



Synthesis, Characterization and Coordination Chemistry of *N,N'*-bis(3-pyridylmethyl)benzene-1,4-dicarboxamide with Palladium and Ruthenium Salts

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Received: 17 January 2017;

Accepted: 17 March 2017;

Published online: 13 May 2017;

AJC-18373

N,N'-bis(3-pyridylmethyl)benzene-1,4-dicarboxamide (**L**) is a diamide bridging ligand. Utilization of bridging ligand such as **L** that exhibits amide moieties has greater potential to encapsulate anion *via* N-H hydrogen bonding donor groups and form metal ligand interaction *via* its pendant group containing pyridine-N atom. The complexes derived from this ligand also capable to form metallosupramolecular assemblies with the presence of the respective moieties. *N,N'*-bis(3-pyridylmethyl)benzene-1,4-dicarboxamide is synthesized from reaction between terephthaloyl chloride and 3-pyridylmethylamine in basic solution. The coordination chemistry between ligand **L** and two metal salts, palladium chloride and ruthenium chloride were attempted. Based on the combination of spectroscopic techniques such as CHNS, FTIR, NMR, TGA and cyclic voltammetry analysis, the molecular formula of the complexes may be suggested as: [Pd₂(**L**)Cl₄] and [Ru₂(**L**)Cl₆(H₂O)₄·2H₂O].

Keywords: Amide ligand, Coordination chemistry, Metal complexes.

INTRODUCTION

Supramolecular chemistry is the aggregates small subunit to larger unit *via* weak intermolecular forces [1]. The importance of weak intermolecular interactions are polar interaction, hydrogen bonding interaction, metal coordination and hydrophobic and hydrophilic interaction [2]. The interaction of hydrogen bonding can be occurred when partially positive hydrogen atom donate its proton to the partially negative atom. Among others, amide group has great ability to increase the strength of intermolecular interaction from its hydrogen bonding interaction and also metal coordination *via* N-H bonding donor group. It has also been reported that N-H bonding donor group can act as an effective neutral anion receptor because its ability to bind anion *via* its hydrogen bond. Ligand contains nitrogen as a donor atom was also reported stable, convenient to synthesis and has unique properties useful in many applications [3-6]. Amide ligand is versatile ligand because its bombastic structure can act as good anion receptor and also form metallosupramolecule when it interacts with metal centre. Realising the special properties and great benefits ligand incorporate amide moieties, hence, it has driven our effort to investigate the compound derivate from amide group. In this study, the ligand *N,N'*-bis(3-pyridylmethyl)benzene-1,4-dicarboxamide was

prepared and its coordination chemistry was studied. The ligand reacted with palladium(II) chloride and ruthenium(III) chloride to form metal complexes.

EXPERIMENTAL

Infrared spectra were carried out on FTIR, Perkin-Elmer spectrum 100 by using KBr disks. CHNS elemental analysis was recorded by using a Flash EA 1112 Series. The ¹H and ¹³C NMR were recorded on a Bruker Advance III 400 spectrometer with DMSO-*d*₆ as a solvent. For thermogravimetric analysis, it was carried out by using TGA/SDTA 851° analyzer METTLER TOLEDO. Melting points were measured from Stuart Scientific Melting Point Apparatus SMP3. The redox reaction was interpreted by using cyclic voltammetry (CV).

***N,N'*-bis(3-Pyridylmethyl)benzene-1,4-dicarboxamide, (**L**):** Terephthaloyl chloride (2.03 g, 10.1 mmol) was dissolved in dichloromethane (20 mL). 3-pyridylmethylamine (2.1 mL, 20.6 mmol) and triethylamine (2.9 mL, 20.9 mmol) were dissolved in dichloromethane (20 mL) and added slowly. The resulting solution was stirred for 48 h to give the diamide compound as a yellowish solid (3.78 g, 92 %). m.p.: 172-174 °C.

Palladium complex in ratio 1:1, 2:1 and 4:1 (metal-to-ligand ratio), (complex 1-3, respectively): Palladium chloride (0.040 g, 0.23 mmol; 0.042 g, 0.24 mmol; 0.041 g, 0.24 mmol)

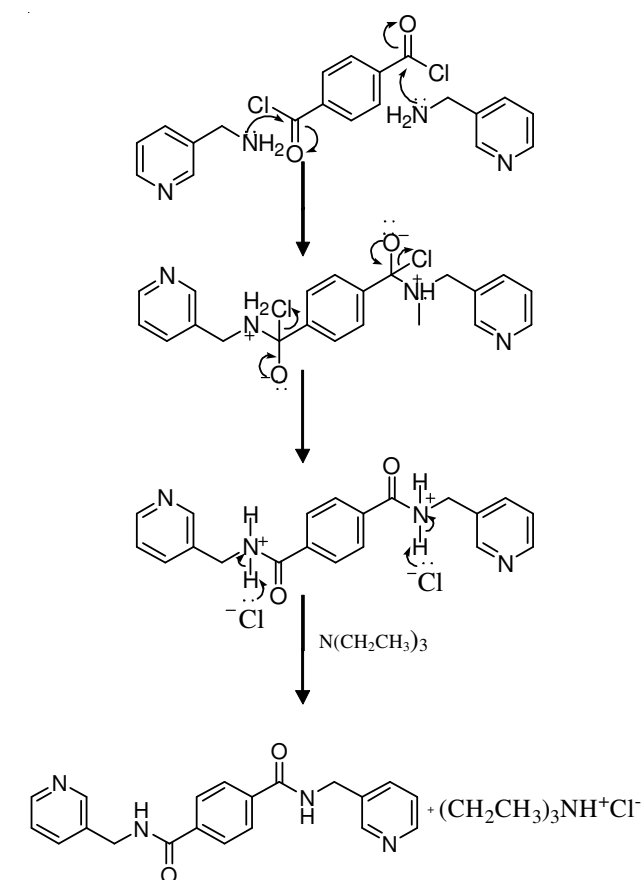
represented to complexes **1-3**, respectively were dissolved in 2 M hydrochloric acid. These solution were added dropwise to a solution of **L** (0.081 g, 0.23 mmol; 0.042 g, 0.12 mmol; 0.021 g, 0.06 mmol) in methanol (20, 15 and 10 mL) for complexes **1-3**, respectively. A yellow precipitate formed after being stirred overnight, collected by filtration, washed with ethanol and dried to give pale yellow solid (0.71 g, 66 %), m.p. 106-255 °C; yellow solid (0.07 g, 86 %), m.p.: 252-299 °C and dark yellow solid (0.01 g, 24 %), m.p.: 268-295 °C represented to complex **1-3**, respectively.

Ruthenium complex in ratio 4:1 (metal-to-ligand ratio)

(complex **4**): Ruthenium(III) chloride (0.25 g, 1×10^{-6} mmol) was dissolved in methanol (25 mL). The solution was heated under reflux for 5 h until the solution turned green. The *N,N'*-bis(3-pyridylmethyl)benzene-1,4-dicarboxamide (0.1 g, 2.7×10^{-7} mmol) was added to the solution. The mixture was refluxed for 2 h. The dark green precipitate was filtered and dried under vacuum. Then, the product was recrystallized with methanol to give dark green solid (0.046 g, 46 %). m.p.: 400-430 °C.

RESULTS AND DISCUSSION

***N,N'*-bis(3-Pyridylmethyl)benzene-1,4-dicarboxamide, (L):** The ligand, **L** was synthesised based on the literature procedures [7]. It was reacted with terephthaloyl chloride, 3-pyridylamine and triethylamine. Triethylamine acts as a base [8,9] to increase the effectiveness of nucleophilic substitution of the amines. The mechanism of the reaction is suggested in Scheme-I.



Scheme-I: Mechanism of **L** (*N,N'*-bis(3-pyridylmethyl)benzene-1,4-dicarboxamide)

FTIR spectrum of **L** showed five absorption bands due to NH stretch (3191 cm^{-1}), C=O stretch (1639 cm^{-1}), C=C stretch (1594 cm^{-1}), NH bend (1543 cm^{-1}) and CN stretch (1318 cm^{-1}). From the comparison between the FTIR spectra of **L** and the literature compound which is the analogue of the ligand namely *N,N'*-2,6-bis(4-pyridylmethyl)pyridinedicarboxamide [7] (Table-1), it has been confirmed that the expected ligand was amide derivatives compound.

TABLE-1
COMPARISON BETWEEN THE FTIR SPECTRA BETWEEN *N,N'*-BIS(3-PYRIDYLMETHYL)BENZENE-1,4-DICARBOXAMIDE (**L**) AND THE LITERATURE LIGAND (*N,N'*-2,6-BIS(4-PYRIDYLMETHYL)PYRIDINEDICARBOXAMIDE)

Bands	Literature compound (cm^{-1})	L (cm^{-1})
N-H stretch	3062	3191
C=O	1640	1639
C=C stretch	1600	1594
N-H bend	1540	1543

^1H NMR spectra of **L** can be observed at δ_{H} 8.0 ppm belongs to phenyl aromatic proton. The inducing ring current of aromatic π electron is affected the downfield position of this peak. NH moieties can be assigned at δ_{H} 9.3 ppm. The higher chemical shift of this molecule due to its position is closer to the stronger electronegativity oxygen atom; so, proton will be decrease the electron density around it [10]. The signal range of δ_{H} 7.4-8.7 ppm were indicated the H atom for pyridine ring. For methylene linker, the signal of proton appears at δ_{H} 4.5 ppm. The ^{13}C NMR spectrum showed the carbon resonance for the $-\text{CH}_2$ peaks at δ_{C} 9 ppm. The resonance observed at δ_{C} 167 ppm belongs to the C atom of C=O amide group. The DMSO- d_6 peak appears at δ_{C} 40 ppm. The carbon resonance for C (aromatic ring) can be observed at δ_{C} 135 ppm. Lastly, peak of $-\text{CN}$ for pyridine was indicated at δ_{C} 46 ppm.

Palladium complexes 1-3: Three different ratios of palladium(II) chloride, complexes **1-3** have been attempted in order to find the most efficient method for coordination polymer. All of three palladium complexes show similar FTIR spectra (Table-2) which represented to palladium complexes with general formula of $[\text{Pd}_2(\text{L})\text{Cl}_4]$. The complex based on palladium transition-metal currently interest because its properties suitable for catalytic applications [11]. Vouti [12] stated the interaction between ligand and metal centre influence the chemical behaviour of a metal ion and its properties as a metal complex.

TABLE-2
COMPARISON OF IR SPECTRA BETWEEN THREE PALLADIUM COMPLEXES

Bands	Complex 1 (cm^{-1})	Complex 2 (cm^{-1})	Complex 3 (cm^{-1})
N-H stretch	3324.80	3326.12	3325.67
C=O	1642.51	1643.05	1643.38
N-H bend	1537.81	1537.51	1537.75
C-N stretch	1293.76	1293.65	1293.74

Meanwhile, the special band was detected at 499.77 cm^{-1} for complex **3**. It shows that palladium was attached on ligand *via* nitrogen atom. The previous studies stated the appearance of band at the range $509\text{--}467\text{ cm}^{-1}$ showed the confirmations of metal coordinate on the respective ligand *via* nitrogen atom [13].

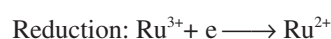
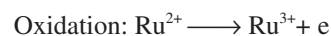
Ruthenium(III) complex (4): FTIR spectrum of complex **4** shows four absorptions for (N-H stretch), $\nu(\text{C}=\text{O})$, $\nu(\text{N-H bend})$ and $\nu(\text{C-N stretch})$ at 3430.60, 1637.56, 1542.14 and 1296.47 cm^{-1} , respectively. As comparing the FTIR spectrum between complex **4** and ligand, the significant changes was observed on the vibration of (N-H stretch). In the complex, the frequency of NH stretch was shifted from 3191.00 to 3430.60 cm^{-1} . It shows that ruthenium was attached to ligand at nitrogen atom.

Elemental analysis: The elemental analysis of ligand (**L**), Pd(II) and Ru(III) complexes also been analyzed to know the general formula and expected structure. Table-3 shows the elemental data of the compounds. All of the results showed the agreement between the theoretical and experimental data, with molecular formula suggested in Table-3.

Thermogravimetric analysis (TGA): The thermal decomposition of Pd(II) and Ru(III) complexes have been studied. The temperature used is the range 200-700 $^{\circ}\text{C}$ at the heating rate of 10 $^{\circ}\text{C}/\text{min}$. Based on the TGA results, it show that the complexes decomposes stepwise (Table-4).

Cyclic voltammetry (CV): The oxidation and reduction state of the metal centre in the complex **4** was analyses by using

cyclic voltammetry. The redox behaviour of complex has been examined in acetonitrile with 1×10^{-5} M of sulphuric acid as a supporting electrolyte. This complex exhibits metal and ligand-centred electrochemistry in the potential range -2 to +2 V. One complete of quasi-reversible for oxidation and reduction process was shown. The scan rate is set at 0.5 V/s to control the time scale of this experiment. Based on voltammogram (Fig. 1), the oxidation process occurs at the initial potential of -2 V where Ru^{2+} begins to be oxidized to the Ru^{3+} . The current was increase as the rate of oxidation increase at more positive potentials. Ru^{3+} begins to reduce to Ru^{2+} . Then, the scan direction was reversed at the 2.0 V where the reduction of Ru^{3+} to Ru^{2+} occurs. In the process of reduction, the layer of Ru^{3+} has been depleted and accumulated the layer of Ru^{2+} . The oxidation and reduction of half-reaction of ruthenium complex are:



Eskelinen and co-workers [14] have reported that the oxidation potential of ($\text{Ru}^{2+}/\text{Ru}^{3+}$) is positively shifted due to the strong electron donor properties of the Cl^{-} ligand in ruthenium complex.

TABLE-3
ELEMENTAL ANALYSIS AND EXPECTED RESULTS OF LIGAND (L), Pd(II) AND Ru(III) COMPLEXES

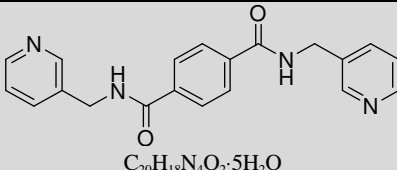
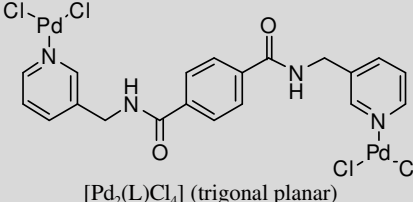
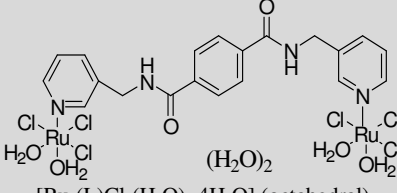
Sample	C (%)		H (%)		N (%)		Expected structure and molecular formula
	Calcd.	Found	Calcd.	Found	Calcd.	Found	
Ligand, L	55.04	56.99	6.47	6.33	12.84	12.78	 $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2 \cdot 5\text{H}_2\text{O}$
Pd(II) complex	34.26	35.24	2.59	2.87	7.99	7.84	 $[\text{Pd}_2(\text{L})\text{Cl}_4]$ (trigonal planar)
Ru(III) complex	28.52	28.44	3.76	2.93	6.34	6.38	 $[\text{Ru}_2(\text{L})\text{Cl}_6(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}]$ (octahedral)

TABLE-4
TGA RESULTS OF PALLADIUM AND RUTHENIUM COMPLEXES

Sample	Decomposition steps	Temp. ($^{\circ}\text{C}$)		Weight loss (%)	Molecule decomposition
		Start	End		
Pd(II) complex	1st	210	250	1.6975	One lattice water molecule
	2nd	250	300	17.6470	Elimination of chloro atom and evolution of CO
	3rd	300	340	13.6012	Two pyridine groups, $\text{C}_{10}\text{H}_{10}\text{N}_2$ from L and liberation of CN gas
	4th	340	420	13.2139	Elimination of $\text{C}_8\text{H}_{10}\text{N}_2$ from L
Ru(III) complex	1st	300	435	1.6975	Loss of two lattice water molecule along with six chloro atoms
	2nd	435	475	5.7926	Loss of four coordinated water
	3rd	475	555	12.3699	Elimination of the of two pyridine groups, $\text{C}_{10}\text{H}_{10}\text{N}_2$ from L and liberation of CN gas
	4th	555	655	11.4403	Loss of $\text{C}_8\text{H}_{10}\text{N}_2$ from L

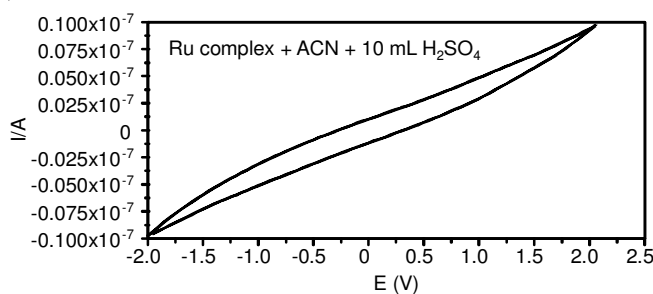


Fig. 1. Cyclic voltammetry for ruthenium complexes

Conclusion

In this study, ligand *N,N'*-bis (3-pyridylmethyl)benzene-1,4-dicarboxamide (**L**) and its complexes with Pd(II) and Ru(III) have been successfully synthesized. All of the compounds obtained in good yield. Three differences ratio of metal to ligand (1:1, 2:1 and 4:1) of palladium complexes have been successfully prepared. But all the complexes show unobvious differences of IR spectra among them. The highest yield (86 %) of palladium salt by using 2:1 ratio is prefer to best procedure for coordination polymer. Furthermore, for preparation of ruthenium complex, the ratio 4:1 for metal to ligand has been used. Based on the analyses have been done, it show that all of the compounds were potentially to be studied in the future.

ACKNOWLEDGEMENTS

The authors thank the School of Agriculture Science and Biotechnology, Faculty of Bioresources and Food Industry, Universiti Sultan Zainal Abidin and School of Fundamental Science, Universiti Malaysia Terengganu and Institute Marine Biotechnology (IMB) and the RMIC, UniSZA for facilities and publication support.

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