



Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

NLO active Cu^{II}/Ru^{II} and Cd^{II}/Ru^{II} coordinationorganometallic complexes: synthesis, structural characterization and photoluminescence properties

B. G. Bharate & S. S. Chavan

To cite this article: B. G. Bharate & S. S. Chavan (2016): NLO active Cu^{II}/Ru^{II} and Cd^{II}/ Ru^{II} coordination-organometallic complexes: synthesis, structural characterization and photoluminescence properties, Journal of Coordination Chemistry, DOI: 10.1080/00958972.2016.1229475

To link to this article: http://dx.doi.org/10.1080/00958972.2016.1229475

ſ	
	+

View supplementary material 🖸

4)	(1
Г			
C			

Published online: 09 Sep 2016.



Submit your article to this journal 🗗





💽 View related articles 🗹



則 🛛 View Crossmark data 🗹

Full Terms & Conditions of access and use can be found at http://www.tandfonline.com/action/journalInformation?journalCode=gcoo20



NLO active Cu^{II}/Ru^{II} and Cd^{II}/Ru^{II} coordination-organometallic complexes: synthesis, structural characterization and photoluminescence properties

B. G. Bharate^{a,b} and S. S. Chavan^a

^aDepartment of Chemistry, Shivaji University, Kolhapur, India; ^bDepartment of Applied Chemistry, Defence Institute of Advanced Technology (DU), Pune, India

ABSTRACT

 $Cu^{\parallel}/Ru^{\parallel}$ and $Cd^{\parallel}/Ru^{\parallel}$ hybrid complexes $[Cu(L_{1-3})(NC_5H_4C=CRu(dppe)_2Cl)]$ (1a-3a) and $[Cd(L_{1,3})(NC_5H_4C=CRu(dppe)_5CI)]$ (1b-3b) have been prepared by reaction of trans-[RuCl(dppe),(C=C-py-3)] (1) with copper or cadmium acetate in the presence of Schiff base ligands $L_{H_{1-3}}$ (where $L_{H} = 2$ -(pyrrole-2-yl-methylidine)aminophenol (L_{H1}), 5-bromo-2-(pyrrole-2-yl-methylidine) aminophenol (L_{H2}) and 5-nitro-2-(pyrrole-2-yl-methylidine)aminophenol (L_{H3})). The hybrid materials were characterized on the basis of elemental analyses, TEM, IR, UV-visible, ¹H NMR, and ³¹P NMR spectral studies. TEM overview observations revealed well-dispersed spherical nanoparticles of ~60 nm are formed. Quasireversible redox behavior is observed for Cu^{II}/Ru^{II} complexes corresponding to Cu^I/Cu^{II} and Ru^{II}/Ru^{III} couples. All the complexes exhibit blue-green emission as a result of fluorescence from the intraligand $(\pi \rightarrow \pi^*)$ emission excited state with good quantum yield. The second-order nonlinear optical (NLO) properties of Cu^{II}/Ru^{II} and Cd^{II}/Ru^{II} complexes have been investigated by the Kurtz-powder method. The second harmonic generation efficiency of these complexes show that these complexes are NLO active and display good second-order nonlinear optical activity.

ARTICLE HISTORY

Received 5 April 2016 Accepted 19 July 2016

KEYWORDS

Schiff base; hybrid complexes; fluorescence; nonlinear optics



1. Introduction

There has been interest in the development of better NLO materials due to their potential applications in optical devices such as optical signal processing, switching, frequency generation, optical data storage, optical communication, and image processing [1–4]. The most widely used NLO materials are inorganic crystals such as LiB₃O₅, BaB₂O₄, and KH₂PO₄. Organic NLO crystals have superior properties to inorganic ones, such as higher susceptibility faster response and the capability of designing components on the molecular level. Effort has been devoted to the metal organic coordination complexes as NLO materials are inorganic and inorganic coordination complexes as NLO materials due to high NLO coefficient, stable physicochemical properties, and better mechanical intension, combining the useful attributes of both organic and inorganic components. The advantage of metal organic coordination complexes are wide variety of central metals varying in size, nature, oxidation states, as well as ligands with different nature and size, facilitating the development of relationships between molecular structures and NLO properties. The most challenging goal to the chemist is to develop new π -conjugated materials with new branches and core to investigate their physical and chemical properties as well as their structure property relationships [5–11].

Metal organic coordination complexes have been growing at a phenomenal rate because of their unique structural, electronic, and functional properties. We are interested in organic and inorganic components of Ru-based hybrid systems to construct structurally organized molecular materials. As continuation of our research we report herein synthesis, characterization, photoluminescence, and nonlinear optical properties of M^{II}/Ru^{II} (M=Cu, Cd) Schiff base complexes by reaction of *trans*-[RuCl(dp-pe)₂(C=C-py-3)] (1) with copper or cadmium acetate in the presence of Schiff base ligands L_{H1-3} (where

L = 2-(pyrrole-2-yl-methylidine)aminophenol (L_{H1}), 5-bromo-2-(pyrrole-2-yl-methylidine)amino phenol (L_{H2}) and 5-nitro-2-(pyrrole-2-yl-methylidine)aminophenol (L_{H2})).

All complexes were characterized by TEM, elemental analyses, IR, UV–visible, ¹H NMR, and ³¹P NMR spectral studies. The photoluminescence, electrochemical behavior, and SHG efficiencies of the complexes have been studied.

2. Experimental

2.1. Materials and general methods

All the chemicals used were of analytical grade. Solvents for synthesis were distilled over appropriate drying agents. *trans*-[RuCl(dppe)₂(C=C-py-3)] (1) was prepared by our previously reported procedure with high yield and purity. Copper acetate, cadmium acetate, and 2-aminophenol were from Spectrochem and 3-ethynylpyridine, NaPF₆, RuCl₃·xH₂O, PdCl₂(PPh₃)₂, and *n*Bu₄NPF₆ were obtained from Aldrich and used as received.

Elemental analyses were performed on a Thermo Finnigan FLASH EA-112 CHNS analyzer. Electronic spectra were recorded on a Cyber-Lab UV-100 Superspec spectrophotometer. Infrared spectra were recorded on a Perkin Elmer FT-IR spectrometer as KBr pellets from 4000–400 cm⁻¹. ¹H NMR spectra of the samples were measured on a Varian Mercury-300 MHz instrument using TMS as an internal standard. ³¹P NMR spectra were recorded using a Varian Mercury-300 FT NMR spectrometer. ESI mass spectra of all the complexes were recorded using a Bruker Apex3. Thermal analyses of the complexes were carried out on a Perkin Elmer thermal analyzer in nitrogen at a heating rate of 10 °C/min. Luminescence properties were determined using a JASCO F.P.750 fluorescence spectrophotometer equipped with a quartz cuvette of 1 cm³ path length at room temperature. 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 reference electrode containing aqueous 3 M KCl were used.

2.2. Synthesis of L_{H1-3}

2.2.1. Synthesis of 2-(pyrrole-2-yl-methylidine)aminophenol (L_{μ_1})

A solution of pyrrole-2-carboxyaldehyde (0.35 g, 3.68 mmol) in 15 mL methanol was added dropwise to a dissolved solution of 2-amino phenol (0.40 g, 3.68 mmol) in methanol (10 mL) with constant stirring at room temperature and the resulting mixture was refluxed at 70 °C until completion of reaction (reaction monitored by TLC). The resultant dark brown product was purified by column chromatography. The solvent was removed under vacuum by a rotary evaporator to receive dark brown product. Yield: (0.51 g, 75%); IR (KBr) (cm⁻¹): 3145, v(N–H); 1618, v(HC=N); 1283, v(C–O); ¹H NMR (CDCl₃) (300 MHz): δ 11.74 (bs, –OH), 8.72 (s, HC=N), 6.74–7.27 (m, Ar–H); MS: 186 (M⁺).

2.2.2. Synthesis of 5-bromo-2-(pyrrol-2-yl-methylidine)aminophenol (L_{H_2})

L_{H2} was prepared similar to the procedure performed in the preparation of L_{H1} except that 2-amino-phenol was replaced by 2-amino-5-bromo phenol (0.69 g, 3.68 mmol). Yield: (0.69 g, 70%); IR (KBr) (cm⁻¹): 3139, v(N–H); 1620, v(HC=N); 1279, v(C–O); ¹H NMR (CDCl₃) (300 MHz): δ 11.76 (bs, –OH), 8.74 (s, HC=N), 6.68–7.29 (m, Ar–H); MS: 265 (M⁺).

2.2.3. Synthesis of 5-nitro-2-(pyrrol-2-yl-methylidine)aminophenol (L_{H3})

 L_{H3} was prepared similar to the procedure performed in the preparation of L_{H1} except that 2-amino phenol is replaced by 2-amino-5-nitrophenol (0.57 g, 3.68 mmol). Yield: (0.58 g, 68%); IR (KBr) (cm⁻¹): 3135, v(N–H); 1625, v(HC=N); 1281, v(C–O); ¹H NMR (CDCl₃) (300 MHz): δ 11.72 (bs, –OH), 8.75 (s, HC=N), 6.71–7.31 (m, Ar–H); MS: 231(M⁺).

2.3. Synthesis of Cu^{II}/Ru^{II} hybrid complexes (1a-3a)

2.3.1. Synthesis of $[Cu(L_1)NC_5H_4C \equiv CRu(dppe)_5CI]$ (1a)

To a solution of *trans*-[RuCl(dppe)₂(C≡C-py-3)] (1) (0.200 g, 0.193 mmol) in CH₂Cl₂ was added a solution of Cu(CH₃COO)₂·H₂O (0.038 g, 0.193 mmol) and L_{H1} (0.036 g, 0.193 mmol) in MeOH dropwise with constant stirring. The reaction mixture was then refluxed for 6 h and the resulting solution was evaporated to small volume under vacuum. The dark yellow complex was collected by filtration, washed with ethanol, and dried in *vacuo*. Yield: (0.192 g, 72%); Elemental analyses (C, H, and N, wt %) Anal. Calcd for C₇₀H₆₀N₃RuP₄OClCu: C, 65.52; H, 4.71; N, 3.27. Found: C, 65.38; H, 4.67; N, 3.41. IR (KBr) (cm⁻¹): 2051 *v*(C≡C); 1590, *v*(HC=N); 1261, *v*(C−O); 1476, 1432, 1167, 695, *v*(dppe); 491 *v*(M-N); UV–Vis (DMF) λ_{max} (nm) ($\varepsilon \times 10^3$, M⁻¹ cm⁻¹): 241 (24), 283 (13), 381(6); 514 (1.2); ¹H NMR (dmso-d₆) (300 MHz): δ 8.95 (s, HC=N), 8.13 (s, 1H, Py-H_{0N,oC≡C}), 8.04 (d, 1H, Py-H_{0N,pC≡C}), 6.56–7.19 (m, 49 H, phenyl), 2.65 (s, 8H, PCH₂CH₂P); ³¹P NMR: δ 46.62. ESI MS: 1306 ([Cu(L₁)NC₅H₄C≡CRu(dppe)₂Cl + Na]⁺, 13); 1105 ([CuNC₅H₄C≡CRu(dppe)₂Cl)]⁺, 28); 1041 ([NC₅H₄C≡CRu(dppe)₂Cl)]⁺, 100); 898 ([Ru(dppe)₂]⁺12).

2.3.2. Synthesis of $[Cu(L_2)NC_5H_4C \equiv CRu(dppe)_2CI]$ (2a)

Complex **2a** was prepared similar to the procedure performed in the preparation of **1a** except that L_{H1} was replaced by L_{H2} (0.051 g, 0.193 mmol). Yield (0.192 g, 78%); Elemental analyses (C, H and N, wt %) Anal. Calcd for $C_{70}H_{59}N_3RuP_4OCuClBr; C, 61.72; H, 4.37; N, 3.08.$ Found: C, 61.39; H, 4.21; N, 3.17. IR (KBr) (cm¹): 2058 v(C=C); 1591 v(HC=N); 1264, v(C–O); 1470, 1431, 1165, 691 (dppe); 509 v(M–N); UV–Vis (DMF) λ_{max} (nm) ($\varepsilon \times 10^3$, M⁻¹ cm⁻¹): 242 (19), 282(11), 382 (7); 517 (0.9); ¹H NMR (dmso- d_6) (300 MHz), δ 9.13 (s, HC=N), 8.15 (s, 1H, Py-H_{0NoC=C}), 8.01 (d,1H, Py-H_{0NoC=C}), 6.75–7.84 (m,48 H, phenyl), 2.63 (s, 8H, PCH₂CH₂P); ³¹P NMR: δ 46.53. ESI MS: 1385 ([Cu(L₂)NC₅H₄C≡CRu(dppe)₂Cl + Na]⁺, 17); 1105 ([CuNC₅H₄C≡CRu(dppe)₂Cl]⁺, 23); 1041 ([NC₅H₄C≡CRu(dppe)₂Cl]⁺, 100); 898 ([Ru(dppe)₂]⁺07).

2.3.3. Synthesis of $[Cu(L_3)NC_5H_4C \equiv CRu(dppe)_5CI]$ (3a)

Complex **3a** was prepared similar to the procedure performed in the preparation of **1a** except that L_{H1} was replaced by L_{H3} (0.044 g, 0.193 mmol). Yield: (0.186 g, 69%); Elemental analyses (C, H, and N, wt %) Anal. Calcd for $C_{70}H_{59}N_4RuP_4O_3CuCl$: C, 63.30; H, 4.48; N, 4.22. Found: C, 62.89; H, 4.39; N, 4.36. IR (KBr) (cm⁻¹): 2047 ν (C=C); 1598, ν (HC=N); 1268, ν (C–O); 1485, 1432, 1174, 695, ν (dppe); 482 ν (M-N); UV–Vis (DMF) λ_{max} (nm) ($\varepsilon \times 10^3$, M⁻¹ cm⁻¹): 249 (24); 281(13), 392 (8); 519 (1.2); ¹H NMR (dmso- d_6) (300 MHz), δ 9.15 (s, HC=N), 8.04 (s, 1H, Py-H_{oN,oC=C}), 8.01 (d, 1H, Py-H_{oN,pC=C}), 6.52–7.69 (m, 48 H, phenyl), 2.71 (s, 8H, PCH₂CH₂P); ³¹P NMR: δ 46.87. ESI MS: 1351 ([Cu(L₃)NC₅H₄C=CRu(dppe)₂Cl + Na]⁺,22); 1105 ([CuNC₅H₄C=CRu(dppe)₂Cl)]⁺, 29); 1041 ([CuNC₅H₄C=CRu(dppe)₂Cl)]⁺, 100); 898 ([Ru(dppe)₃]⁺ 11).

2.4. Synthesis of Cd^{II}/Ru^{II} hybrid complexes (1b-3b)

2.4.1. Synthesis of $[Cd(L_1)NC_5H_4C \equiv CRu(dppe)_2Cl]$ (1b)

To a solution of *trans*-[RuCl(dppe)₂(C=C-py-3)] (**1**) (0.200 g, 0.193 mmol) in CH₂Cl₂ was added a solution of Cd(CH₃COO)₂·2H₂O (0.051 g, 0.193 mmol) and L_{H1} (0.036 g, 0.193 mmol) in MeOH dropwise with constant stirring. The reaction mixture was then refluxed for 6 h and the resulting solution then evaporated to small volume under vacuum. The pale yellow complex was collected by filtration, washed with ethanol, and dried in *vacuo*. Yield (0.184 g, 71%). Elemental analyses (C, H, and N, wt %) Anal. Calcd for C₇₀H₆₀N₃RuP₄OCdCl: C, 63.12; H, 4.54; N, 3.15. Found: C, 62.85; H, 4.21; N, 3.21. IR (KBr) (cm⁻¹): 2053 v(C=C); 1588, v(HC=N); 1267, v(C–O); 1481, 1435, 1095, 693, v (dppe); 512 v(M–N); UV–Vis (DMF) λ_{max} (nm) ($\varepsilon \times 10^3$, M⁻¹ cm⁻¹): 246 (26); 278 (12); 379 (8); ¹H NMR (dmso-d₆) (300 MHz): δ 9.01 (s, HC=N), 8.15 (s, 1H, Py-H_{0N,0C=C}), 8.01 (d, 1H, Py-H_{0N,pC=C}), 6.59–7.25 (m, 49 H, phenyl), 2.69 (s, 8H, PCH₂CH₂P); ³¹P NMR: δ 46.74. ESI MS: 1355 ([Cd(L₁)NC₅H₄C≡CRu(dppe)₂Cl + Na]⁺, 18); 1153 ([CuNC₅H₄C≡CRu(dppe)₂Cl)]⁺, 18); 1041 ([CuNC₅H₄C≡CRu(dppe)₂Cl)]⁺, 100); 898 ([Ru(dppe)₃]⁺15).

2.4.2. Synthesis of $[Cd(L_2)NC_5H_4C \equiv CRu(dppe)_2Cl]$ (2b)

Complex **2b** was prepared similar to the procedure performed in the preparation of **1b** except that L_{H1} was replaced by L_{H2} (0.0512 g, 0.193 mmol). Yield: (0.202 g, 74%); Elemental analyses (C, H and N, wt %) Anal. Calcd for $C_{70}H_{59}N_3RuP_4OCdClBr$: C, 59.59; H, 4.21; N, 2.98. Found: C, 59.12; H, 4.01; N, 3.13. IR (KBr) (cm⁻¹): 2051 ν (C=C); 1601, ν (HC=N); 1262, ν (C–O); 1482, 1434, 1159, 691, ν (dppe); 487, ν (M-N); UV–Vis (DMF) λ_{max} (nm)($\varepsilon \times 10^3$, M⁻¹ cm⁻¹): 249 (27); 279 (13); 378 (9); ¹H NMR (dmso- d_6) (300 MHz), δ 9.12 (s, HC=N), 8.12 (s, 1H, Py-H_{oNoC=C}), 8.04 (d,1H, Py-H_{oNoC=C}), 6.93–7.42 (m,48 H, phenyl), 2.69 (s, 8H, PCH₂CH₂P); ³¹P NMR: δ 46.58. ESI MS: 1434 ([Cd(L₂)NC₅H₄C=CRu(dppe)₂Cl + Na]⁺, 10), 1149 ([CdNC₅H₄C=CRu(dppe)₂Cl)]⁺, 14) 1041([NC₅H₄C=CRu(dppe)₂Cl]⁺, 100), 957 ([Ru(dppe)₂]ClNa.]⁺ 21).

2.4.3. Synthesis of $[Cd(L_3)NC_5H_4C \equiv CRu(dppe)_5Cl]$ (3b)

Complex **3b** was prepared similar to the procedure performed in the preparation of **1b** except that L_{H1} was replaced by L_{H3} (0.0446 g, 0.193 mmol). Yield: (0.190 g, 76%); Elemental analyses (C, H, and N, wt %) Anal. Calcd for $C_{70}H_{59}N_4RuP_4O_3CdCl$: C, 61.05; H, 4.32; N, 4.07. Found: C, 60.87; H, 4.02; N, 4.28. IR (KBr) (cm⁻¹): 2054 v(C=C); 1605, v(HC=N); 1261, v(C–O); 1478, 1439, 1166, 693, v(dppe); 495 v(M-N); UV–Vis (DMF) λ_{max} (nm)($\varepsilon \times 10^3$, M^{-1} cm⁻¹): 252 (28); 280 (14); 381 (7); ¹H NMR (dmso- d_6) (300 MHz), δ 9.06 (s, HC=N), 8.04 (s, 1H, Py-H_{0N,OC=C}), 8.01 (d, 1H, Py-H_{0N,PC=C}), 6.57–7.62 (m, 48 H, phenyl), 2.68 (s, 8H, PCH_2CH_2P); ³¹P NMR: δ 46.82. ESI MS: 1400 ([Cd(L_3)NC_5H_4C=CRu(dppe)_2CI + Na]⁺, 29); 1153 ([CdNC_5H_4C=CRu(dppe)_2CI]⁺, 31) 1041 ([CuNC_5H_4C=CRu(dppe)_2CI]⁺, 100), 898 ([Ru(dppe)_2]⁺ 12).

3. Results and discussion

3.1. Synthesis and characterization

The reaction of equimolar quantities of *trans*-[RuCl(dppe)₂(C≡C-py-3)] (1) with Cu^{II} or Cd^{II} acetate in the presence of Schiff base ligands L_{H1-3} in CH₂Cl₂/MeOH afforded bimetallic complexes [Cu(L₁₋₃) (NC₅H₄C≡CRu(dppe)₂Cl)] (**1a-3a**) and [Cd(L₁₋₃)(NC₅H₄C≡CRu(dppe)₂Cl)] (**1b-3b**) (where L=2-(pyrrole-2-yl-methylidine)aminophenol-H (L₁), 5-bromo-2-(pyrrole-2-yl-methylidine)aminophenol-H (L₂) and 5-nitro-2-(pyrrole-2-yl-methylidine)aminophenol-H (L₃)]. Cu^{II} is one of the most labile metal centers even though it forms air stable, moisture insensitive complexes due to π -acceptor ability of ligands. These complexes are partially soluble in chloroform, dichloromethane, methanol, *etc.*, but show maximum solubility in DMF and DMSO. All the complexes were characterized by elemental analyses, IR, UV–Visible, ¹H NMR, and ³¹P NMR spectral studies. The results of elemental analyses confirm the compositions of the complexes.

To study the bonding of L_{H1-3} and organometallic moiety **1** to Cu^{II} or Cd^{II} , IR spectra of L_{H1-3} and **1** are compared with the spectra of their corresponding binuclear complexes. The IR spectrum of **1** shows the band at 2074 cm⁻¹ corresponding to C=C bonds of pyridyl acetylide ligand; upon coordination this band shifted to lower frequency at *ca*. 2047–2058 cm⁻¹ for **1a-3a** and 2051–2054 cm⁻¹ for **1b-3b** [12]. The band at 1618–1625 cm⁻¹ in spectra of uncomplexed L_{H1-3} is due to v(HC=N), shifted to lower frequency at 1590–1598 cm⁻¹ in **1a-3a** and 1588–1605 cm⁻¹ in **1b-3b**, indicating involvement of imine (HC=N) nitrogen in coordination with the metal ion [13]. A new band at *ca*. 482–512 cm⁻¹ is observed in all complexes which is not present in either L_{H1-3} nor in **1**, which is assigned to v(M-N) stretch. The involvement of deprotonated phenolic moiety in all heterobimetallic complexes is confirmed by shift of the stretching band at 1279–1283 cm⁻¹ in L_{H1-3} to lower frequency by 10–20 cm⁻¹. The shift of v(C-O) at 1283 cm⁻¹ to lower frequency of L_{H1-3} at 3135–2900 cm⁻¹ disappeared in all heterometallic complexes, indicating participation of deprotonated N-H [15]. The spectra of all complexes also exhibit bands for dppe ligand at 1483, 1435, 1168, and 693 cm⁻¹ [16].

Electronic absorption spectra of **1a-3a** and **1b-3b** were measured in DMF solution at room temperature. The spectra show intense bands at *ca*. 241–249 and 278–283 nm for **1a-3a** and 249–252 and 278–281 nm for **1b-3b** assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the coordinated ligands. In addition



Figure 1. Proposed molecular structure of the complexes.

to the high energy band, low energy absorptions at *ca*. 381–392 nm in **1a-3a** and 378–382 nm in **1b-3b** are likely assigned as a mixture of intraligand ($\pi \rightarrow \pi^*$) transition with metal-ligand charge transfer (MLCT) transitions, similar to their precursor complexes [17]. The slight bathochromic shift in these complexes relative to **1** indicates coordination of the pyridyl group to Cu^{II} or Cd^{II}. A very weak absorption at 519 nm for **1a-3a** which is absent in **1b-3b** is assigned for d-d transition of four-coordinate square planer geometry around Cu^{II} [18].

¹H NMR spectra of **1a-3a** and **1b-3b** recorded in dmso-*d*₆ are given in the Experimental section. The ¹H NMR spectroscopic data of **1a-3a** and **1b-3b** are consistent with their formulation as heterometallic ruthenium acetylide complexes. A comparison of the chemical shifts of **1** with **1a-3a** and **1b-3b** shows that some of the resonances are shifted on complexation in each case. The ¹H NMR spectra of L_{H1-3} shows a singlet at δ 8.72–8.75 ppm for imine proton. This imine proton signal is easily identified as a singlet at δ 8.79–9.15 ppm for **1a-3a** and 9.01–9.12 ppm for **1b-3b**. Downfield shift of imine proton signal of complex as compared to L_{H1-3} is attributed to deshielding arising from coordination of imine nitrogen [19, 20]. The ¹H NMR spectra also show several coupled multiplets at δ 6.57–7.84 ppm for **1a-3a** and **1b-3b** typical for the ring protons of L₁₋₃ and **1**. A peak observed at δ 11.76 ppm in L_{H1-3} characteristic of intramolecular hydrogen bonded phenolic OH disappears in spectra of **1a-3a** and **1b-3b** indicating deprotonation of phenolic proton, confirming coordination through phenolic oxygen [21]. A broad singlet at $\sim \delta$ 2.69 ppm observed in spectra of all complexes corresponds to CH₂ protons of dppe. ³¹P NMR spectra of the Cu^{II}/Ru^{II} and Cd^{II}/Ru^{II} complexes show a singlet at ~ 47 ppm, confirming *trans* geometry at ruthenium in which the two dppe ligands occupy the equatorial plane with the Cl⁻ and alkynyl group *trans* in axial positions [22].

Proposed molecular structures of the complexes are confirmed by ESI mass spectra. The formulation of Cu^{II}/Ru^{II} and Cd^{II}/Ru^{II} complexes is assigned from the presence of molecular ion peak and other prominent peaks in mass spectra. The mass spectra of **1a-3a** and **1b-3b** show that the molecular ion peak is present in all the complexes at low abundance. The formation of Cu^{II}/Ru^{II} hybrid complexes is clearly supported from the molecular ion peak at m/e 1306, 1385, and 1351 in **1a-3a**, respectively, with base peak at 1041; mass spectra of **1b-3b** showed molecular ion peaks at m/e 1355, 1434, and 1400, respectively, equal to theoretical molecular weight for Cd^{II}/Ru^{II} complexes. The peaks centered at *m/z* 1041 in **1a-3a** and **1b-3b** are due to a charged fragment ([NC₅H₄C≡CRu(dppe)₂Cl)]⁺, obtained by the loss of the Schiff base ligand and Cu or Cd ion from the organometallic moiety (**1**). A further loss of pyridine acetylene ligand from the ruthenium center gives the intense group of charged ions centered around *m/z* 957. The peaks at *m/z* 898 in **1a-3a** are due to a singly charged species ([Ru(dppe)₂]⁺. The



Figure 2. TEM image of as synthesized Cu^{II}/Ru^{II} complexes.

Cu^{II}/Ru^{II} and Cd^{II}/Ru^{II} complexes also show prominent peaks due to elimination of Cl⁻, C₆H₅, Schiff base, dppe, tropylium, iodide, CH=CH, *etc.* from the parent ion and subsequent fragment. The fragmentation patterns of all the complexes are in general agreement with proposed chemical formulation. ESI mass spectra of coordination organometallic complexes are quite complex with number of peaks due to the presence of numerous ions containing isotopes. Complex **2b** contains ruthenium, cadmium, bromine, and chlorine atoms so the expected isotope pattern is complex. Figure 3S Inset spectrum shows the theoretical isotopic pattern of the expected molecular species (**2b**). Figure 3S shows that the isotopic profile for the acquired data closely matches that predicted by the isotope model. The peak at 1085 corresponded to fragment ions that have the characteristic isotopic distribution pattern of one bromine and one chlorine (**3b**) at M, M + 2, M + 4 in the ratio 3:4:1. The ESI mass spectra of Cu^{II}/Ru^{II} and Cd^{II}/Ru^{II} complexes also show the mutual location of bands as well as their ion composition and isotopic pattern are specific for each complex. Figure 1 provides a schematic drawing of the complexes.

Figure 2 shows the representative TEM image of as synthesized Cu^{II}/Ru^{II} complexes. The TEM image clearly indicates that complex nanoparticles are formed with well-arranged spheres. On the basis of TEM image the size of Cu^{II}/Ru^{II} hybrid complexes is ~60 nm. TEM image also shows well-dispersed spherical nanoparticles without agglomeration.

3.2. Cyclic voltammetry

The electrochemical features of the bimetallic complexes were investigated in DMF containing 0.05 M n-Bu₄NClO₄ as supporting electrolyte by cyclic voltammetry. All measurements were carried out in 10^{-3} M solutions at room temperature from +1.5 to -1.5 V with scan rate 100 mVs⁻¹. The cyclic voltammetric (CV) data of the Cu^{II}/Ru^{II} and Cd^{II}/Ru^{II} complexes are summarized in table 1.

	Cu ^I /Cu ^{II}			Ru ^{II} /Ru ^{III}		
	$E_{\rm pa}(V)$	$E_{\rm pc}(V)$	E _{1/2} (V)	$E_{\rm pa}(V)$	$E_{\rm pc}(V)$	E _{1/2} (V)
1a	0.971	0.863	0.917	1.183	1.093	1.138
2a	0.980	0.876	0.928	1.226	1.132	1.179
3a	0.982	0.882	0.932	1.255	1.171	1.213
1b	-	-	-	1.131	1.066	1.098
2b	-	-	-	1.152	1.072	1.112
3b	-	-	-	1.162	1.081	1.121

 Table 1. Electrochemical data of Cu^{II} /Ru^{II} and Cd^{II}/Ru^{II} complexes (1a-3a and 1b-3b).

Note: Supporting electrolyte: n-Bu₄NClO₄ (0.05 M); complex: 0.001 M; solvent: DMF; $E_{1/2} = \frac{1}{2} (E_{na} + E_{nc})$; scan rate: 100 mVs⁻¹.

Complex	Excitation (nm)	Emission (nm)	φ
1a	342	447	0.037
2a	345	451	0.038
3a	348	454	0.041
1b	354	459	0.042
2b	355	465	0.046
3b	357	477	0.047

 Table 2. Fluorescence spectral data of Cu^{II}/Ru^{II} and Cd^{II}/Ru^{II} complexes (1a-3a and 1b-3b).

B. G. BHARATE AND S. S. CHAVAN

8



Figure 3. Emission spectra of 1a-3a.

Cyclic voltammetry studies **1a-3a** reveal that the complexes undergo quasireversible oxidation processes at 0.917–0.932 V assigned to Cu¹/Cu^{II}. Another oxidation process in **1a-3a** at 1.138–1.213 V is assigned to the Ru^{II}/Ru^{III} couple. In **1b-3b** only oxidation of Ru^{II}/Ru^{III} couple is observed at 1.098–1.121 V. Compared to **1** the oxidation of the Ru^{II} unit shifted more positive, indicating it is difficult to oxidize upon coordination of M^{II} unit which increases the electron density around M^{II} [23, 24].

3.3. Thermogravimetric analyses

The thermal stabilities of Cu^{II}/Ru^{II} and Cd^{II}/Ru^{II} complexes were investigated by thermogravimetric analyses (TGA). TGA were performed at a heating rate of 10 °C min⁻¹ under flowing nitrogen to 800 °C. TGA data suggest that **1a-3a** are stable to 258 °C revealing the absence of either water or solvent. In the temperature range of 259–350 °C, these complexes underwent complicated multiple weight loss steps with total loss corresponding to Schiff base and pyridylacetyl ligands (obsd. 21.68 (**1a**), 26.41 (**2a**), 24.37 (**3a**) %; Calcd 22.29 (**1a**), 26.79 (**2a**), and 24.93 (**3a**) %). All the complexes collapse due to release of dppe ligand along with Cl⁻ per formula unit between 351 and 534 °C with an observed weight loss of 64.37 (**1a**), 60.73 (**2a**), 62.08 (**3a**), respectively (Calcd 64.85 (**1a**), 61.09 (**2a**), and 62.59 (**3a**)%). For **1b**-**3b**, the decomposition stage with mass loss of 20.96 in **1b**, 25.67 in **2b**, and 23.69% in **3b** correspond to Schiff base and pyridyl acetyl ligand at 261–357, 268–365, and 263–351 °C, respectively (theoretical mass loss: 21.48, 25.86, 24.04%). Another stage at 362–612, 370–597, and 355–619 °C with mass loss

of 62.21, 58.74, and 60.15% may be assigned to decomposition of the remaining half of dppe ligand which is in agreement with a calculated mass loss of 62.48 (**1b**), 58.98 (**2b**), and 60.43 (**3b**) %.

3.4. Fluorescence spectral studies

The photoluminescence properties of binuclear complexes and **1** and the effect of ligand substituents on photophysical properties have been investigated. The emission spectra of all the Cu^{II}/Ru^{II} and Cd^{II}/ Ru^{II} complexes were recorded in DMF at room temperature as summarized in table 2 and the spectra of the complexes are depicted in Figures 3 and 4. **1a-3a** show blue-green emission at *ca*. 447–454 nm upon excitation with λ_{ex} 342–348 nm. However, Cd^{II}-Ru^{II} complexes show emission at 459–477 nm for **1b-3b** excited at 354–357. On comparing the emission maxima of heterobimetallic complexes and **1** (441 nm) a slight red shift is observed. These results are consistent with what we observed in absorption spectra in which a red shift occurs in heterobimetallic complexes. Hence emission spectra also confirm the formation of binuclear species leading to increased energy gap between ground state and excited state. These results also confirm an emission origin predominantly not only due to $\pi \rightarrow \pi^*$ intraligand transition but also with some metal-ligand charge transfer (MLCT) character, which enhance the rigidity of the ligands and thus reduces the loss of energy through radiationless decay of the intraligand emission excited state [25, 26].

Fluorescence quantum yields of all the complexes were measured by the integration sphere method using quinine sulfate as a reference with known Φ_{R} . The area of emission spectrum was integrated using the software available in the instrument and the quantum yield was calculated by using

$$\phi_{s} = A_{s}/A_{R}X (Abs)_{R}/(Abs)_{s}X \phi_{R}$$

where ϕ_s and ϕ_R are the fluorescence quantum yield of sample and reference, respectively, A_s and A_R are the area under the fluorescence spectra of the sample and reference, respectively, and (Abs)_s and (Abs)_p are the respective optical densities of the sample and the reference solution at the wavelength of



10 🕒 B. G. BHARATE AND S. S. CHAVAN

Table 3. Measured SHG values of Cu^{II} /Ru^{II} and Cd^{II}/Ru^{II} complexes (1a-3a and 1b-3b).

Complex	Efficiency (relative to urea)
1a	0.16
2a	0.18
3a	0.19
1b	0.19
2b	0.21
3b	0.25

excitation. All the complexes exhibit good quantum yields of 0.037–0.047 for **1a-3a** and **1b-3b**, slightly higher than structurally related compounds reported [27–29].

3.5. Nonlinear optical properties of the complexes

The nonlinear optical properties of the Cu^{II}/Ru^{II} and Cd^{II}/Ru^{II} complexes have been studied by the Kurtzpowder technique and second harmonic generation (SHG) efficiencies are given in table 3. The SHG efficiency observed for Cu^{II}/Ru^{II} **1a-3a** is 0.16–0.19 times that of urea. However, **1b-3b** show SHG efficiency 0.20–0.25 times that of urea. SHG efficiency clearly indicates that the second-order NLO response of Cd^{II}/Ru^{II} complexes is a little larger than the Cu^{II}/Ru^{II} complexes. The SHG efficiency of **1** is compared with the binuclear complexes, showing that binuclear complexes are two times more active. The best value of SHG efficiency is reached for the Cd^{II}/Ru^{II} complex having a 5-nitro-2-(pyrrole-2-yI-methylidine) aminophenol (L₃) ligand.

4. Conclusion

The heterobimetallic complexes $[Cu(L_{1-3})(NC_5H_4C\equiv CRu(dppe)_2Cl)]$ (**1a-3a**) $[Cd(L_{1-3})(NC_5H_4C\equiv CRu(dppe)_2Cl)]$ (**1a-3a**) $[Cd(L_{1-3})(NC_5H_4C\equiv CRu(dppe)_2Cl)]$ (**1b-3b**) have been prepared and characterized. The electrochemical behavior of the complexes indicates that the complexes exhibit a quasireversible redox process. TEM analyses confirmed the formation of Cu^{II}/Ru^{II} hybrid nanomaterials with well-dispersed nanospheres of ~60 nm size. According to the quantum yields and fluorescence spectra, the complexes have relatively good fluorescence properties. The SHG efficiencies of the complexes were measured by the Kurtz-powder technique, indicating that all the complexes are NLO active with good NLO response.

Acknowledgements

We gratefully acknowledge financial support from Department of Science and Technology (DST Ref. No. SR/FT/CS-004/2008), New Delhi, India. Council of Scientific and Industrial Research (CSIR), New Delhi for awarding Senior Research Fellowship (SRF). We thank Prof. P. K. Das, IPC Department, IISc, Bangalore for providing NLO facility.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was financially supported by the Department of Science and Technology, New Delhi, India [grant number DST Ref. number SR/FT/CS-004/2008]; and Council of scientific and Industrial Research (CSIR), New Delhi [grant number 124183/2k11/1].

References

- [1] S.R. Marder, D.W. Bruce, D. O'Hare (Eds.), Inorganic Materials, Wiley, New York, NY (1992).
- [2] M.R.S.A. Janjua, S. Jamil, T. Ahmad, Z. Yang, A. Mahmood, S. Pan. Comp. Theor. Chem., 1033, 6 (2014).

- [3] E. Cariati, M. Pizzotti, D. Roberto, F. Tessore, R. Ugo. Coord. Chem. Rev., 250, 1210 (2006).
- [4] P.G. Lacroix, I. Malfant, C. Lepetit. Coord. Chem. Rev., 308, 381 (2016).
- [5] H. Zhang, S. Dechert, J. Maurer, M. Linseis, R.F. Winter, F. Meyer. J. Organomet. Chem., 692, 2956 (2007).
- [6] K. Green, M. Cifuentes, M. Samoc, M. Humphrey. Coord. Chem. Rev., 255, 2530 (2011).
- [7] V. Guerchais, L. Ordronneau, H.L. Bozec. Coord. Chem. Rev., 254, 2533 (2010).
- [8] T. Guerrero, P.G. Lacroix, H. García-Ortega, O.G. Morales-Saavedra, D. Agustin, N. Farfán. Inorg. Chim. Acta, 442, 10 (2016).
- [9] H. Zhang, S. Dechert, M. Linseis, R. Winter, F. Meyer. Eur. J. Inorg. Chem., 29, 4679 (2007).
- [10] O. Tamer, D. Avcı, Y. Atalay. Spectrochim. Acta, Part A, **136**, 644 (2015).
- [11] C.L. Hu, J.G. Mao. Coord. Chem. Rev., 288, 1 (2015).
- [12] J.L. Zuo, E. Herdtweck, F.E. Kuhn. J. Chem. Soc., Dalton Trans., 7, 1244 (2002).
- [13] R. Shanmugakala, P. Tharmaraj, C.D. Sheela. J. Mol. Struct., 1076, 606 (2014).
- [14] T. Hamdi, H. Halil. Transition Met. Chem., 27, 609 (2002).
- [15] A. Datta, N.K. Karan, S. Mitra, V. Gramlich. J. Chem. Cryst., 33, 579 (2003).
- [16] S.S. Chavan, B.G. Bharate. Inorg. Chim. Act, 394, 598 (2013).
- [17] P.J. Burke, D.R. McMillin, W.R. Robinson. Inorg. Chem., 19, 1211 (1980).
- [18] H. Ünver, Z. Hayvali. Spectrochim. Acta, Part A, 75, 782 (2010).
- [19] M. Morshedi, M. Amirnasr, A. Slawin, J. Woollins, A. Khalaji. Polyhedron, 28, 167 (2009).
- [20] M. Ruthkosky, F.N. Castellano, G.J. Meyer. Inorg. Chem., 35, 6404 (1996).
- [21] J.A. Castro, J. Romero, J.A. Garcia-Vazquez, A. Castineiras, A. Sousa. Allg. Chem., 619, 601 (1993).
- [22] B.G. Bharate, A.N. Jadhav, S.S. Chavan. Polyhedron, 33, 179 (2012).
- [23] C. Zúñiga, I. Crivelli, B. Loeb. Polyhedron, 85, 511 (2015).
- [24] W.Y. Yang, H. Schmider, Q.G. Wu, Y.S. Zhang, S.N. Wang. Inorg. Chem., 39, 2397 (2000).
- [25] J.B. Brikes, J.E. Dyson. Proc. Roy. Soc., 275, 135 (1963).
- [26] H. Qian, Y. Dai, J. Geng, L. Wang, C. Wang, W. Huang. Polyhedron, 67, 314 (2014).
- [27] M. Royzen, J.W. Canary. Polyhedron, 58, 85 (2013).
- [28] J. Jee, Y. Kim, S. Lee, K. Park, C. Kwak. Inorg. Chem. Commun., 6, 946 (2003).
- [29] C.K.M. Chan, C.-H. Tao, K.-F. Li, K.M-C. Wong, N. Zhu, K.-W. Cheah, V.W-W. Yam. J. Organomet. Chem., 696, 1163 (2011).