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Coordination-organometallic hybrid materials based on the trinuclear M(II)-Ru(II) (M=Ni and Zn) complexes: Synthesis, structural characterization, luminescence and electrochemical properties

S.B. Pawal, S.R. Lolage, S.S. Chavan^{*}

Department of Chemistry, Shivaji University, Kolhapur, 416 004, MS, India

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ABSTRACT

A new series of trinuclear complexes of the type Ni[R-C₆H₄N=CH(O)C₆H₃C≡CRu(dppe)₂Cl]₂ (**1a-c**) and Zn[R-C₆H₄N=CH(O)C₆H₃C≡CRu(dppe)₂Cl]₂ (**2a-c**) have been prepared from the reaction of *trans*-[RuCl(dppe)₂C≡C-C₆H₃(OH)(CHO)] (**1**) with aniline, 4-nitroaniline and 4-methoxyaniline (R₁₋₃) in presence of nickel acetate and zinc acetate in CH₂Cl₂/MeOH (1:1) mixture. The structural properties of the complexes have been characterized by elemental analyses and spectroscopic techniques *viz*. FTIR, UV-Visible, ¹H NMR and ³¹P NMR spectral studies. The crystal structure and morphology of the hybrid complexes was investigated with the help of X-ray powder diffraction (XRPD), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). The thermal properties of **1a-c** and **2a-c** were studied by thermogravimetric (TG) analysis. The electrochemical behaviour of the complexes reveals that all complexes displayed a quasireversible redox behaviour corresponding to Ru(II)/Ru(III) and Ni(II)/Ni(III) couples for **1a-c** and only Ru(II)/Ru(III) couple for **2a-c**. All complexes are emissive in solution at room temperature revealing the influence of substituents and solvent polarity on emission properties of the complexes.

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1. Introduction

Advances in molecular materials with heteronuclear or multicomponent complexes are strongly motivated because of their interesting synthetic, structural and magnetic properties [1–3]. Among different strategies used for the synthesis of such systems, one of the most efficient method is the use of multifunctional bridging ligand that contain two or more functional groups associated with different metal centers. Such heteronuclear and/or multicomponent systems exhibit remarkable physical and chemical properties with potential applications in catalysis, molecular sensing, biological systems as well as in the magnetic and optoelectronic field [4–7]. Schiff base ligands particularly with N, O donor atoms have drawn special attention for fabrication of such molecular assemblies because of their ability to generate a much greater diversity with potential applications in many fields such as catalysis [8], pharmaceuticals [9], luminescent [10] and nonlinear optics [11]. Such systems are more attractive with respect to their

* Corresponding author. E-mail address: sanjaycha2@rediffmail.com (S.S. Chavan). base ligands which play an essential role in stabilizing the metal ion and modifying the physical and chemical properties of the synthesized complexes [12-15]. Organometallic compounds particularly with σ -alkynyl ligands have also attracted considerable attention for their use in the preparation of heteronuclear and/or multicomponent system with desired electronic and optical properties. The interest in σ -alkynyl complexes are not only due to their rich structural diversity and interesting chemical reactivity but also due to their increasing potential applications in nonlinear optics [16], electronic communication [17], luminescence [18] and liquid crystalline materials [19]. In order to prepare the heteronuclear and/or multicomponent complexes, metal-acetylides are attractive precursor due to their electronic, structural features and their ability to interact with metal centers via $p\pi$ -d π overlap. The interest in such multifunctional molecular systems are not only due to their excellent candidature for exploration of intramolecular triplet energy transfer between organometallic subunits but also for achieving materials with long-lived luminescence with high quantum efficiency [20].

steric, electronic and conformational effects imparted by the Schiff

In order to explore new materials with interesting structural topology and novel physical properties, we have been recently









engaged in the research of synthesis of new hybrid complexes composed of coordination and organometallic sites. A previous report from our laboratory has developed some heterobimetallic complexes of the type $[Ni(R-C_6H_4HC = N(O))]$ hybrid $C_6H_3N = NC_6H_4C \equiv CRu(dppe)_2Cl)$ (L')] and $[Zn(R-C_6H_4HC = N(O))]$ $C_6H_4N = NC_6H_4C \equiv CRu(dppe)_2Cl)$ (L')] by the reaction of $[(R-C_6H_4HC = N(O)C_6H_3N = NC_6H_4C \equiv CRu(dppe)_2Cl)]$ with nickel acetate or zinc acetate in presence of 8-hydroxyguinoline (where L' = 8-hydroxyquinoline, R = Cl, Br, I) and reported their promising application as a luminescent material [21]. As a continuation of our previous report, we explore herein synthesis of new trinuclear M(II)/Ru(II) coordination-organometallic hybrid complexes of the type Ni[R-C₆H₄N = CH(O)C₆H₃C \equiv CRu(dppe)₂Cl]₂ (**1a-c**) and Zn $[R-C_6H_4N = CH(O)C_6H_3C \equiv CRu(dppe)_2Cl]_2$ (**2a-c**) derived from the reaction of *trans*-[RuCl(dppe)₂C \equiv C-C₆H₃(OH)(CHO)] (1) with aniline, 4-nitroaniline and 4-methoxy aniline (R_{1-3}) in presence of Ni(II) and Zn(II) in CH₂Cl₂/MeOH (1:1) mixture. These complexes were characterized by elemental analyses, IR, UV–Visible, ¹H NMR, ³¹P NMR and ESI-MS spectral studies. X-ray powder diffraction (XRPD), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) are used for confirmation of morphology and structural behaviour of the complexes. The influence of π -conjugation, the donor/acceptor substituent on photoluminescence, electrochemical and thermal properties of the complexes have also been reported.

2. Experimental

2.1. Materials and general methods

All manipulations were carried out under dry nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. All solvents were dried over appropriate drying agents and freshly distilled by suitable procedures prior to use. All chemicals used were of AR grade and used without further purification. NaPF₆ and *n*-Bu₄NClO₄ were purchased from Aldrich and used as received. RuCl₂(dmso)₄ [22] and *cis*-RuCl₂(dppe)₂ [23] were synthesized according to standard procedure.

Microanalyses (C, H and N) were performed on a Thermo Finnigan FLASH EA-112 CHNS analyzer. UV-Visible absorption spectra of the samples were measured at room temperature on a Shimadzu UV-Vis-NIR-100 spectrophotometer. Infrared spectra were recorded on Perkin Elmer FTIR spectrometer as KBr pellets in the 4000-400 cm⁻¹ spectral range. ¹H NMR spectra of the samples were measured on Bruker-300 MHz instrument using TMS [(CH₃)₄Si] as an internal standard. ³¹P NMR spectra were recorded using a Varian Mercury-300 FTNMR spectrometer. ESI mass spectra were recorded using Finnigan LCQ mass spectrometer. Thermal analysis of the complexes was carried out on a Perkin Elmer thermal analyzer in nitrogen atmosphere at a heating rate of 10°C/min. The fluorescence spectra were collected on Perkin Elmer LS 55 spectrofluorometer equipped with quartz cuvette of 1 cm path length at room temperature. Luminescence lifetime measurement was carried out by using time-correlated single photon counting from HORIBA Jobin Yvon. Scanning electron microscopy (SEM) images were captured on Carl Zeiss (Ultra plus) field emission scanning electron microscope using AC voltage of 10 kV. TEM image was obtained on instruments of Philips CM120 microscope. X-ray powder diffraction (XRD) spectra were recorded on a Rigaku diffractometer (Cu-Ka radiation, k = 0.15418 nm) having angle range 5–70. The electrochemical measurements were performed with a CH-400A Electrochemical Analyzer. A three component electrochemical cell was used with Pt disk as the working electrode, Pt wire counter electrode and Ag/AgCl reference electrode. All the measurements have been carried out with scan rate 100 mV/s in CH₂Cl₂ solution containing n-Bu₄NClO₄ as the supporting electrolyte. The peak potentials reported were referenced to Ag/AgCl and were converted to the SCE scale.

2. Synthesis

2.2.1. Synthesis of trans-[RuCl(dppe)₂C \equiv C-C₆H₃(OH)(CHO)] (1)

The mixture of 5-ethynylsalicyladehyde (0.09048 g, 0.619 mmol), *cis*-RuCl₂(dppe)₂ (0.500 g, 0.516 mmol) and NaPF₆ (0.266 g, 1.583 mmol) was refluxed in CH₂Cl₂/MeOH (30 ml, 2:1 v/v) for 16 h. NEt₃ (1 ml) was added and the solution was immediately passed through a short pad of alumina eluting with CH₂Cl₂. The solvent was removed from the eluate under reduced pressure and the resulting yellow powder was stirred with diethyl ether to remove unreacted *cis*-[RuCl₂(dppe)₂]. The product was further purified by column chromatography on alumina using 4:1 CH₂Cl₂: petroleum ether as eluent to afford yellowish green coloured solid.

Yield: 78% (0.4605 g, 0.426 mmol); Elemental analyses (C, H and N, Wt %) Anal. Cal for $C_{61}H_{53}O_2RuP_4Cl$: C, 67.93; H, 4.95; Found: C, 67.63; H, 4.71%; IR (KBr) (cm⁻¹): 2076, υ (C=C); 3280, υ (-OH); 1289, υ (C-O); 1474, 1433, 1163, 689, υ (dppe); ¹H NMR (CDCl₃) (300 MHz): δ 10.68 (s, 1H, OH), 9.66 (s, 1H, O=CH), 6.45–7.53 (m, 43H, Ph), 2.65 (s, 8H, CH₂); ³¹P NMR: δ 49.43. ESI-MS: 1102 ([RuCl(dppe)₂C=C-C₆H₃(OH)(CHO)+Na]⁺, 30), 898 ([Ru(dppe)₂]⁺, 100).

2.2.2. Synthesis of Ni[H-C₆H₄N = CH(O)C₆H₃C \equiv CRu(dppe)₂Cl]₂ (1a)

To a solution of *trans*-[RuCl(dppe)₂C \equiv C-C₆H₃(OH)(CHO)] (0.200 g, 0.185 mmol) in dichloromethane was added a solution of Ni(CH₃COO)₂.4H₂O (0.0230 g, 0.0927 mmol) (5 ml) and aniline (0.0172 g, 0.185 mmol) (5 ml) in methanol dropwise with constant stirring. The reaction mixture was then rfluxed for 4 h on water bath. The resulting solution was then evaporated to small volume under *vacuum*. The brown coloured complex was collected by filtration, washed with ethanol and dried in *vacuo*.

Yield: 72% (0.2231 g, 0.094 mmol); Elemental analyses (C, H and N, Wt %) Anal. Cal for NiC₁₃₄H₁₁₄N₂O₂Ru₂P₈Cl₂: C, 68.08; H, 4.86; N, 1.19. Found: C, 67.85; H, 4.75; N, 1.35%; IR (KBr) (cm⁻¹): 2053, υ (C=C); 1581, υ (C=N); 1273, υ (C-O); 1476, 1436, 1165, 695, υ (dppe); ¹H NMR (CDCl₃) (300 MHz): δ 8.37 (s, 2H, C=N), δ 6.53–7.57 (m, 96H, phenyl), δ 2.67 (m, 16H, PCH₂CH₂P); ³¹P NMR: δ 49.46. ESI-MS: 2387 ([Ni{H-C₆H₄N = CH(O)C₆H₃C=CRu (dppe)₂Cl]₂+Na]⁺, 29), 1153 ([{H-C₆H₄N = CH(O)C₆H₃C=CRu (dppe)₂Cl]⁺, 100), 898 ([Ru(dppe)₂]⁺, 41).

2.2.3. Synthesis of Ni[NO₂-C₆H₄N = CH(O)C₆H₃C \equiv CRu(dppe)₂Cl]₂ (**1b**)

The complex **1b** was prepared similar to the procedure performed in the preparation of **1a** except that aniline was replaced by 4-nitroaniline (0.0256 g, 0.185 mmol).

 $\begin{array}{l} \label{eq:2.1} Yield: 67\% \ (0.2132 \ g, 0.086 \ mmol); \ Elemental analyses \ (C, H \ and N, Wt \ \%) \ Anal. \ Cal \ for \ NiC_{134}H_{112}N_4O_6Ru_2P_8Cl_2: \ C, 65.59; \ H, 4.60; \ N, 2.28. \ Found: \ C, 65.25; \ H, 4.45; \ N, 2.48\%; \ IR \ (KBr) \ (cm^{-1}): \ 2056, \ \upsilon(C=C); \ 1590, \ \upsilon(C=N); \ 1275, \ \upsilon(C-O); \ 1477, \ 1435, \ 1164, \ 696, \ \upsilon(dppe); \ ^1H \ NMR \ (CDCl_3) \ (300 \ MHz): \ \delta \ 8.40 \ (s, \ 2H, \ C=N), \ \delta \ 6.60-7.79 \ (m, 94H, \ phenyl), \ \delta \ 2.68 \ (m, 16H, \ PCH_2CH_2P); \ ^{31}P \ NMR: \ \delta \ 49.47. \ ESI-MS: \ 2477 \ ([Ni{NO}_2-C_6H_4N=CH(O) \ C_6H_3C=CRu(dppe)_2Cl_2+Na]^+, \ 32), \ 1198 \ ([{NO}_2-C_6H_4N=CH(O) \ C_6H_3C=CRu(dppe)_2Cl_2+Na]^+, \ 100), \ 898 \ ([Ru(dppe)_2]^+, \ 43). \end{array}$

2.2.4. Synthesis of Ni[OCH₃-C₆H₄N = CH(O)C₆H₃C \equiv CRu(dppe)₂Cl]₂ (**1c**)

The complex **1c** was prepared similar to the procedure performed in the preparation of **1a** except that aniline was replaced by 4-methoxyaniline (0.0228 g, 0.185 mmol).

Yield: 75% (0.2366 g, 0.097 mmol); Elemental analysis (C, H and N, Wt %) Anal. Cal for NiC₁₃₆H₁₁₈N₂O₄Ru₂P₈Cl₂: C, 67.39; H, 4.91; N, 1.16. Found: C, 67.18; H, 4.69; N, 1.33%; IR (KBr) (cm⁻¹): 2058, υ (C=C), 1583, υ (C=N); 1274, υ (C-O); 1479, 1436, 1166, 696, υ (dppe); ¹H NMR (CDCl₃) (300 MHz): δ 8.38 (s, 2H, C=N), δ 6.65–7.81 (m, 94H, phenyl), δ 3.88 (s, 6H, OCH₃), δ 2.68 (m, 16H, PCH₂CH₂P); ³¹P NMR: δ 49.46. ESI-MS: 2447 ([Ni{OCH₃-C₆H₄N = CH(O)C₆H₃C=CRu(dppe)₂Cl]₂+Na]⁺, 35), 1183 ([{OCH₃-C₆H₄N = CH(O)C₆H₃C=CRu(dppe)₂Cl]]⁺, 100), 898 ([Ru(dppe)₂]⁺, 39).

2.2.5. Synthesis of $Zn[H-C_6H_4N = CH(O)C_6H_3C \equiv CRu(dppe)_2Cl]_2$ (2a)

To a solution of *trans*-[RuCl(dppe)₂C \equiv C-C₆H₃(OH)(CHO)] (0.200 g, 0.185 mmol) in dichloromethane was added a solution of Zn(CH₃COO)₂.2H₂O (0.0203 g, 0.092 mmol) (5 ml) and aniline (0.0172 g, 0.185 mmol) (5 ml) in methanol dropwise with constant stirring. The reaction mixture was refluxed for 4 h on water bath. The resulting solution was then evaporated to small volume under *vacuum*. The pink coloured complex was collected by filtration, washed with ethanol and dried in *vacuo*.

 $\begin{array}{l} \label{eq:2.1} Yield: 83\% \ (0.1971 \ g, 0.083 \ mmol); \ Elemental analyses \ (C, H \ and N, Wt \ \%) \ Anal. \ Cal \ for \ ZnC_{134}H_{114}N_2O_2Ru_2P_8Cl_2: \ C, 67.89; \ H, 4.85; \ N, 1.18. \ Found: \ C, \ 67.70; \ H, \ 4.65; \ N, \ 1.35\%; \ IR \ (KBr) \ (cm^{-1}): \ 2055, \ \upsilon(C=C); \ 1589, \ \upsilon(C=N); \ 1276, \ \upsilon(C-O); \ 1479, \ 1435, \ 1164, \ 693, \ \upsilon(dppe); \ ^1H \ NMR \ (CDCl_3) \ (300 \ MHz): \ \delta \ 8.39 \ (s, \ 2H, \ C=N), \ \delta \ 6.54-7.60 \ (m, \ 96H, \ phenyl), \ \delta \ 2.69 \ (m, \ 16H, \ PCH_2CH_2P); \ ^{31}P \ NMR: \ \delta \ \ 49.48. \ \ ESI-MS: \ \ 2394 \ ([Zn\{H-C_6H_4N=CH(O)\ C_6H_3C=CRu(dppe)_2Cl\}_2+Na]^+, \ \ 33), \ \ 1153 \ ([\{H-C_6H_4N=CH(O)\ C_6H_3C=CRu(dppe)_2Cl\}_{+}, \ 100), \ 898 \ ([Ru(dppe)_2]^+, \ 38). \end{array}$

2.2.6. Synthesis of $Zn[NO_2-C_6H_4N = CH(O)C_6H_3C \equiv CRu(dppe)_2Cl]_2$ (**2b**)

The complex **2b** was prepared similar to the procedure performed in the preparation of **2a** except that aniline was replaced by 4-nitroaniline (0.0256 g, 0.185 mmol).

Yield: 78% (0.1918 g, 0.077 mmol); Elemental analyses (C, H and N, Wt %) Anal. Cal for ZnC₁₃₄H₁₁₂N₄O₆Ru₂P₈Cl₂: C, 65.41; H, 4.59; N, 2.28. Found: C, 65.20; H, 4.29; N, 2.55%; IR (KBr) (cm⁻¹): 2060,

 $u(C=C); 1588, u(C=N); 1278, u(C-O); 1481, 1436, 1167, 697 u(dppe); ¹H NMR (CDCl₃) (300 MHz): δ 8.38 (s, 2H, C=N), δ 6.85−7.80 (m, 94H, phenyl), δ 2.68 (m, 16H, PCH₂CH₂P); ³¹P NMR: δ 49.47. ESI-MS: 2484 ([Zn{NO₂-C₆H₄N = CH(O)C₆H₃C=CRu(dppe)₂Cl]₂+Na]⁺, 29), 1198 ([{NO₂-C₆H₄N = CH(O)C₆H₃C=CRu(dppe)₂Cl]]⁺, 100), 898 ([Ru(dppe)₂]⁺, 46).$

2.2.7. Synthesis of $Zn[OCH_3-C_6H_4N = CH(O)C_6H_3C \equiv CRu(dppe)_2Cl]_2$ (2c)

The complex **2c** was prepared similar to the procedure performed in the preparation of **2a** except that aniline was replaced by 4-methoxyaniline (0.0228 g, 0.185 mmol).

Yield:87% (0.2114 g, 0.087 mmol); Elemental analyses $ZnC_{136}H_{118}N_2O_4Ru_2P_8Cl_2$: C, 67.20; H, 4.89; N, 1.15. Found: C, 66.99; H, 4.76; N, 1.37%; IR (KBr) (cm⁻¹): 2058, υ (C=C); 1586, υ (C=N); 1279, υ (C-O); 1478, 1437, 1165, 692, υ (dppe); ¹H NMR (CDCl_3) (300 MHz): δ 8.39 (s, 2H, C=N), δ 6.74–7.55 (m, 94H, phenyl), δ 3.87 (s, 6H, OCH₃), δ 2.70 (m, 16H, PCH₂CH₂P); ³¹P NMR: δ 49.49. ESI-MS: 2454 ([Zn{OCH₃-C₆H₄N=CH(O)C₆H₃C=CRu(dppe)₂Cl]₂+Na]⁺, 33), 1183 ([{OCH₃-C₆H₄N=CH(O)C₆H₃C=CRu(dppe)₂Cl]⁺, 100), 898 ([Ru(dppe)₂]⁺, 43).

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of ruthenium-alkynyl complex 1 and its trimetallic hybrid complexes 1a-c and 2a-c is shown in Scheme 1. The reaction of *cis*-[RuCl₂(dppe)₂] with 5-ethynylsalicyaldehyde in $CH_2Cl_2/MeOH$ mixture (2:1) assisted by NaPF₆ at room temperature followed by column chromatography (Al₂O₃) afforded trans- $[RuCl(dppe)_2C \equiv C - C_6H_3(OH)(CHO)]$ (1) (dppe = 1,2-bis(diphenyl)phosphinoethane)) as a mononuclear complex in 78% yield. The trinuclear complexes $Ni[R-C_6H_4N = CH(O)]$ of the type $C_6H_3C \equiv CRu(dppe)_2Cl]_2$ $Zn[R-C_6H_4N = CH(O)]$ (1a-c), $C_6H_3C \equiv CRu(dppe)_2Cl]_2$ (**2a-c**) (where R = H, NO₂, OCH₃) were prepared by the reaction of trans-[RuCl(dppe)₂C=C-C₆H₃(OH)(-CHO)] (1) with nickel acetate or zinc acetate in the presence of aniline, 4-nitroaniline and 4-methoxyaniline, respectively. All the complexes were air stable at room temperature, non-hygroscopic



R= H, NO2, OCH3; M=Ni, Zn

Scheme 1. The Synthetic route to 1 and its hybrid complexes 1a-c and 2a-c.

and soluble in solvents like chloroform, dichloromethane, ethanol, methanol etc. The composition and identity of the complexes were confirmed from satisfactory elemental analyses, ESI-MS, IR, UV–Visible, ¹H NMR and ³¹P NMR spectroscopy.

The IR frequencies of selected groups in the spectra of **1** and its hybrid complexes **1a-c** and **2a-c** are given in experimental section. A weak band at 2076 cm⁻¹ due to internal triple bond (C=C) in the IR spectrum of **1** is slightly shifted to lower frequency region at *ca* 2053–2058 cm⁻¹ for **1a-c** and *ca* 2055–2060 cm⁻¹ for **2a-c** suggesting perturbation of the phenyl site leads to electron dissipation at the triple bond through conjugation [24]. The band observed at 1581-1590 cm⁻¹ in **1a-c** and 1586-1589 cm⁻¹ in **2a-c** indicate the presence of imine (HC=N) group in the complexes [25]. This view was further supported by the appearance of a band corresponding to the metal-nitrogen stretching vibration at *ca* 501-519 cm⁻¹ in **1a-c** and *ca* 515-519 cm⁻¹ in **2a-c**. In the IR spectrum of **1**, a band observed at 3280 cm⁻¹ due to phenolic –OH proton disappeared in the spectra of **1a-c** and **2a-c** upon coordination. The involvement of deprotonated phenolic moiety in all heteronuclear complexes is deduced by shifting of v(C-O) stretching frequency observed at 1289 cm^{-1} in **1** to a lower frequency region by $14-16 \text{ cm}^{-1}$ in **1a-c** and 10-13 cm⁻¹ in **2a-c** indicating weakening of v(C-O) and formation of strong M – O bond [26]. Further proof for complexation of oxygen is obtained from the appearance of (M - O) band at *ca* $537-569 \text{ cm}^{-1}$ for **1a-c** and $543-564 \text{ cm}^{-1}$ for **2a-c**. The spectra of all complexes exhibit bands at around 1478, 1435, 1168, 694 cm^{-1} are due to the presence of the dppe ligand. The complexes **1b** and **2b** exhibit two bands at ~1565 cm^{-1} and ~1409 cm^{-1} which can be attributed to $\upsilon_{asym}(NO_2)$ and $\upsilon_{sym}(NO_2)$ modes whereas; 1c and 2c exhibit band at around 1165 cm^{-1} ascribed to $-OCH_3$ group in the complexes [27].

The ¹H NMR spectra of mononuclear ruthenium-acetylide complex 1 and its corresponding trinuclear Ni(II)/Ru(II) (1a-c) and Zn(II)/Ru(II) (2a-c) complexes were recorded in CDCl₃ and are given in experimental section. Comparison of the chemical shift of the ruthenium-acetylide complex **1** with its respective Ni(II)/Ru(II) and Zn(II)/Ru(II) complexes shows that the resonance peaks are shifted at different level in each case. In the ¹H NMR spectrum of **1**, a characteristic resonance observed at δ 10.68 ppm due to phenolic OH proton disappeared in the spectra of **1a-c** and **2a-c** indicating deprotonation of **1** and coordination of phenolic –OH to the central metal ion. Another singlet observed at δ 9.66 ppm in the ¹H NMR spectrum of 1 corresponds to aldehydic proton. Upon imine formation this singlet disappeared and a new singlet was observed at around δ 8.39 ppm in **1a-c** and **2a-c** identified as -CH=N resonance of the imine proton [28]. However, the signal due to aromatic protons observed as multiplets in the region δ 6.45–7.53 ppm in **1** shifted towards downfield region in **1a-c** and **2a-c** confirming the complexation with Ni(II) and Zn(II) ion in the complexes. The 1 H NMR spectra of all complexes exhibit single resonance characteristic of the CH₂ protons in the dppe of acetylide ligand at δ 2.69 ppm [29]. A sharp singlet observed at δ 3.87 ppm in the spectra of **1c** and **2c** corresponds to $-OCH_3$ protons in the complexes [30].

The ³¹P NMR spectra of **1a-c** and **2a-c** and their mononuclear counterpart **1** displayed a single resonance at ~49.47 ppm corresponding to the phosphine ligand attached to the ruthenium. This suggests that two dppe ligands of each ruthenium occupy the equatorial plane with Cl^- and alkynyl group *trans* disposed at the axial sites in all the complexes [31].

3.2. Absorption and emission behaviour

The electronic absorption spectra of ruthenium-acetylide complex **1** and its trinuclear Ni(II)/Ru(II) (**1a-c**) and Zn(II)/Ru(II) (**2a-c**) complexes were recorded in CH_2Cl_2 (10^{-4} M) at room temperature

Table 1UV-Visible absorption data of 1a-c and 2a-c in CH2Cl2.

-	Complex	$\lambda_{\rm max}({\rm nm})~(e~{\rm x10^3},{\rm M^{-1}}~{\rm cm^{-1}})$
-	1	278 (13.3), 320 (3.4)
	1a	283 (17.1), 347 (4.3), 516 (0.6)
	1b	285 (16.6), 349 (3.9), 521 (0.5)
	1c	282 (18.0), 345 (5.4), 513 (0.7)
	2a	289 (17.2), 348 (5.3)
	2b	292 (15.4), 356 (3.9)
	2c	285 (18.1), 347 (6.2)
$\epsilon / M^{-1} cm^{-1}$	15000 - 10000 - 5000 - 0	
	270	370 470 570
		Wavelength (nm)

Fig. 1. UV-Visible absorption spectra of 1 in CH₂Cl₂ solutions.

and their corresponding data are summarized in Table 1. The absorption spectrum of **1** in CH₂Cl₂ is displayed in Fig. 1. The dppe phenyl group is primarily responsible for the intraligand $\pi \rightarrow \pi^*$ transition band at λ_{max} at 278 nm while the absorption band at λ_{max} 320 nm are due to the $d\pi(Ru) \rightarrow \pi^*(C \equiv CR)$ MLCT transition in **1**. Similar absorption spectra were observed for the complexes exhibiting two intense bands with λ_{max} at around 283 and 347 nm for 1a-c and 288 and 350 nm for 2a-c (Fig. 2) which can be attributed to an intraligand $(\pi \rightarrow \pi^*)$ transition and MLCT transition, respectively. A weak absorption at around 516 nm in the spectra of **1a-c** is assigned to the spin allowed transition $({}^{1}A_{1g} \rightarrow {}^{1}A_{2g})$ for four-coordinated square-planar Ni-Salen complexes [32]. Upon coordination, absorption bands of the complexes **1a-c** and **2a-c** are shifted to longer wavelength region compared to those of their monometallic precursor 1. The absorption shift and intensity change in the spectra of **1a-c** and **2a-c** relative to metallic precursor **1** is most likely originated from the metallation, increased π conjugation and increased delocalization of the whole electronic system [33].

Emission spectra of **1** as well as its trimetallic complexes **1a-c** and **2a-c** were recorded in CH_2Cl_2 solution (10^{-5} M) and spectral data are displayed in Table 2. The ruthenium-alkynyl complex **1** exhibit emission at 495 nm upon excitation at 371 nm (Fig. 3). This emission belong to MLCT transition similar to that of other luminescent ruthenium(II)-alkynyl complexes reported earlier [34]. Upon complexation of **1** with Ni(II) and Zn(II), the trinuclear complexes exhibit strong red shifted emission at 534–552 nm for **1a-c** and 539–554 nm for **2a-c** with lifetime of 2.56–2.78 and 3.77–3.91 ns, respectively. The significant red shift observed in **1a-c** and **2a-c** in comparison to their metallic precursor **1** results from the formation of trinuclear species which leads to an increased energy gap between ground state and excited state. These results also confirm that the emission origin in **1a-c** and **2a-c** predominantly not only



Fig. 2. UV–Visible absorption spectra of (A) 1a-c (B) 2a-c in CH₂Cl₂ solutions.

Table 2 Photoluminescence data of 1a-c and 2a-c in CH_2Cl_2 (10^{-5} M).

Complex	λ_{ex} (nm)	λ_{em} (nm)	φ	τ (ns)	$K_r(s^{-1}/10^7)$	$K_{nr}(s^{-1}/10^9)$
1	371	495	0.049	1.90	2.578	0.500
1a	380	538	0.056	2.60	2.153	0.363
1b	383	552	0.059	2.78	2.122	0.338
1c	378	534	0.053	2.56	2.070	0.369
2a	390	549	0.068	3.85	1.766	0.242
2b	393	554	0.069	3.91	1.764	0.238
2c	388	539	0.064	3.77	1.697	0.248



Fig. 3. Emission spectra of 1 in CH₂Cl₂ solutions.

due to MLCT transition but also due to chelation enhanced fluorescence (CHEF) caused by coordination of imine group to Ni(II) and Zn(II) ion in the complexes [35]. The remarkable increase in fluorescence emission by CHEF is attributed to the formation of comparatively rigid structure by strong complexation with central metal ion which minimizes the nonradiative energy loss [36]. Compared to **1a**, **1c**, **2a** and **2c** the slight red shift of the absorption and emission wavelengths observed in **1b** and **2b** is probably as a result of the higher electron withdrawing ability of $-NO_2$ group which offers an extra conjugated backbone which lower the $\pi^*(C=CH)$ orbital energy and lead to narrowing the HOMO-LUMO energy gap. The substituent's on the coordinated imine group also affect the emission intensities in the complexes. The fluorescence intensity is significantly quenched in **1b** and **2b** due to presence of electron withdrawing $-NO_2$ group as compared to electron donating $-OCH_3$ group in **1c** and **2c**. However, the emission intensities in **1a** and **2a** with 'H' group in the complexes are in between above two intensities. The emission quantum yield (ϕ) of all the complexes was determined with reference to quinine sulfate ($\phi = 0.52$) and are listed in Table 2. The fluorescence quantum yield (ϕ) of the complexes is approximately at 0.053–0.059 for **1a-c** and 0.064–0.069 for **2a-c** which are higher than for their mononuclear counterpart **1** (0.049). These values are in conformity with the values reported in the literature [37].

3.3. Solvatochromism of the complexes

The solubility of the complexes in variety of organic solvents allowed a detailed investigation of its solvatochromism behaviour. Thus in order to study the solvatochromism of the complexes their emission spectra were obtained in different solvents (chlorobenzene, dichloromethane and tetrahydofuran). It was observed from Fig. 4 that, emission band maxima of the complexes 1a-c and 2a-c shows clear differences. The complexes **1a-c** shows their emission peak at 524-539 nm in chlorobenzene, 534-552 nm in dichloromethane and 544-565 nm in tetrahydrofuran whereas, the complexes 2a-c shows emission peak at 528-540 nm in chlorobenzene, 539-554 nm in dichloromethane and 551-564 nm in tetrahydrofuran. From Table 3 it is revealed that emission maxima increases with increase in solvent polarity in the order chlorobenzene < dichloromethane < tetrahydrofuran. The observed shift of band maxima to higher wavelength in the solvents of increasing polarity were indicative of, excited states are more stabilized with increasing polarity of the solvents which leads to a red shifted emission [38].

3.4. SEM and TEM studies

The SEM analysis of representative complexes **1a** and **2c** was carried out in order to evaluate the surface morphology and particle size of the trimetallic complexes. From the SEM image in Fig. 5(A) and 5(B) it is observed that, the shape of complex **1a** is irregular with crushed ice like morphology having average size of ~110 nm. On other hand the SEM of **2c** exhibit plate like morphology with average size of ~200 nm. Fig. 6 shows various TEM images with different magnifications and the calculated histogram for zinc complex. The TEM image indicate the sphere-like structure for Zn(II)/Ru(II) hybrid complex (**2c**) with well dispersed spherical particle size between 200 and 300 nm without agglomeration.



Fig. 4. Emission spectra of 1a-c and 2a-c in different solvents: chlorobenzene, dichloromethane and tetrahedrofuran.

3.5. X-ray powder diffraction studies

Single crystal X-ray technique is a powerful analytical tool which provides detailed information about internal lattice, unit cell dimensions, particle size, crystal system, bond length and bond angles of crystalline substances. However, the difficulties in obtaining crystalline complexes in proper symmetric form rendered us to study the X-ray powder diffraction method of prepared complexes. The X-ray diffraction pattern of representative complexes **1a** and **2c** revealed well defined crystalline peaks indicating that the complexes **1a** and **2c** are crystalline in nature (Fig. 7). The diffractogram of **1a** records eight reflections between 5 and 80° (2 θ) with maximum at $2\theta = 12.61°$ corresponding to value

of d = 7.012 Å. The diffractogram of **2c** consists of six reflections with maxima at $2\theta = 10.44^{\circ}$ corresponding to value of d = 8.470 Å. The main peaks of **1a** and **2c** have been indexed by using computer software by trial and error method [39] keeping in mind characteristics of various symmetry systems till good fit could be obtain between observed and calculated 2θ and $sin^2\theta$ values. The method also yielded *hkl* values. The relative intensities corresponding to the prominent peaks have been measured. The indexing of the diffractogram of **1a** and **2c** are identical. Based on this it can be proposed that these compounds belong to same structural class. A comparison of values of 2θ and $sin^2\theta$ for the **1a** and **2c** reveals that, there is good agreement between the calculated and observed values of 2θ and $sin^2\theta$ on the basis of assumption of monoclinic S.B. Pawal et al. / Journal of Molecular Structure 1154 (2018) 131-139

 Table 3

 Emission maxima and Quantum yield data in various solvents of 1a-c and 2a-c

Complex	Solvent	$\lambda_{\rm ex} ({\rm nm})$	λ_{em} (nm)	Quantum Yield (ϕ)
1a	Chlorobenzene	379	531	0.057
	Dichloromethane	380	538	0.056
	Tetrahydrofuran	382	553	0.054
1b	Chlorobenzene	383	539	0.061
	Dichloromethane	383	552	0.059
	Tetrahydrofuran	386	565	0.058
1c	Chlorobenzene	375	524	0.053
	Dichloromethane	378	534	0.053
	Tetrahydrofuran	379	544	0.052
2a	Chlorobenzene	388	536	0.069
	Dichloromethane	390	549	0.068
	Tetrahydrofuran	391	557	0.065
2b	Chlorobenzene	392	540	0.069
	Dichloromethane	393	554	0.069
	Tetrahydrofuran	397	564	0.067
2c	Chlorobenzene	387	528	0.068
	Dichloromethane	388	539	0.064
	Tetrahydrofuran	390	551	0.061

structure [40]. The structure of **1a** yields values for lattice constant a = 10.9308 Å, b = 8.8289 Å, and c = 15.2709 Å; $\alpha = \gamma = 90^{\circ}$ and $\beta = 103.7^{\circ}$, unit cell volume $V = 1431.92 \text{ Å}^3$. However, the structure of **2c** yields values for lattice constant a = 14.6848 Å, b = 8.4702 Å and c = 11.4494 Å; $\alpha = \gamma = 90^{\circ}$ and $\beta = 99.035^{\circ}$, unit cell volume $V = 1406.45 \text{ Å}^3$. In conjunction with these parameters the conditions such as $a \neq b \neq c$ and $\alpha = \gamma \neq \beta$ required for the samples to be monoclinic were tested and found to be satisfactory. The particle size of **1a** and **2c** was determined using Scherrer's formula [41] and was found to be 231.62 and 247.13 Å, respectively.

3.6. Thermogravimetric analysis

To characterize the compounds in terms of thermal stability, the thermal properties of **1a-c** and **2a-c** complexes were studied by thermogravimetric analysis. For TG measurement the samples were heated in the range of 25–800 °C at heating rate of 10 °C min⁻¹ under nitrogen atmosphere. TG curve of Ni(II)/Ru(II) complexes showed that the complexes are thermally stable upto *ca* 245 °C revealing absence of either water or solvent molecules. In the temperature range of 246–350 °C, the complexes were then underwent complicated and significant multiple weight loss of 18.19 (**1a**), 21.35(**1b**) and 20.22 (**1c**), respectively corresponding to the



Fig. 6. TEM photograph of 2c.

total loss of salicylidine moiety (calcd. 18.52 (1a), 21.51(1b) and 20.54 (1c). All the complexes collapse due to release of dppe ligand along with Cl⁻ per formula unit between 351 and 535 °C with an observed weight loss of 70.28 (1a), 67.69 (1b) and 68.40 (1c), respectively (calcd. 70.41 (1a), 67.83 (1b) and 68.66 (1c)). The Zn(II)/Ru(II) complexes 2a, 2b and 2c shows very similar behaviour to the above; once again an absence of water or solvent is indicated by stability of the complexes up to ca. 243, 246 and 251 °C for 2a, 2b and 2c respectively. For 2a-c the decomposition stage with mass loss of 17.97 in 2a, 21.03 in 2b and 20.18 in 2c can be ascribed to the loss of coordinated salicylidine moiety (calcd 18.47 (2a), 21.45 (2b) and 20.48 (2c)) in the temperature ranges 244-353, 247-357 and 252-362 °C, respectively. Another stage at 354-569, 358-567, 363-615 and 363-620 °C with observed mass loss of 69.89 (2a), 67.27 (2b) and 68.08 (2c) respectively due to loss of the remaining dppe ligands (calcd 70.21 (2a), 67.64 (2b) and 68.48 (2c)).

3.7. Cyclic voltammetry

In order to gain insight into the electronic environment; the electrochemical properties of all complexes were probed by cyclic voltammetry. All measurements were performed in dichloromethane solution (10^{-3} M) containing 0.05 M *n*-Bu₄NClO₄ as a supporting electrolyte at room temperature in the potential range +1.50 to -1.50 V. The electrochemical behaviour of all the complexes is characterized by a well defined redox process on the positive potential side in dichloromethane and the representative cyclic voltammogram of **1c** and **2c** are presented in Fig. 8. The



Fig. 5. Scanning electron micrographs of (A) 1a and (B) 2c.



Fig. 7. Powder X-ray diffraction patterns of 1a and 2c.

ruthenium-acetylide complex **1** oxidized at a potential 1.021 V ($E_{1/}$ 2) ascribed to the Ru(II)/Ru(III) couple. Cyclic voltammetry studies on Ni(II)/Ru(II) complexes (1a-c) reveal that, all complexes undergo quasireversible oxidation processes in the range 0.528-0.549 V assigned to the Ni(II)/Ni(III) couple by analogy with earlier observations [42]. Another oxidation process observed at 1.051-1.078 V $(E_{1/2})$ in **1a-c** is attributed to Ru(II)/Ru(III) couple. However, the half wave potential for Ru(II)/Ru(III) couple is only observed at 1.040–1.061 V (E_{1/2}) for **2a-c**. On comparing cyclic voltammetry data of mononuclear precursor 1 with its respective Ni(II)/Ru(II) and Zn(II)/Ru(II) complexes, it was found that the oxidation of ruthenium(II) units shifted to more positive value which is presumably due to increase in electron density around Ni(II) and Zn(II) in the complexes [43]. It is noticeable from Table 4 that, the electrochemical properties of all the complexes are interdependent with the substituent groups on the coordinating ligands. The electron donating -OCH₃ shifts both oxidation and reduction towards cathode while electron withdrawing -NO₂ groups shift the redox potentials towards anode.

4. Conclusion

In summary, some trimetallic complexes of the type Ni $[R-C_6H_4N = CH(O)C_6H_3C \equiv CRu(dppe)_2Cl]_2$ (1a-c) and Zn $[R-C_6H_4N = CH(O)C_6H_3C \equiv CRu(dppe)_2Cl]_2$ (2a-c) have been synthesized and characterized. X-ray powder diffraction, SEM and TEM

Table 4Electrochemical data of the complexes 1a-c and 2a-c.

Compound	Ni(II)/Ni(III)			Ru(II)/Ru(III)		
	$E_{pa}(V)$	E _{pc} (V)	E _{1/2} (V)	E _{pa} (V)	$E_{pc}(V)$	E _{1/2} (V)
1a	0.587	0.486	0.536	1.079	1.044	1.061
1b	0.610	0.488	0.549	1.087	1.069	1.078
1c	0.575	0.482	0.528	1.063	1.039	1.051
2a	-	-	_	1.085	1.019	1.052
2b	-	-	_	1.096	1.027	1.061
2c	-	-	-	1.075	1.006	1.040

Supporting electrolyte: n-Bu₄NClO₄ (0.05 M); complex: 0.001 M; solvent: CH₂Cl₂; $E_{1/2} = \frac{1}{2}(E_{pa} + E_{pc})$; scan rate: 100 mVs⁻¹. All potentials vs. SCE.

studies of representative complexes **1a** and **2c** are used to investigate the crystal structure and morphology of the complexes. The electrochemical study of the complexes showed quasireversible redox behaviour corresponding to Ni(II)/Ni(III) and Ru(II)/Ru(III) for **1a-c** and only Ru(II)/Ru(III) for **2a-c**. Oxidation of Ru(II) unit in **1a-c** and **2a-c** is shifted towards more positive value than their mononuclear precursor **1** upon coordination to Ni(II) and Zn(II). All the complexes are photoluminescent in solution state at room temperature which can be tuned by the variation of the substituent group and follow the trend NO₂ >H > OCH₃ whereas; reverse effect was found in emission intensity of the complexes. Emission maxima increases with increase in polarity of the solvent indicative of excited states of all the complexes are more stabilized in polar



Fig. 8. Cyclic voltammograms of 1c and 2c measured in CH₂Cl₂ (10⁻³ M) and 0.05 M n-Bu₄NClO₄ as supporting electrolyte. Potentials vs. SCE.

solvents.

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