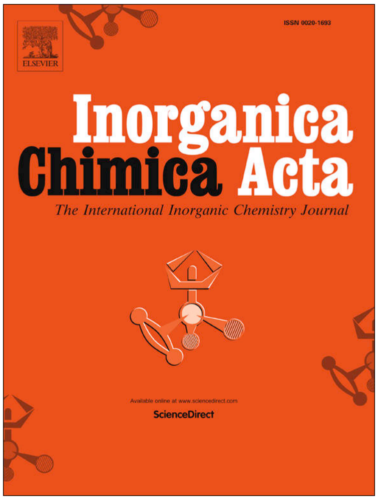

Research paper

Ru(III)-pseudohalide complexes with alkynyl functionalized salicylaldimine ligand and heterocyclic coligand: Synthesis, characterization, electrochemical and luminescence properties

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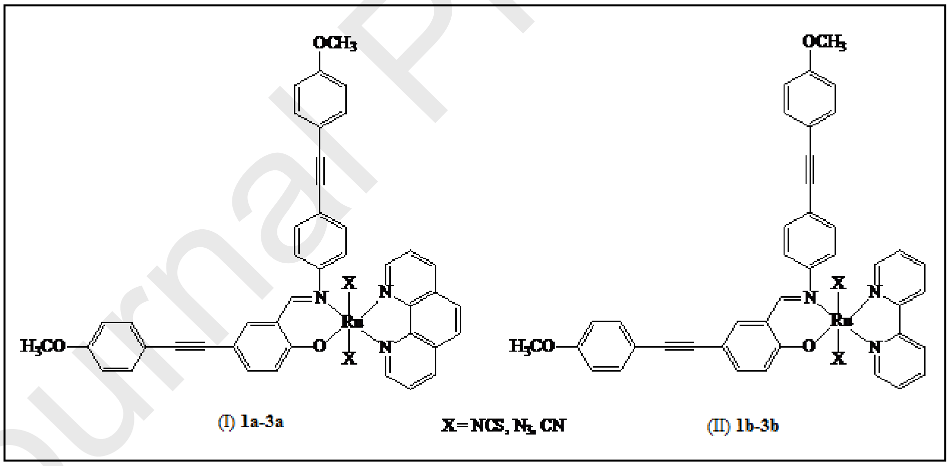
Abstract:

The hexa-coordinated Ru(III)-pseudohalide complexes of the type [Ru(**L**)(**phen**)X_2] and [Ru(**L**)(**bipy**)X_2] [where X=NCS, N_3, CN; **L**=2-((E)-(4-(2-(4-methoxyphenyl)ethynyl)phenylimino) methyl)-4-(2-(4-methoxyphenyl)ethynyl)phenol, **Phen**=1,10-phenanthroline, **bipy**=2,2'- bipyridine] have been prepared and characterized. The EPR spectra and magnetic susceptibility measurement indicate octahedral geometry around Ru(III). All complexes exhibit a quasireversible redox behaviour corresponding to Ru(III)/Ru(IV) and Ru(III)/Ru(II) couple and are variable to π-acidic character of coligands. Room temperature luminescence is observed for all complexes correspond to ILCT with some LMCT character.



Keywords: Ru(III) complexes, EPR spectra, Cyclic voltammetry, Photoluminescence

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Ru(III)-pseudohalide complexes with alkynyl functionalized salicylaldimine ligand and heterocyclic coligand: Synthesis, characterization, electrochemical and luminescence properties

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Abstract

A new series of hexa-coordinated Ru(III) complexes of the type [Ru(**L**)(**phen**)X_2] (**1a-3a**) and [Ru(**L**)(**bipy**)X_2](**1b-3b**) [where, X=NCS, N_3, CN] have been prepared by the reaction of $RuCl_3.H_2O$ with 2-((E)-(4-(2-(4-methoxyphenyl)ethynyl)phenylimino)methyl)-4-(2-(4-methoxy phenyl)ethynyl)phenol (**L**) in presence of 1,10-phenanthroline (**phen**) or 2,2′-bipyridine (**bipy**) as a ligand. The molecular structure of ligand **L** was confirmed by single crystal X-ray diffraction. All complexes were characterized on the basis of elemental analysis, magnetic moment, TGA, IR, UV-Vis, EPR and mass spectral studies. The EPR spectral data and magnetic susceptibility measurement showed octahedral geometry around Ru(III). The electrochemical properties of all complexes indicate quasireversible redox behaviour corresponding to Ru(III)/Ru(IV) and Ru(III)/Ru(II) couple and are variable to π-acidic character of **phen** and **bipy**. All complexes exhibit strong emissions from lowest energy ILCT state with some LMCT character in DMF (10^{-4} M) at room temperature indicating that alkynyl functionality on salicylaldimine ligand enhances the emission property of the complexes and varies considerably with quenching ability of pseudohalides.

Keywords: Ru(III) complexes, EPR spectra, Cyclic voltammetry, Photoluminescence

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1. Introduction

Over the decades, the transition metal complexes containing ruthenium as metal centre have been the focus of continues research interest because of their rich photocatalytic, photochemical and electrochemical properties [1-3]. The choice of this metal ion is of interest because it possesses stable and accessible oxidation states ranging from I to III. Also the photophysical, photochemical and electrochemical properties of these complexes can be tuned by introducing specific ligands in a controlled manner. In recent years, considerable research efforts have been focused on synthesis and properties of ruthenium complexes of hybrid ligands because they can provide new material with useful properties such as electrochemical, photo-physical, photo-electrochemical and catalytic properties [4-7]. Of the various ligands, Schiff base containing N, O donors are interesting ligands that have been widely exploited for the fabrication of this molecular architecture because of their structural diversity and potential applications in analytical [8], biological [9] and industrial [10] field. More recently considerable interest has been paid on incorporation of additional functionalities into Schiff base ligands which are reported to exhibit very interesting luminescence and optical properties [11, 12]. Addition of alkynyl functionality particularly, with π-conjugation in Schiff base ligand constitutes an important class of compounds as a luminescent material due to their advanced structural and electronic properties [13]. These two properties cause a large π–delocalization over the ligand which results into increase in rigidity of the structure and dipole moment of the complexes [14]. The literature survey reveals that the 1, 10-phenanthroline and 2,2'-bipyridine have attracted special interest from many researchers in the perspective of their various structural and chemical properties such as planarity, rigidity, aromaticity, basicity and chelating capability [15, 16]. All these advantages make them important starting materials for synthesis of metallodendrimers [17], supramolecular assemblies [18] as well as photoactive materials [19].

Pseudohalides such as thiocyanate (NCS), azide (N_3) and cyanide (CN) are also versatile building blocks which can link to one or more metal ions in variety of ways to form different mono-, di- or polynuclear coordination molecules and supramolecular entities. There is a vast amount of literature available on numerous transition metal complexes with interesting molecular or supramolecular assemblies by using organic ligands in combination with pseudohalides [20-22].

Influenced by all these facts, recently we have reported Ru(III)-bypyridyl complexes with 2-((E)-((4-((4-bromophenyl)ethynyl)phenyl)imino)methyl-4-((E)-phenyldiazenyl)phenol and N_3^- or NCS^- and anticipated that, the azo chromophore with extended π-conjugation lead to perturb the electronic properties of the complexes and thus their emission properties [23]. Also, these complexes are found to be suitable precursor for the preparation of nanoscale structure. Herein we report synthesis of new series of Ru(III)-pseudohalide complexes by the reaction $RuCl_3.H_2O$ with alkynyl functionalized salicylaldimine ligand 2-((E)-(4-(2-(4-methoxyphenyl)ethynyl)phenylimino)methyl)-4-(2-(4-methoxyphenylethynyl)phenol in presence of 1,10-phenanthroline and 2,2′-bipyridine as a coligand. All the complexes were characterized by elemental analysis, magnetic moment, IR, UV-Vis, EPR and mass spectral studies. The electrochemical behavior and luminescence properties of the complexes have also been studied.

2. Experimental

2.1 Materials and General Methods

All chemicals used were of AR grade. Solvents used for synthesis were distilled over appropriate drying reagents. 4-(-2-(4-methoxyphenyl)ethynyl)benzenamine [24] was prepared according to the literature procedure. Elemental analyses (C, H and N) were performed on a Thermo Finnigan FLASH EA-112 CHNS analyzer. Electronic spectra were recorded on a Shimadzu UV-Vis-NIR-100 spectrophotometer. Magnetic susceptibility was measured on Gouy balance at room temperature using a Johnson Matthey

Alfa MKI magnetic susceptibility balance with Hg[Co(SCN)$_4$] as calibrant. The EPR spectra of the complexes were recorded at room temperature on Varian E-112 spectrometer using TCNE as the standard. Infrared spectra were recorded on Perkin-Elmer FTIR spectrometer as KBr pellets in the 4000-400 cm^{-1} spectral range. ^{1}H NMR spectra of the sample was measured on Bruker-300 MHz instrument using TMS [(CH$_3$)$_4$Si] as an internal standard. ESI mass spectra were recorded using Finnegan LCQ mass spectrometer. Luminescence properties were measured using a Perkin Elmer LS 55 spectrofluorometer equipped with quartz cuvette of 1 cm path length at room temperature. Luminescence lifetime measurements were carried out by using time-correlated single photon counting from HORIBA Jobin Yvon. Thermogravimetric analysis of the complexes was carried out on a Perkin Elmer thermal analyzer in nitrogen atmosphere at a heating rate of 10 ^{o}C min. Cyclic voltammetry measurements were performed with a CH-400A electrochemical analyzer. A standard three electrode system, consisting of Pt disk working electrode, Pt wire counter electrode and Ag/AgCl as a reference electrode.

2.2. X-Ray Crystallography

Single crystal X-ray structural study of **L** was performed on Bruker KAPPA APEX-II diffractometer. Data were collected in omega and phi scan mode, MoKα=0.71073 Å at room temperature with scan width of 0.3^o at θ (0^o, 90^o and 180^o) by keeping the distance at 40 nm between sample to fixed detector at 24^o. The X-ray generator was operated at 50 kV and 30 mA. The details of crystal data, data collection and refinements are given in Table 1. The X-ray data collection was monitored by SMART program (Bruker, 2003). All the data were corrected using SAINT and SADABS programs (Bruker, 2003).SHELX-97 was used to solution of structure and full matrix least squares refinement on F2 [25]. Molecular and packing diagram were generated using ORTEP-3and Mercury-3.

2.3. *Synthesis* of 2-((E)-(4-(2-(4-methoxyphenyl)ethynyl)phenylimino)methyl)-4-(2-(4-methoxy phenyl)ethynyl)phenol (L)

2-((E)-(4-(2-(4-methoxyphenyl)ethynyl)phenylimino)methyl)-4-(2-(4-methoxyphenyl)ethynyl) phenol (**L**) was prepared by mixing of methanolic solution (10 ml) of 2-hydroxy-5-(2-(4-methoxyphenylethynyl)benzaldehyde (1.500 g, 5.937 mmol) with methanolic solution (10 ml) of 4-(-2-(4-methoxyphenyl)ethynyl)benzenamine (1.327 g, 5.946 mmol). The resulting mixture was refluxed for 3h at 80 °C. The separated brick red coloured solid was collected by filtration, washed with diethyl ether and recrystallized from ethanol.

Yield: 82%. (2.536 g, 5.561 mmol); Elemental analysis (C, H, N, wt %) Anal. Calc. for $C_{31}H_{23}NO_3$: C, 81.38; H, 5.07; N, 3.06; Found: C, 81.12; H, 4.88; N, 3.30 %; IR (KBr, cm^{-1}): 3064 υ(O-H), 2067 υ(C≡C), 1623 υ(HC=N), 1273, υ(C-O); ^1H NMR ($CDCl_3$; 300 MHz): δ 8.62 (s, 1H, HC=N), δ 13.35 (s, 1H, OH), δ 3.83 (s, 6H, OCH_3), 6.86-7.59 (m,15H Ar): ESI-MS: Found m/z = 457.51 (M^+) (calculated m/z = 457.70 for M^+).

2.4. Synthesis of [Ru(L)(phen)X_2] (1a-3a)

To a stirring solution of $RuCl_3.H_2O$ (1 mmol, 0.270 g) in methanol (10 ml) was added a solution of 1, 10 phenanthroline (1mmol, 0.180 g) and solution of two equivalent of appropriate pseudohalides (2 mmol, 0.152 g, NH_4SCN; 2 mmol, 0.129 g, NaN_3; 2 mmol, 0.130 g, KCN) in methanol (10 ml). After half an hour solution of 2-((E)-(4-(2-(4-methoxyphenyl)ethynyl)phenyl imino)methyl)-4-(2-(4-methoxyphenyl)ethynyl)phenol (**L**) (0.457 g, 1 mmol) in dichloromethane (10 ml) was added drop wise. The resulting solution was refluxed for 4h at 80 °C. The solid complex precipitated was collected by filtration, washed with 1:1 ethanol: water mixture and dried under *vacuum* over $CaCl_2$.

1a: Yield: 79%. (0.405 g, 4.747 mmol); Elemental analysis (C, H, N, wt%) Anal. Calc for $C_{45}H_{30}N_5O_3S_2Ru$: C, 63.29; H, 3.54; N, 8.20% Found: C, 63.05; H, 3.41; N, 8.40%; IR (KBr cm^{-1}): 2067, υ(C≡C); 2149, υ(NCS); 1609, υ(HC=N), 1281, υ(C-O); ESI-MS: 877 ([Ru(**L**)(**phen**)$(NCS)_2$+Na]$^+$, 22), 457 ([**L**]$^+$, 100), 397 ([Ru(**phen**)$(NCS)_2$]$^+$, 41). **2a:**Yield: 82%. (0.417 g, 5.075

mmol); Elemental analysis (C, H, N, wt%) Anal. Calc for $C_{43}H_{30}N_9O_3Ru$: C, 62.84; H, 3.68; N, 15.34% Found: C, 62.56; H, 3.45; N, 15.56%; IR (KBr cm^{-1}): 2067, υ(C≡C); 2040, υ(N_3); 1606, υ(HC=N); 1278, υ(C-O);. ESI-MS: Found: 845 ([Ru(**L**)(**phen**)$(N_3)_2$+Na]$^+$, 24), 457 ([**L**]$^+$, 100), 365 ([Ru(**phen**)$(N_3)_2$]$^+$, 43). **3a:**Yield: 84%. (0.426 g, 5.398 mmol); Elemental analysis (C, H, N, wt%) Anal. Calc for $C_{45}H_{30}N_5O_3Ru$: C, 68.43; H, 3.83; N, 8.87 % Found: C, 68.12; H, 3.57; N, 9.05%; IR (KBr cm^{-1}): 2067, υ(C≡C); 2093, υ(CN); 1607, υ(HC=N); 1279, υ(C-O); ESI-MS: 813 ([Ru(**L**)(**phen**)$(CN)_2$+Na]$^+$, 22), 457 ([**L**]$^+$, 100), 333 ([Ru(**phen**)$(CN)_2$]$^+$, 45).

2.5. Synthesis of [Ru(L)(bipy)X_2] (1b-3b)

To a stirring solution of $RuCl_3.H_2O$ (1 mmol, 0.270 g) in methanol (10 ml) was added a solution of 2,2'-bypyridine (1mmol, 0.156 g) and solution of two equivalents of appropriate pseudohalides (2 mmol, 0.152 g, NH_4SCN; 2 mmol, 0.129 g, NaN_3; 2 mmol, 0.130 g, KCN) in methanol (10 ml). After half an hour solution of 2-((E)-(4-(2-(4-methoxyphenyl)ethynyl)phenylimino)methyl)-4-(2-(4-methoxyphenyl)ethynyl)phenol (**L**) (0.457 g, 1 mmol) in dichloromethane (10 ml) was added drop wise. The resulting solution was refluxed for 4h at 80 °C. The solid complex precipitated was collected by filtration, washed with 1:1 ethanol: water mixture and dried under *vacuum* over $CaCl_2$.

1b: Yield: 83%. (0.409 g, 4.924 mmol); Elemental analysis (C, H, N,wt%) Anal. Calc for $C_{43}H_{30}N_5O_3S_2Ru$: C, 62.23; H, 3.64; N, 8.44% Found: C, 61.97; H, 3.49; N, 8.63%; IR (KBr cm^{-1}): 2067, υ(C≡C); 2153 υ(NCS), 2148; 1611, υ(HC=N); 1280, υ(C-O); ESI-MS: 853 ([Ru(**L**)(**bipy**)$(NCS)_2$+Na]$^+$, 20), 457 ([**L**]$^+$, 100), 373 ([Ru(**bipy**)$(NCS)_2$]$^+$, 40). **2b:** Yield: 85%. (0.410 g, 5.137 mmol); Elemental analysis (C, H, N, wt%) Anal. Calc for $C_{41}H_{30}N_9O_3Ru$: C, 61.72; H, 3.79; N, 15.80 % Found: C, 61.54; H, 3.57; N, 15.98%; IR (KBr cm^{-1}): 2067, υ(C≡C); 2039, υ(N_3); 1613, υ(HC=N); 1278, υ(C-O); ESI-MS: 821 ([Ru(**L**)(**bipy**)$(N_3)_2$+Na]$^+$, 22), 457 ([**L**]$^+$, 100), 341 ([Ru(**bipy**)$(N_3)_2$]$^+$, 43). **3b:** Yield: 81%. (0.390 g, 5.101 mmol); Elemental analysis (C, H, N, wt%) Anal. Calc for $C_{43}H_{30}N_5O_3Ru$: C, 67.44; H, 3.95; N, 9.15 % Found: C, 67.22; H, 3.69; N, 9.38%;

IR (KBr cm^{-1}): 2067, υ(C≡C); 2092, υ(CN); 1612, υ(HC=N); 1282, υ(C-O); ESI-MS: 798 ([Ru(**L**)(**bipy**)$(CN)_2$+Na]$^+$, 21), 457 ([**L**]$^+$, 100), 309 [Ru(**bipy**)$(CN)_2$]$^+$, 42).

3. Results and discussion

3.1 Synthesis of L and Ru(III) complexes

Initially, 5-ethynylsalicylaldehyde was prepared by Sonogashira $PdCl_2(PPh_3)_2$/CuI catalyzed coupling of 5-bromosalicylaldehyde with trimethylsilylacetylene followed by treatment with KOH in methanol according to the procedure reported earlier [26]. The reaction of 5-ethynylsalicylaldehyde with 4-iodoanisole yielded 2-hydroxy-5-(-2-(4-methoxyphenylethynyl)benzaldehyde in good yield. Further condensation of 2-hydroxy-5-(-2-(4-methoxyphenylethynyl)benzaldehyde with 4-(-2-(4-methoxy phenyl)ethynyl)benzenamine in methanol afforded corresponding Schiff base ligand 2-((E)-(4-(2-(4-methoxyphenyl)ethynyl)phenylimino)methyl)-4-(2-(4-methoxyphenyl)ethynyl)phenol (**L**) in excellent yield (Scheme 1). The Ru(III) complexes [Ru(**L**)(**phen**)X_2] [X=NCS (**1a**), N_3 (**2a**), CN (**3a**) and [Ru(**L**)(**bipy**)X_2] [X=NCS (**1b**), N_3 (**2b**), CN (**3b**) were prepared by the reaction of **L** with $RuCl_3.H_2O$ in presence of 1,10-phenanthroline and 2,2'-bipyridine followed by addition of NH_4SCN, NaN_3 and KCN in CH_2Cl_2:MeOH (1:1) mixture, respectively, All complexes are coloured, moisture insensitive and insoluble in common organic solvents but shows maximum solubility in DMF and DMSO. The results of elemental analyses (C, H and N) which are given in section 2 confirm the assigned composition of the complexes (Fig.1)

3.2 X-ray structure of L

Single crystal of ligand **L** suitable for X-ray diffraction was obtained by slow evaporation of saturated solution of **L** in dichloromethane. The ligand **L** crystallizes in a monoclinic system with the space group Pc and Z=2. The molecular structure of **L** along with atom numbering scheme is illustrated in Fig. 2 and the selected bond lengths and bond angles are summarized in Table 2. The crystal and molecular structure of **L** reveals some interesting findings. First the structure exhibits a strong intramolecular (O2-H2A-N1) hydrogen bond between the nitrogen atom of -HC=N- of Schiff base and hydrogen atom of the -OH group of salicylaldehyde ring with a distance of 2.581(9) Å which is in good agreement with the values reported in the literature [27]. Individually, each benzene ring in the molecule is almost planar in which the C3, C14 and C20 atom from each benzene ring has best plane by 0.042(3), 0.036(2) and 0.037(2) Å. The molecular packing of the structure is stabilized by C-H-O intermolecular hydrogen bond. All bond lengths and angles in (C1-C6), (C9-C14), (C16-C21) and (C24-C29) benzene rings have normal values 1.375(12), 1.376(13), 1.394(11) and 1.404(13) Å, respectively. The two benzene rings along with HC=N displayed the *trans* configuration and torsion angles of N(1)-C(16)-C(17)-C(18) is 177.2(8)°, C(14)-C(13)-C(15)-N(1) is −177.0(8)°. These angles are reported in the literature with values of 175.5(2)° and −176.8(2)° [28]. The bond distance C(7)-C(8) 1.188(12) Å and C(22)-C(23) 1.189 Å is smaller due to presence of C≡C. These results are comparable with those of the ligands reported earlier containing the similar moiety [29].

3.3 IR and NMR Spectra

The IR spectra of selected groups in the spectra of **L** and their **1a-3a** and **1b-3b** complexes are given in section 2. The IR spectrum of **L** and representative spectrum of **1a** are depicted in Fig 3 and 4, respectively. In the IR spectrum of **L** a broad band observed at 3064 cm^{-1} is assigned to ν(OH) vibration associated intramolecularly with the nitrogen atom of -HC=N- group. This band disappeared in **1a-3a** and **1b-3b** confirmed the coordination of phenolic oxygen to Ru(III) centers. Another medium intensity band observed at *ca* 2067 cm^{-1} due to internal triple bond (C≡C) and *ca* 1160 cm^{-1} due to OCH_3 group remain unaltered in all Ru(III) complexes. A strong absorption at 1623 cm^{-1} observed in the spectrum of **L** is slightly shifted to lower frequency at 1606-1609 cm^{-1} in **1a-3a** and 1611-1613 cm^{-1} for **1b-3b**. This change in frequency indicating imine nitrogen coordination [30]. The characteristic band appeared at 1273 cm^{-1} in **L** has been ascribed to the phenolic C-O stretch. On complexation, this band shifted to higher frequency by *ca* 7-9 cm^{-1} in **1a-3a** and *ca* 8-11 cm^{-1} in **1b-3b** relative to **L** suggesting involvement of C-O moiety in coordination. In addition to this, the bands at *ca* 1500, 805 and 735 cm^{-1} due to **phen** in **1a-3a** and bands at *ca* 760 and 740 cm^{-1} due to **bipy** in **1b-3b** confirmed the coordination of these ligands with Ru(III). The complexes **2a**, **2b** exhibit bands at around 2039 cm^{-1} and strong band at 1348 cm^{-1} assigned to υ_a and υ_s vibration of the coordinated azido group [31]. The cynide complexes **3a**, **3b** exhibit band at around 2094, 2065 cm^{-1} [32] whereas, thiocyanato complexes **1a**, **1b** shows a strong band at around 2148 cm^{-1}, a weak band at 771 and 484 cm^{-1} which can be attributed to υ(CN), υ(CS) and υ(NCS), respectively. The ^{1}H NMR spectrum of **L** exhibit hydroxyl proton and the imine proton as a singlet at δ 13.35 and 8.62 ppm, respectively. The resonance due to aromatic protons appeared as a multiplet in the region δ 6.86-7.59 ppm. Moreover, a signal of two methoxy protons is observed at δ 3.83 ppm.

3.4 Magnetic moment and EPR spectra

The room temperature (300 K) magnetic moment of **1a-3a** and **1b-3b** in the powdered phase are in the range 1.82-1.94 μ_B, and are listed in Table.3. These values are consistent with the low spin character and S = ½ ground state of metal ion, which corresponds to unpaired electron (low spin Ru^{III}, t_{2g}^5) in an octahedral environment [33]. To obtain further information about the stereochemistry and the site of the metal-ligand bonding and to determine the magnetic interaction in the complexes, the X-band EPR spectra of **1a-3a** and **1b-3b** complexes were recorded in polycrystalline state at room temperature. The g values obtained are given in Table 3 and a representative spectrum of **1a** is shown in Fig 5. The EPR spectra of all complexes exhibit two different g values (g_x=g_y≠g_z) with $g_\perp$ at 2.47-2.66 and $g_{||}$ at 1.99-2.11 indicating octahedral field with tetragonal distortion. Two g values indicate an axial symmetry and hence *trans* positions are assigned to the pseudohalide group in these complexes. Overall, the position of lines and nature of the EPR spectra of the complexes are characteristic of low spin Ru(III) octahedral complexes. These results are consistent with those obtained for other similar octahedral Ru(III) complexes [34].

3.5 Electrochemical Properties

The electrochemical properties of **1a-3a** and **1b-3b** were screened cyclic voltammetrically in 10^{-3} M DMF solution containing 0.05 M *n*-Bu_4NClO_4 as supporting electrolyte. The electrochemical data are listed in Table 4 and the representative cyclic voltammogram of **1a** and **2b** is shown in Fig 6 (A and B). Cyclic voltammogram of all complexes displayed a quasireversible oxidation (Ru^{IV}/Ru^{III}) and reduction (Ru^{III}/Ru^{II}) at the scan rate of 100 mV s^{-1}. All the complexes showed well-defined waves $E_{1/2}$ lies at +0.20 to +0.28 V (Ru^{III}/Ru^{IV}) and -0.36 to -0.48 V (Ru^{III}/Ru^{II}). The large peak-to-peak separation (ΔEp) of 120-180 mV in **1a-3a** and 100-130 mV in **1b-3b** and the current height measurement revel one electron redox processes [35]. It was observed that, the electrochemical properties of all the complexes are highly sensitive to the nature of coligand. The, redox processes for **1a-3a** appeared at more positive potential by 0.010-0.019 V as compared to those for corresponding **1b-3b**. These results could be attributed to better stabilization of the **phen** based complexes as compared to **bipy** based complexes as a consequence of their strong π-acidic character [36]. Further, the redox process for Ru(III) thiocynato complexes (**1a**, **1b**) appeared at less positive potential (140 V) as compared to those for corresponding azido (**2a**, **2b**) and cyano (**3a**, **3b**) complexes (167 V). This is might be due to the differences between π-acidic characters of the pseudohalides [37].

3.6 Thermogravimetric (TG) analysis

The thermal stabilities of **1a-3a** and **1b-3b** were investigated by thermogravimetric analysis (TGA) under flowing nitrogen to 800 °C. Typical TG curve of **1a** is presented in Fig. 7 and thermal analysis data is depicted in Table 5. TGA data suggest that, complexes **1a-3a** is stable up to 162 °C revealing the absence of either water or solvent molecule. In the temperature range of 162-474 ^{o}C, the complexes **1a-3a** underwent complicated multiple weight loss with total loss of 35.05 (**1a**), 32.60 (**2a**), 36.16 (**3a**)%, (Calcd. 35.96 (**1a**), 33.18 (**2a**), 36.81 (**3a**)%) which corresponds to loss of azido/thiocynato/cynato ion along with **phen** ligand. All the complexes collapse due to release of ligand **L** which occurs between 475-576^{o}C with an observed weight loss of 49.57(**1a**), 53.70 (**2a**), 52.70 (**3a**)% (Calcd.50.14 (**1a**), 54.23 (**2a**), 53.13 (**3a**)%). The complexes **1b-3b** shows slight changes in their thermal behaviour as compare to **1a-3a**, once again indicating absence of water or solvent molecule and decomposition ranges from 164 to 460 ^{o}C. The rapid and significant weight loss observed of 33.15 (**1b**), 31.64 (**2b**), 34.11 (**3b**)% (Calcd 33.82 (**1b**), 31.09 (**2b**), 34.61 (**3b**)%) which are presumably due to collapse of azido/thiocynato/cynato ion along with **bipy** ligand. The weight loss due to **L** in temperature range 461-562 ^{o}C observed at about 51.90 (**1b**), 55.48 (**2b**), 53.19 (**3b**)% (Calcd 52.23 (**1b**), 56.00 (**2b**), 53.73 (**3b**)%). From the thermogravimetric profile, it is clear that **phen** based complexes are found to be thermally more stable as compared to **bipy** based complexes.

3.7 Photophysical properties

The UV-Vis absorption spectra of free ligand **L** and its complexes **1a-3a** and **1b-3b** were carried out in DMF solution (10^{-4} M) at room temperature and resulting data are summarized in Table 6. In DMF, ligand **L** exhibit two absorption bands at λ_{max} 233 and 341 nm (Fig. 8) are due to intra-ligand π- π^* and n- π^* transitions. These peaks shows bathochromic shift in **1a-3a** and **1b-3b** and observed at 246-256, 241-247 nm and 354-361, 352-367 nm, respectively which support the coordination of **L** to Ru(III) ion. Besides the π-π^* and n-π^* transitions, **1a-3a** exhibit an intense absorption at λ_{max} 421-448 nm whereas, **1b-3b** exhibit absorption at λ_{max} 412-438 nm which can be attributed to charge transfer (CT) transitions. In a d^5 system and especially Ru(III) which has relatively high oxidizing properties, the charge transfer bands of the type $L\pi y \rightarrow t_{2g}$ are prominent in the low energy region which obscure the weaker bands due to d-d transitions. However, low energy absorption bands observed at λ_{max} 637-658 nm in **1a-3a** and λ_{max} 621-643 nm in **1b-3b** are attributed to d-d transition ($^2T_{2g}\rightarrow^2A_{2g}$) which is in conformity with the assignment made for similar octahedral ruthenium(III) complexes [38]. Low value of d-d transition observed in **phen** complexes (**1a-3a**) indicating that, in these complexes basel planes are comparatively more distorted than the **bipy** complexes (**1b-3b**). Also, d-d transition of cyano complexes (**3a**, **3b**) are blue shifted by 13-15 nm as compared to thiocynato (**1a** and **1b**) and azido (**2a**, **2b**) complexes. Moreover, the high intensity of cyano complexes may be suggestive of stronger distortion compared to thiocynato and azido complexes. These results are consistent with the higher ligand field factor of N-coordinated –CN than -NCS and -N_3 [39].

The emission and corresponding excitation spectra of **L** and its **1a-3a** and **1b-3b** complexes were systematically investigated in DMF solution (10^{-4}M) at room temperature. The excitation and emission spectra of representative complex **1a** is shown in Fig. 9 and the resulting data are summarized in Table 6. The ligand **L** exhibit emission at λ_{max} 558 nm (Fig. 8) upon excitation at 399 nm with stoke shift of 159 nm. The emission observed in **L** is due to emission stemming from a ligand centered π-π* transition. In contrast, **1a-3a** and **1b-3b** shows steady state marked differences in their emission behaviour in DMF solution. The spectra of **1a-3a** exhibit a broad emission profile at λ_{max} 654-669 nm with life time 6.74-7.01 ns upon excitation at λ_{max} 420-445 nm. Whereas, **1b-3b** shows emission profile at λ_{max} 645-658 nm with life time 6.49-6.86 ns upon excitation of λ_{max} 410-435 nm resulting in higher stokes shifts. The emission observed in these complexes can be attributed to π→π* intra-ligand charge transfer (ILCT) fluorescence in combination with some ligand to metal charge transfer (LMCT) character. The enhancement of fluorescence efficiency in all these complexes can be attributed to coordination of the ligands to Ru(III) ion which effectively increases the rigidity of the ligands and reduces loss of energy *via* radiation less thermal vibration decay [40]. It was observed that, all the complexes under study offer an extra conjugated back bone resulting in significantly increase in fluorescence efficiency as compare to previously reported similar Ru(III) complexes [23]. It was also observed that, the emission efficiency of **phen** complexes (**1a-3a**) appear at longer wavelength with enhanced intensity and large stoke shifts as compared to **bipy** complexes (**1b-3b)**. This may be due to non-radiative decay process which is more effective in **bipy** complexes as compared to **Phen** complexes [41]. Moreover, cyano complexes (**3a** and **3b**) shows high emissivity as compare to thiocynato (**1a** and **1b**) and azido **2a** and **2b**) complexes and fallow the path N_3<NCS<CN due to better quenching ability of pseudohalides [42]. The fluorescence quantum yield (ϕ) of all the complexes was determined with reference to quinine sulfate (ϕ=0.52 at 298 K) and appeared at 0.082-0.089 for **1a-3a** and 0.066-0.077 for **1b-3b** which are in good agreement with those are reported in the literature [43]. The observed emission decay of all the complexes are fit well with single exponential decay with average life time of **1a-3a** is longer than those observed for **1b-3b**. These results could be attributed due to red shifted emission and decreased emission intensity observed in **1b-3b** as compare to **1a-3a**. The experimentally measured τ and ϕ values were used to calculate the radiative K_r and the non radiative K_{nr} rate constant. The K_r values of **1a-3a** are slightly greater whereas, K_{nr} values are slightly lower than the **1b-3b**. All these results are in good agreement with those values reported in the literature [44].

4. Conclusion

Some new Ru(III)-pseudohalide complexes of the type [Ru(**L**)(**phen**)X_2] (**1a-3a**) and [Ru(**L**)(**bipy**)X_2] (**1b-3b**) [where; X=NCS, N_3, CN; **phen** = 1,10-phenanthroline, **bipy** = 2,2′-bipyridine] have been prepared and characterized. Based on magnetic susceptibility and EPR spectra, an octahedral structure was confirmed for the new complexes. All complexes exhibit quasireversible redox behaviour corresponding to Ru(III)/Ru(IV) and Ru(III)/Ru(II) couple. Further, significant effect of **phen**/**bipy** coligands on redox state of metal in complexes has been examined. The **phen** (**1a-3a**) complexes are thermally more stable than the **bipy** (**1b-3b**) complexes. At room temperature all complexes shows large stokes shift and act as fluorescent in blue-green region due to π-π* intra-ligand charge transfer (ILCT) transition with some ligand to metal charge transfer (LMCT) character. Moreover, cyano (**3a** and **3b**) complexes shows high emissivity as compare to thiocynato (**1a** and **1b**) and azido (**2a** and **2b**) complexes and fallow the path N_3<NCS<CN due to better quenching ability of pseudohalides.

Supplementary material

CCDC 1945674 contain the supplementary crystallographic data 2-((E)-(4-(2-(4-methoxyphenyl) ethynyl)phenylimino)methyl)-4-(2-(4-methoxyphenyl)ethynyl)phenol (**L**)

Acknowledgments

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References:

[1] E. Muller, M.K. Nazeeruddin, M. Gratzel, K. Kalyanasundaram, J.C. Prome, New J. Chem. 20 (1996) 759.
[2] M.T. Indelli, F. Scandola, J.P. Collin, J.-P. Sauvage, A. Sour, Inorg chem. 35 (1996) 303.
[3] A. Hagfeldt, M. Gratzel, Chem. Rev. 95 (1995) 49.
[4] N. Fay, E. Dempsey, A. Kennedy, T. McCormac, J. Electroanal. Chem. 556 (2003) 63.
[5] N. Fay, V.M. Hultgren, A.G. Wedd, T.E. Keyes, R.J. Forster, D. Leane, A.M. Bond, Dalton Trans. 35 (2006) 4218.
[6] M.K. Seery, N. Fay, T. McCormac, E. Dempsey, R.J. Forster, T.E. Keyes, Phys. Chem. Chem. Phys. 7 (2005) 3426.
[7] X.L. Wang, Q. Zhang, Z.B. Han, E.B. Wang, Y.Q. Guo, C.W. Hu, J. Electroanal. Chem. 563 (2004) 221.
[8] S.Kannan, R.Ramesh, Polyhedron 25 (2006) 3095.
[9] Z. Albobaledi, M.H. Esfafani, M. Behzad, A. Abbasi, Inorg. Chim. Acta. 499 (2020) 119185.
[10] Z.M. Zaki, S.S. Haggag, A.A. Soayed, Spectroscopy Letters 31 (1998) 757.
[11] C. Schmitz, P. Posch, M. Thelakkat, H.W. Schmidt, A. Montali, K. Felman, P. Smith, C. Weder, Adv. Funct. Mater 11 (2001) 41.
[12] N.P. Priya, S. Arunachalam, A. Manimaran, D. Muthupriya, C. Jayabalakrishnan, Spectrochim. Acta 72 (2009) 670.

[13] P. Gull, M.A. Malik, O.A. Dar, A.A. Hashmi, J. Mol. Struct.1134 (2017) 734.

[14] M. Muthukumar, P. Viswanthamurthi, R. Prabhakaran, K. Natarajan, J. Coord. Chem 21 (2010) 3833.

[15] C. Schmitz, P. Posch, M. Thelakkat, H.W. Schmidt, A. Montali, K. Felman, P. Smith, C. Weder, Adv. Funct. Mater 11 (2001) 41.

[16] M.A. Malik, M.K. Raza, O.A. Dar, Amadudin, M. Abid, M.Y. Wani, A.S. Al-Bogami, A.A. Hashmi, Bioorg Chem 87 (2019) 773.

[17] G. Accorsi, A. Listorti, K. Yoosaf, N. Armaroli, Chem. Soc. Rev 38 (2009) 1690.

[18] C. Wallenhorst, G. Kehr, H. Luftmann, R. Frohlich, G. Erker. Organometallics 27 (2008) 6547.

[19] Y. Sunatsuki, Y. Motoda, Y. Matsumoto, Coord. Chem. Rev 226 (2002) 199.

[20] S. Basak, S. Sen, C. Marschner, J. Baumgartner, S.R. Batten, D.R. Turner, S. Mitra. Polyhedron 27 (2008) 1193.

[21] S. Das, S. Satapathi, S. Roy, K. Bhar, P. Mitra, B.K. Ghosh, J. Mol. Struct 982 (2010) 113

[22] Y.W. Dong, R.Q. Fan, P. Wang, L.G. Wei, X.M. Wang, H.J. Zhang, S. Gao, Y.L. Yang Y.L.Wang, Dalton Trans 44 (2015) 5306.

[23] S.S. Mohite, A.B. Patil-Deshmukh, S.S. Chavan, J. Mol. Struct 1176 (2019) 386.

[24] C. Shu, J.G. Moxey, A. Barlow, M. Morshedi, Acta. Crystallogr 71 (2015) 321.

[25] G.M. Sheldrick, Acta Crystallogr 64 (2008) 112.

[26] I.P. Evans, A. Spencer, G. Wikinson, J. Chem. Soc. Dalton Trans 2 (1973) 204.

[27] H. Dal, Y. Suzen, E. Sahin, Spectrochim. Acta Part A 67 (2007) 808.

[28] M. Ikiz , E. Ispir, E. Aytar, M. Ulusoy, S. Karabug, M. Aslantas, O. Celik, New J Chem 39 (2015) 7786.

[29] R. Ziessel, J. Suffert, M.T. Youinou, J. Org Chem 61 (1996) 6535.

[30] J.A. Castro, J. Romero, J.A. Garcia-Vazoquez, Polyhedron 12 (1993) 1391.

[31] M. Shebl, S.M.E. Khalil, S.A. Ahmed, H.A.A. Medien, J. Mol. Struct 39 (2010) 980.

[32] M.C. Ribeiro, R.S. Correa, M.F. Barbosa, F.G. Delolo, J. Ellena, A.L. Bogado, A.A. Batista, Polyhedron 137 (2017) 311.

[33] K. Jone, J. Saranya, N. Sathya, I.V.M.V. Enoch, P. Mosae Selvakumar, S. Chitra, Appl. Organomet. Chem 31 (2017) 3760.

[34] T.D. Thangadurai, K. Natarajan, Trans. Met. Chem.26 (2001) 717.

[35] G.Venkatachalam, R. Ramesh, S.M. Mobin, J. Oragnomet. Chem 690 (2005) 3937.

[36] C.V. Krishnan, C. Creutz, H.A. Schwarz, N. Sutin, J. Am. Chem. Soc 105 (1983) 5617.

[37] A.M. Maron, J.G. Małecki, Polyhedron 85 (2015) 549.

[38] A. Manimaran, V. Chinnusamy, C. Jayabalakrishnan, Appl. Organomet. Chem 25 (2011) 87.

[39] U. Ray, D. Banerjee, G. Mostafa, T.H. Lu, C. Shina, New. J. Chem 28 (2004) 1437.

[40] M.S. Chen, Q. Hau, Z.S. Bai, Polyhedron 29 (2010) 2454.

[41] J.L. Kahl, K. Hanck, K. Dearmond, J. Inorg. Nucl. Chem 41 (1979) 495.

[42] J.R. Lakowicz, third ed, Springer. USA 2006.

[43] J.E. Jee, Y.M. Kim, S.S. Lee, K.M. Park, C.H. Kwak, Inorg. Chem. Commum 6 (2003) 946.

[44] S.R Lolage, S.B Pawal, S.S Chavan, Opt. Mater 67 (2017) 162.

Figure captions:

Scheme. 1 Synthetic route to the preparation of **L**

Fig. 1 Proposed molecular structure of the complexes (I) **1a-3a** and (II)**1b-3b**

Fig. 2 Single crystal X-ray diffraction of **L**

Fig. 3 IR spectrum of **L**

Fig. 4 IR spectrum of **1a**

Fig. 5 EPR spectrum of [Ru(**L**)**phen**(NCS)$_2$] (**1a**)

Fig. 6 Cyclic voltammogram of (A) **1a** and (B) **2b**

Fig. 7 Thermogram of **1a**

Fig. 8 Absorption and Emission Spectra of **L**

Fig. 9 Excitation (red line) and Emission (blue line) spectra of **1a**

Table.1. Crystal data and structure refinement details for **L**

Empirical formula	$C_{31}H_{23}NO_3$
Formula weight	457.50

Crystal system	Monoclinic
Space group	Pc
a (Å)	26.489(3)
b (Å)	7.2195(7)
c (Å)	6.2098(6)
ɑ (°)	90
β (°)	b= 93.279(5)°
γ (°)	90
V (A^3)	1185.6(2)
Z	2
Density (mg/m^3)	1.282 Mg/m^3
μ (M_0K_α)(mm^{-1})	0.656
F (000)	480
Data collection	3.342 to 65.986°
Temperature (K)	296 (2)
θ mini-maxi (deg)	0.7536 and 0.5441
Data set [*h k l*]	-30/31, -8/8, -7/7
Total unique data R_{int}	10184 [R(int) = ?]
Extinction coefficient	0.010(4)
Refinement	Full-matrix least-square on F^2
No of reflection collected	10184
Data / restraints / parameters	10184 / 2 / 318
R_1, R_1	0.0732, 0.1220
wR_2, wR_2	0.1781, 0.2045
Goodness-of-fit	1.023

Table.2. Selected bond lengths (Å) and bond angles (°) for **L**

Bond length	(Å)	Bond angle	(°)
C(1)-O(1)	1.373(11)	C(7)-O(8)-C(9)	174.7(10)
C(7)-C(8)	1.188(12)	N(1)-C(15)-C(13)	121.2(8)
C(13)-C(15)	1.462(11)	C(23)-C(22)-C(19)	177.2(10)
C(15)-N(1)	1.276(10)	C(22)-C(23)-C(24)	176.5(10)
C(16)-N(1)	1.403(11)	O(3)-C(27)-C(28)	115.5(9)
C(22)-C(23)	1.189(12)	C(1)-O(1)-C(31)	118.1(7)
C(27)-O(3)	1.370(11)	C(12)-O(2)-H(2A)	109.5
C(30)-O(3)	1.422(12)	C(27)-O(3)-C(30)	118.2(8)

Table.3. EPR and magnetic susceptibility data of **1a-3a** and **1b-3b**

Complexes	g_x	g_y	g_z	(g)*	$\mu_{eff(BM)}$
1a	2.47	2.47	2.04	2.69	1.82
2a	2.54	2.54	1.99	2.77	1.90
3a	2.52	2.52	2.07	2.79	1.88
1b	2.57	2.57	2.08	2.88	1.94
2b	2.66	2.66	2.11	3.06	1.87
3b	2.63	2.63	2.06	2.96	1.81

$< g >^* = [\ 1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2]^{1/2}$

Table.4 Electrochemical data of **1a-3a** and **1b-3b** in DMF (10^{-3}M)

Complexes	Ru^{III} - Ru^{IV}							Ru^{III} - Ru^{II}						
	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	$E_{1/2}$ (V)	Band gap	EA	IP	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	$E_{1/2}$ (V)	Band gap	EA	IP
1a	0.45	0.25	200	0.35	0.20	-0.125	-4.875	-0.42	-0.30	120	-0.36	-0.12	-0.675	-4.005
2a	0.39	0.28	110	0.33	0.11	-0.095	-4.815	-0.47	-0.28	190	-0.37	-0.19	-0.655	-3.955
3a	0.38	0.24	140	0.31	0.14	-0.135	-4.805	-0.50	-0.32	180	-0.41	-0.18	-0.695	-3.925
1b	0.40	0.22	180	0.31	0.18	-0.155	-4.825	-0.45	-0.34	100	-0.39	-0.11	-0.715	-3.975
2b	0.47	0.25	220	0.36	0.22	-0.125	-4.895	-0.40	-0.39	110	-0.39	-0.01	-0.765	-4.025
3b	0.36	0.20	160	0.28	0.16	-0.175	-4.785	-0.55	-0.42	130	-0.48	-0.13	0.795	-3.875

Supporting electrolyte: n-Bu_4NClO_4 (0.05 M); complex: 0.001 M; solvent: DMF; $E_{1/2} = ½(E_{pa} + E_{pc})$; scan rate: 100 mV s^{1}.

Table.5 Thermoanalytical data of **1a-3a** and **1b-3b**

Complex	Thermogravimetric (TG)		Mass loss (%)		Decomposition product loss
	Stage	Temp range(°C)	Found	Calc	
1a	I	162-474	35.05	35.96	$C_{14}H_8N_4S_2$
	II	475-576	49.57	50.14	$C_{30}H_{23}NO_3$
2a	I	165-473	32.60	33.18	$C_{12}H_8N_8$
	II	474-574	53.70	54.23	$C_{30}H_{23}NO_3$
3a	I	164-470	36.16	36.81	$C_{14}H_8N_4$
	II	471-575	52.70	53.13	$C_{30}H_{23}NO_3$
1b	I	164-460	33.15	33.82	$C_{12}H_8N_4S_2$
	II	461-562	51.90	52.23	$C_{30}H_{23}NO_3$
2b	I	167-458	32.64	31.09	$C_{10}H_8N_8$
	II	459-560	55.48	56.00	$C_{30}H_{23}NO_3$
3b	I	165-558	34.11	34.61	$C_{12}H_8N_4$
	II	559-560	53.19	53.73	$C_{30}H_{23}NO_3$

Table.6 Absorption and Emission data of **L** and **1a-3a** and **1b-3b** in DMF (10^{-4} M)

Compound	λmax(nm) (ε x10^3, M^{-1} cm^{-1})	λ_{ex}	λ_{em}	Stoks Shift	ϕ	$\tau_{(ns)}$	$K_r(S^{-1}/10^7)$	$K_{nr}(S^{-1}/10^9)$
L	233, 341	399	558	159	0.061	4.87	1.21	0.1992
1a	246, 356, 438, 649	420	662	242	0.084	6.74	1.23	0.1506
2a	251, 354, 448, 658	445	654	209	0.082	6.76	1.21	0.1479
3a	256, 361, 421, 637	436	669	233	0.089	7.01	1.25	0.1408
1b	246, 352, 429, 631	428	651	223	0.068	6.49	1.05	0.1555
2b	241, 359, 438, 643	410	645	235	0.066	6.51	1.01	0.1536
3b	247, 367, 412, 621	435	658	223	0.077	6.86	1.12	0.1457

Research Highlights:

- Synthesis of Ru(III)-pseudohalide complexes.
- Characterization by elemental analyses, IR, EPR and mass spectral studies.
- Room temperature luminescence is observed for all complexes.

‘A’ Reaccredited by NAAC

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2 February 2020

To
Editor,
Inorganica Chimica Acta

Dear Sir,

We have revised the manuscript titled ‘Ru(III)-pseudohalides complexes with alkynyl functionalized salicylaldimine ligand and heterocyclic coligand: Synthesis, characterization electrochemical and luminescence properties' by taking into consideration the suggestions made by the respected reviewers. The work presented in the manuscript contributes examining the structural aspects as well as luminescence properties of new Ru(III) complexes. The data and ideas of the prepared complexes are of our own and are not under consideration for publication elsewhere, and that all authors are aware of the submission and agree to its publication. I hope that the manuscript will be worth for publication in your esteemed journal

Thanking you

Yours faithfully

Prof. (Dr.) Sanjay Chavan

Scheme 1.

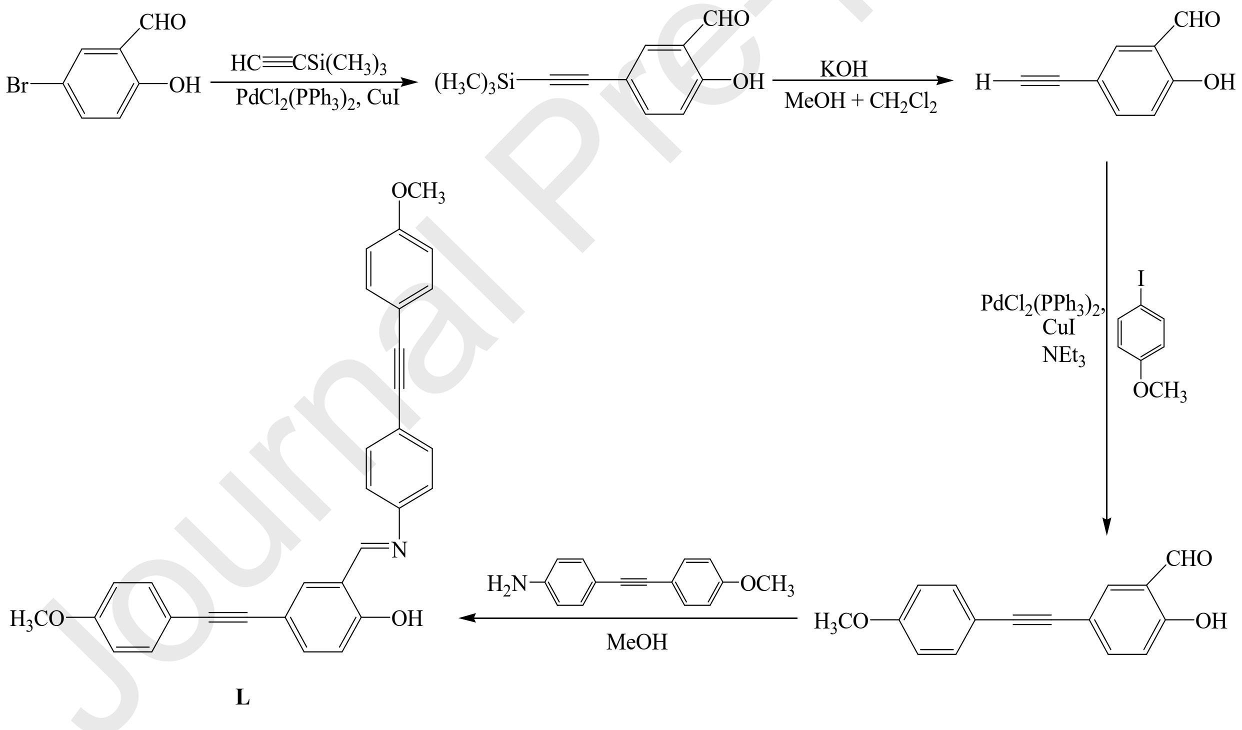
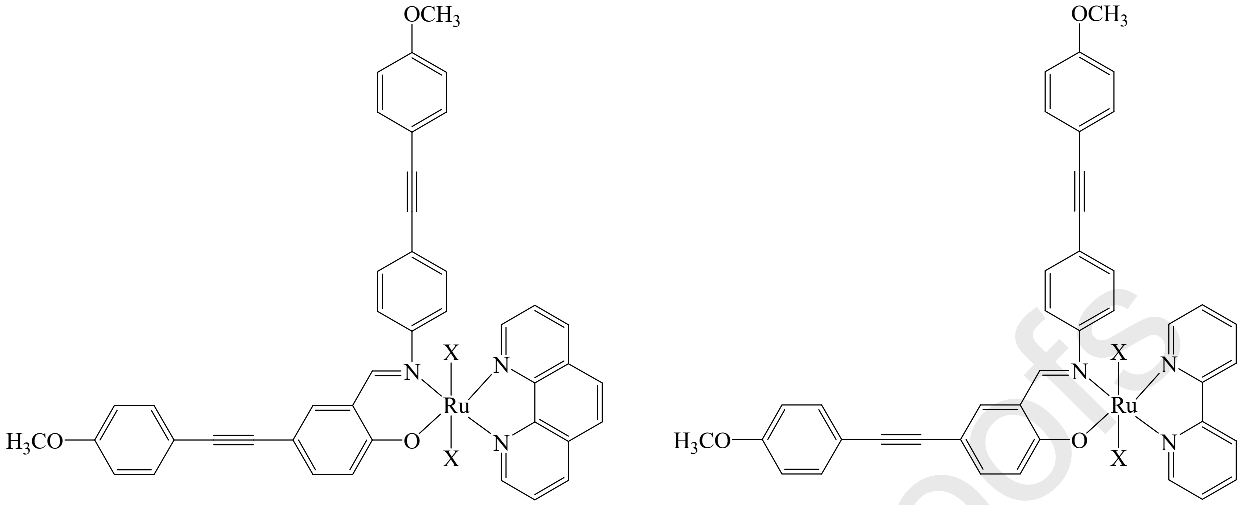


Fig. 1.



(I) **1a-3a** X = NCS, N_3, CN (II) **1b-3b**

Fig. 2.

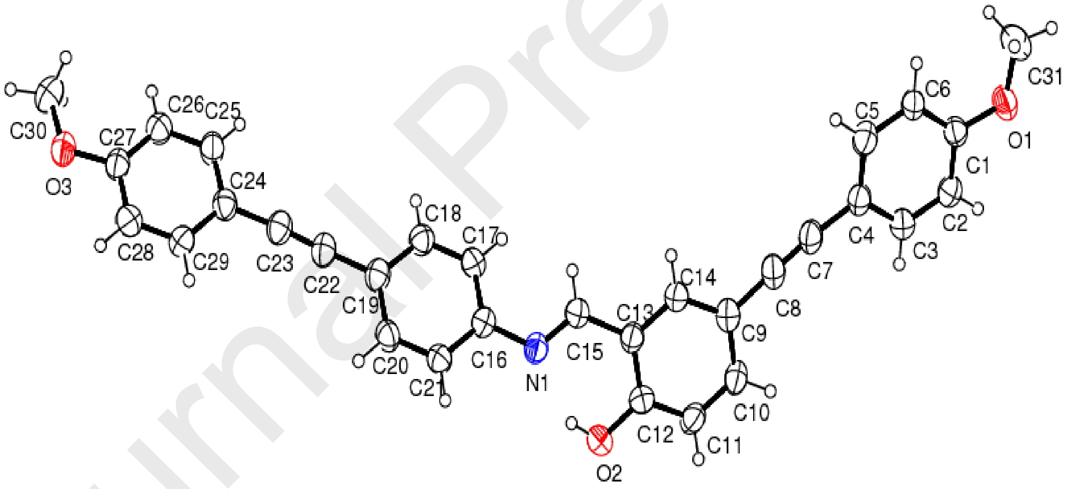
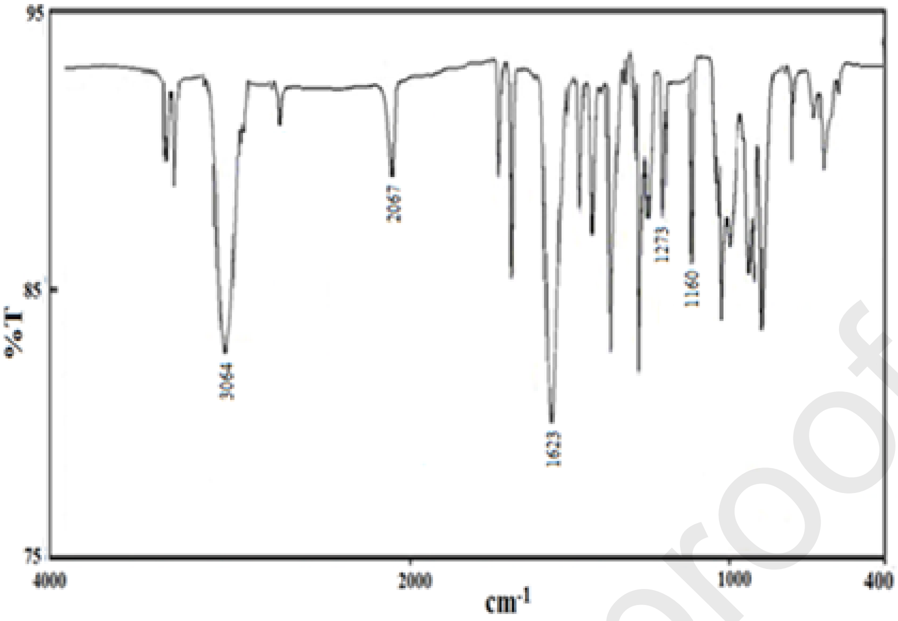


Fig. 3.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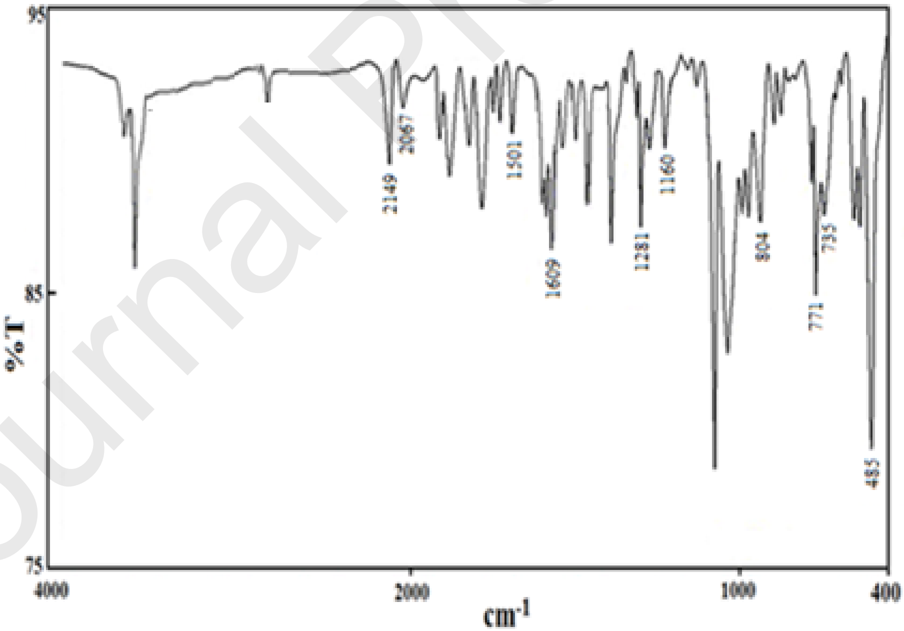
1160

Fig. 4.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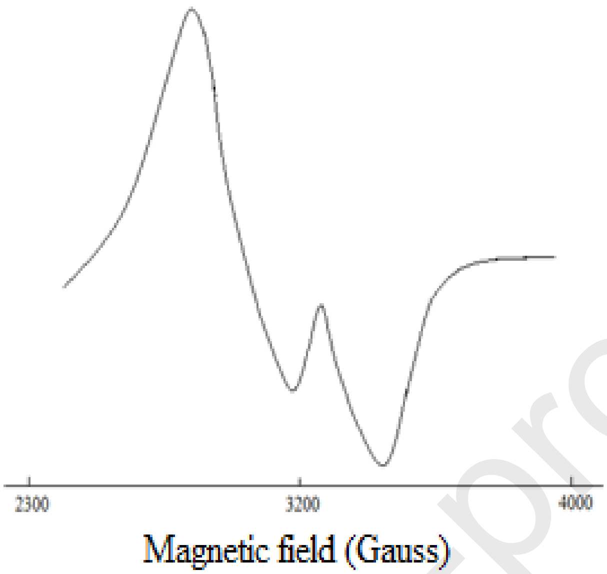
735
485

Fig. 5.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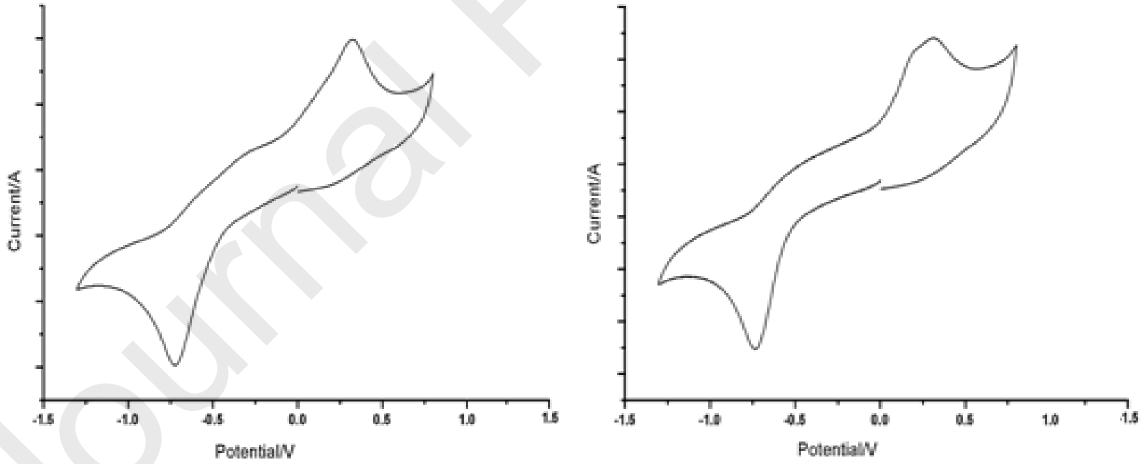
3200
4000
Magnetic field (Gauss)

Fig. 6.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-1.0
-0.5
0.0
0.5
1.0
1.5
Potential/V

(A) (B)

Fig. 7.

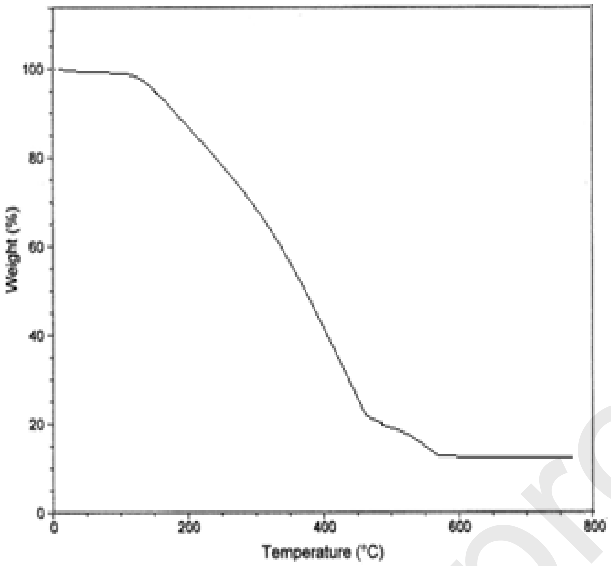


Fig. 8.

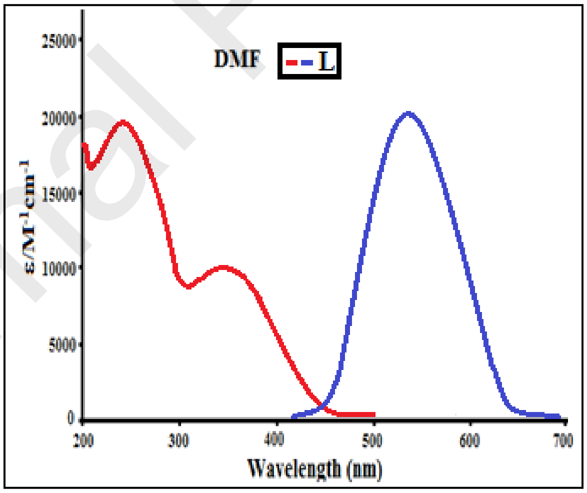
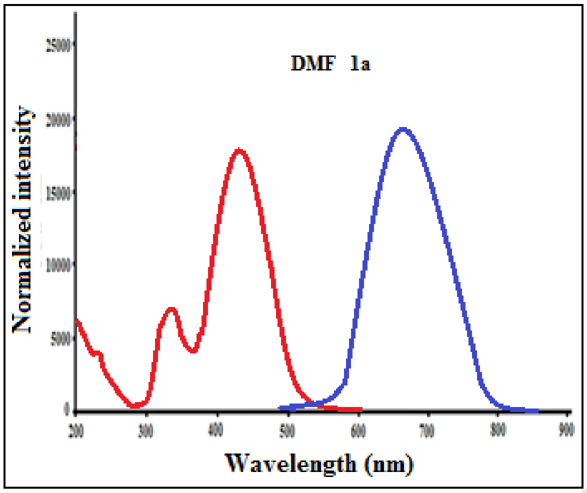


Fig. 9.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20000
15000
10000
5000
0
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300
400
500
600
700
800
900
Wavelength (nm)

Conflict of Interest:

No any conflict of interest of this research article

Graphical Abstract:

Ru(III)-pseudohalide complexes with alkynyl functionalized salicylaldimine ligand and heterocyclic coligand: Synthesis, characterization, electrochemical and luminescence properties