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Collaborative Activity 1

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A series of ruthenium(II) organometallic complexes incorporating pyridine-2-carboxylato ligand: Detailed spectroscopic and computional studies

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ABSTRACT

The reaction of $Ru(\kappa^2C,O\text{-}RL)(PPh_3)_2(CO)Cl$, **1** with excess sodium salt of pyridine-2-carboxylic acid (Napic) furnishes the complexes of the type $Ru(\kappa^1C\text{-}RL)(PPh_3)_2(CO)$ (pic), **2**(R) with excellent yield (κ^2C,O-RL is C_6H_2O-2-$CHNHC_6H_4R(p)$-3-Me-5, κ^1C-RL is C_6H_2OH-2-$CHNC_6H_4R(p)$-3-Me-5 and R is Me, OMe, Cl). The chelation of pic is attended with the cleavage of Ru–O and Ru–Cl bonds and iminium–phenolato→imine–phenol prototropic shift. The **1** → **2** conversion is irreversible and the type **2** species are thermodynamically more stable than the acetate, nitrite and nitrate complexes of **1**. The spectral (UV–vis, IR, ^1H NMR) and electrochemical data of the complexes are reported. In dichloromethane solution the complexes display one quasi-reversible RuIII/RuII cyclic voltammetric response with $E_{1/2}$ in the range 0.72–0.80 V *vs.* Ag/AgCl. The crystal and molecular structure of $Ru(\kappa^1C\text{-}MeOL)(PPh_3)_2(CO)(pic)\cdot CH_3CN$ is reported which revealed distorted octahedral RuC_2P_2NO coordination sphere. The pairs (P, P), (C, O) and (C, N) define the three *trans* directions. The electronic structures of the complexes are also scrutinized by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations.

1. Introduction

Picolinic acid (Hpic) is related to α-amino acid and is a naturally occurring ligand [1]. It has two significantly different donor sites (N, O) and can exhibit a variety of coordination modes [2–15]. It plays important roles in some enzymes and is active agent in a number of drugs [16–23]. Picolinate ion (pic) is a distinguished terminal tryptophan metabolite [24] and can also induce cell death by DNA fragmentation [25]. It is documented that Hpic reduces intra macrophage growth of the mycobacterium avium complex [26]. Several Co, Cu, Zn and Ru complexes with the picolinate ligand have been synthesized [27–32]. Some metal-picolinate complexes show *in vitro* antimycobactrial activity against M. tuberculosis [33] and are active catalyst for ring closing metathesis (RCM), cross metathesis and enzyme metathesis reactions [34].

Almost two decades ago, ruthenium organometallics of type $Ru(\kappa^2C,O\text{-}RL)(PPh_3)_2(CO)Cl$, **1** was synthesized by decarbonylative orthometallation reaction of $Ru(PPh_3)_3Cl_2$ and 4-methyl-2,6-diformylphenol in presence of primary amine [35]. In the literature the reactivity of **1** is well-documented. It has been found that displacement of labile chloride ligand of **1** can be achieved by various mono-anionic [36–44] and neutral chelating ligands [45]. Insertion of alkynes and isonitrile respectively into the Ru–C(aryl) and Ru–O bonds of **1** have also been studied [46,47]. Cleavage of Ru–C(aryl) bond of **1** has been found in the reaction of **1** with 2-mercaptopyrimidine and pyridine-2, 6-dicarboxylate ligands [48]. The thiolato bridged binuclear ruthenium complexes have also been synthesized by the reaction of **1** with sodium *p*-chlorothiophenolate in refluxing ethanol [49].

We were fascinated with the reaction chemistry of **1**, so far studied, and it has prompted us to investigate this further. Herein we present the facile reaction of **1** with the sodium salt of picolinic acid (Napic). This ligand choice was based on the documented affinity of ruthenium for picolinate ligands [1,33,50–53]. The reaction of **1** with the picolinate ligand indeed furnished a new class of picolinate chelated ruthenium organometallics. The synthetic procedures, structure, spectroscopic and electrochemical properties of the complexes have been narrated in the present work. It has been found that in the course of the reaction RL ligand changes its coordination mode from κ^2C,O to κ^1C with the concomitant changes in the tautomeric state and rotameric conformation. The complexes are potentially luminescent in the visible region. The

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Collaborative Activity 2

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Provisional Ph.D. Certificate

No. Ph.D./Chem./A1/256(30)/2021

March 01, 2021

This is to certify that on the recommendation of the Board of Examiners, the thesis submitted by ***Anikul Islam*** *for the award of* ***Ph.D. Degree*** *of this University and on the performance of his/her Ph.D. Open Viva vide Reg.12 (D.D.) & Reg.13 (D.D.)* (as per Regulation 2014, K.U.), *he/she has been admitted to the aforesaid degree on* ***12.02.2021*** *in* ***Chemistry*** *under the faculty of* ***Science.***

The Ph.D. Degree has been awarded in accordance with the provisions of UGC (Minimum Standards and Procedure for Awards of M.Phil./Ph.D. Degree) Regulation, 2009.

Title of the Thesis:
"Chemistry of Ruthenium and Rhodium Incorporating (N,O) Donor Ligands"

His/Her Degree will be conferred by the Hon'ble Chancellor at the next Convocation of this University.

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1/3/21
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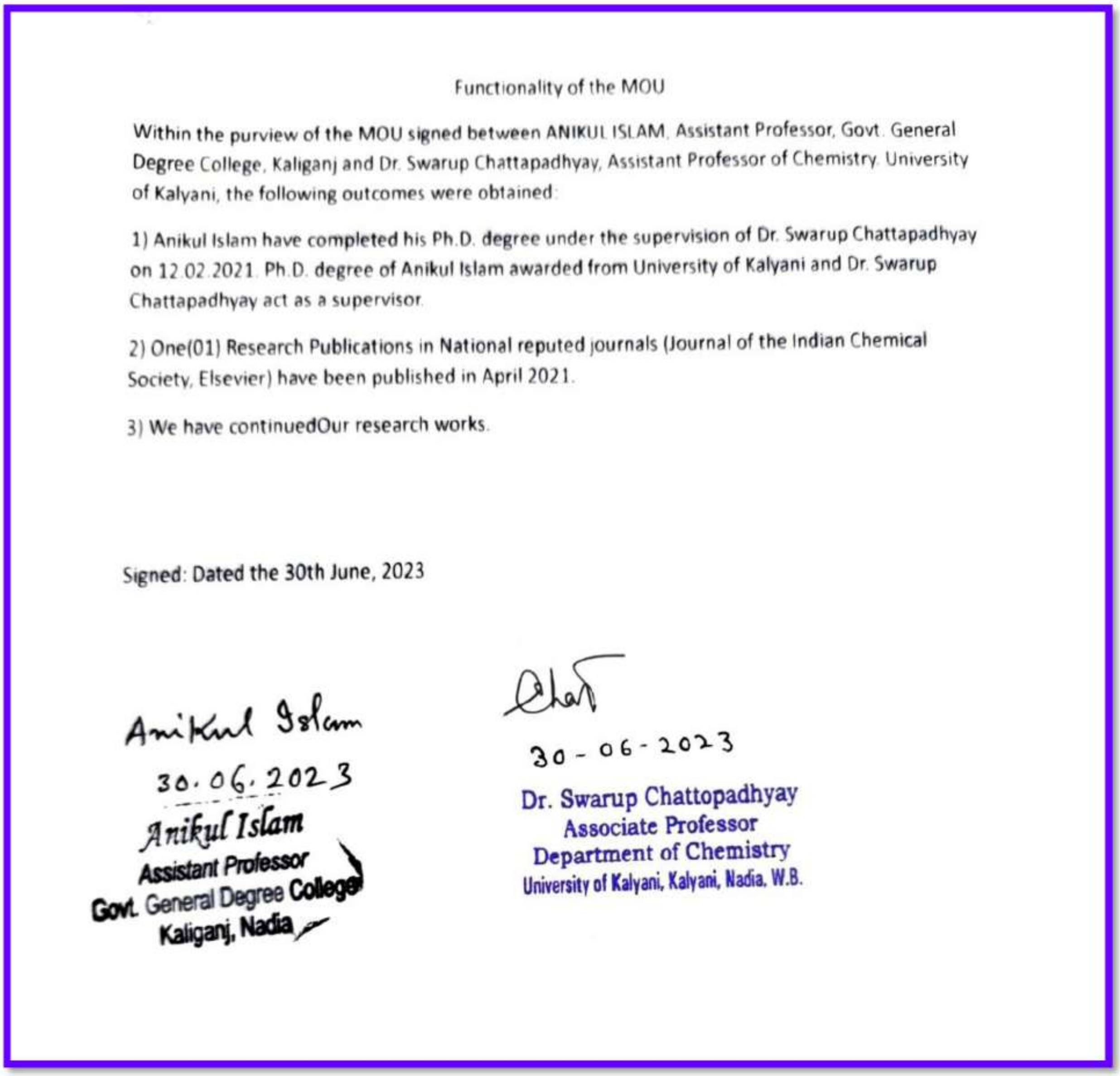

Functionality of the MOU

Within the purview of the MOU signed between ANIKUL ISLAM, Assistant Professor, Govt. General Degree College, Kaliganj and Dr. Swarup Chattapadhyay, Assistant Professor of Chemistry. University of Kalyani, the following outcomes were obtained:

1) Anikul Islam have completed his Ph.D. degree under the supervision of Dr. Swarup Chattapadhyay on 12.02.2021. Ph.D. degree of Anikul Islam awarded from University of Kalyani and Dr. Swarup Chattapadhyay act as a supervisor.

2) One(01) Research Publications in National reputed journals (Journal of the Indian Chemical Society, Elsevier) have been published in April 2021.

3) We have continuedOur research works.

Signed: Dated the 30th June, 2023

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