclusion

The high reactivity of Schiff base product of *p*-toluidine with pyridine-2-carboxaldehyde was observed, leading to methyl group immigration to *ortho*-position followed by the dimerization reaction to form biphenyl system, forming the highly conjugated ligand with two bidentate coordination sites. The coordination behaviour of the Schiff base was examined

against many metal salts and some organometallic centers. Two metal complexes were only isolated and identified by X-ray crystallography for ruthenium(II) and zinc(II), showing that metals promote the catalyzed oxidation of the azomethine bond in case of the ruthenium center followed by the coordination of ruthenium center to pyridine-2-carboxylic acid while zinc is coordinated to NN site on the ligand followed by the catalyzed oxidation. The crystal structure of zinc(II) complex showed trigonal pyramidal geometry, enforced by the methyl steric hindrance. Further studies are ongoing to explore the behaviour of the ligand with different metal centers and to synthesize more ligands derived from pyridine-2-carboxaldehyde.

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