



Synthesis and Characterization of Ruthenium(II) Carbonyl Complexes of Substituted Quinazoline Derivatives and their Catalytic Activity

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A series of ruthenium(II) carbonyl complexes of the types $[\text{RuCl}_2(\text{CO})_2\text{L}]_2 \cdot n\text{H}_2\text{O}$ $\{n = 1, \text{L} = \text{L}^1, \text{L}^3\}$; $[\text{RuCl}_2(\text{CO})_2(\text{L})(\text{H}_2\text{O})] \cdot n\text{H}_2\text{O}$ $\{n = 1, \text{L} = \text{L}^2, \text{L}^4, \text{L}^6 \text{ and } n = 2, \text{L} = \text{L}^7\}$; $[\text{RuCl}(\text{CO})_2(\text{L}-\text{H})(\text{H}_2\text{O})]_2$ $\{\text{L} = \text{L}^5\}$; $[\text{RuCl}_2(\text{CO})_2]_3(\text{L})_2$ $\{\text{L} = \text{L}^8\}$ were synthesized where L is 6R-5,6-dihydrobenzoimidazo[1,2-c]quinazoline (R-Diq; R = phenyl: L^1 /furyl: L^2 /thiophenyl: L^3 /o or p-hydroxyphenyl: L^4, L^5 /o or p-chlorophenyl: L^6, L^7 /dimethylaminophenyl: L^8). The Ru(II) complexes were characterized by elemental analyses, conductivity measurements, TGA, infrared, electronic, NMR and mass spectral techniques. An octahedral geometry around the metal ion was proposed for all the complexes and monomeric, dimeric and trimeric stereochemistry was suggested. The catalytic activity for few ruthenium(II) complexes towards oxidation of benzyl alcohol, hydroquinone and cyclohexanol was also investigated.

Keywords: Dihydrobenzoimidazoquinazoline derivatives, Mass spectra, Ru(II) carbonyl complexes.

INTRODUCTION

The chemistry of ruthenium has been extensively studied as it offers a wide range of stable oxidation states and the impetus of developing their coordination chemistry is due to their physico-chemical properties and significant biological and catalytic activities [1,2]. The complexes of ruthenium(II) are redox active and find application as redox reagents in different chemical reactions. Numerous studies have been conducted on the Ru(II) complexes due to their numerous catalytic uses and they are also known to catalyze photosplitting of water, solar energy conversion and hydroformylation reactions [3,4]. Diruthenium tetracarboxylate complexes have been reported to exhibit interesting electronic [5-7], mesomorphic [8-10], gas sorption [11, 12] and catalytic properties [13-16]. Grubbs type ruthenium catalysts have been successively utilized for olefin metathesis [17-20]. Dinuclear organometallic complexes of Ru(II) has generated a lot of interest as they can be used to model materials for optical and electronic devices [21-23], since such complexes can form supramolecules with an ability to absorb or emit visible light and reversibly exchange electrons, which are essential for solar energy conversion and information storage devices [24].

Quinazolines are an important class of N-heterocycles and the quinazoline ring systems along with many alkaloids [25-27] are widely recognized for their medicinal applications. In view of the multifaceted applications of this class of N-heterocyclic compounds and ruthenium(II) complexes, synthesis and characterization of ruthenium(II) carbonyl complexes with quinazoline derivatives (Fig. 1) were undertaken. The catalytic activity of some of the complexes towards oxidation of benzyl alcohol, hydroquinone and cyclohexanol was also investigated.

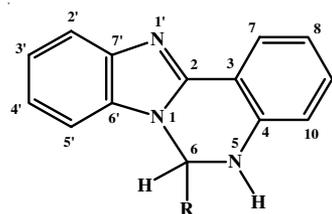


Fig. 1. Structure of the quinazoline derivative

EXPERIMENTAL

All the reagents were of Analar grade. The solvents used were purified according to standard procedures [28]. Ruthenium

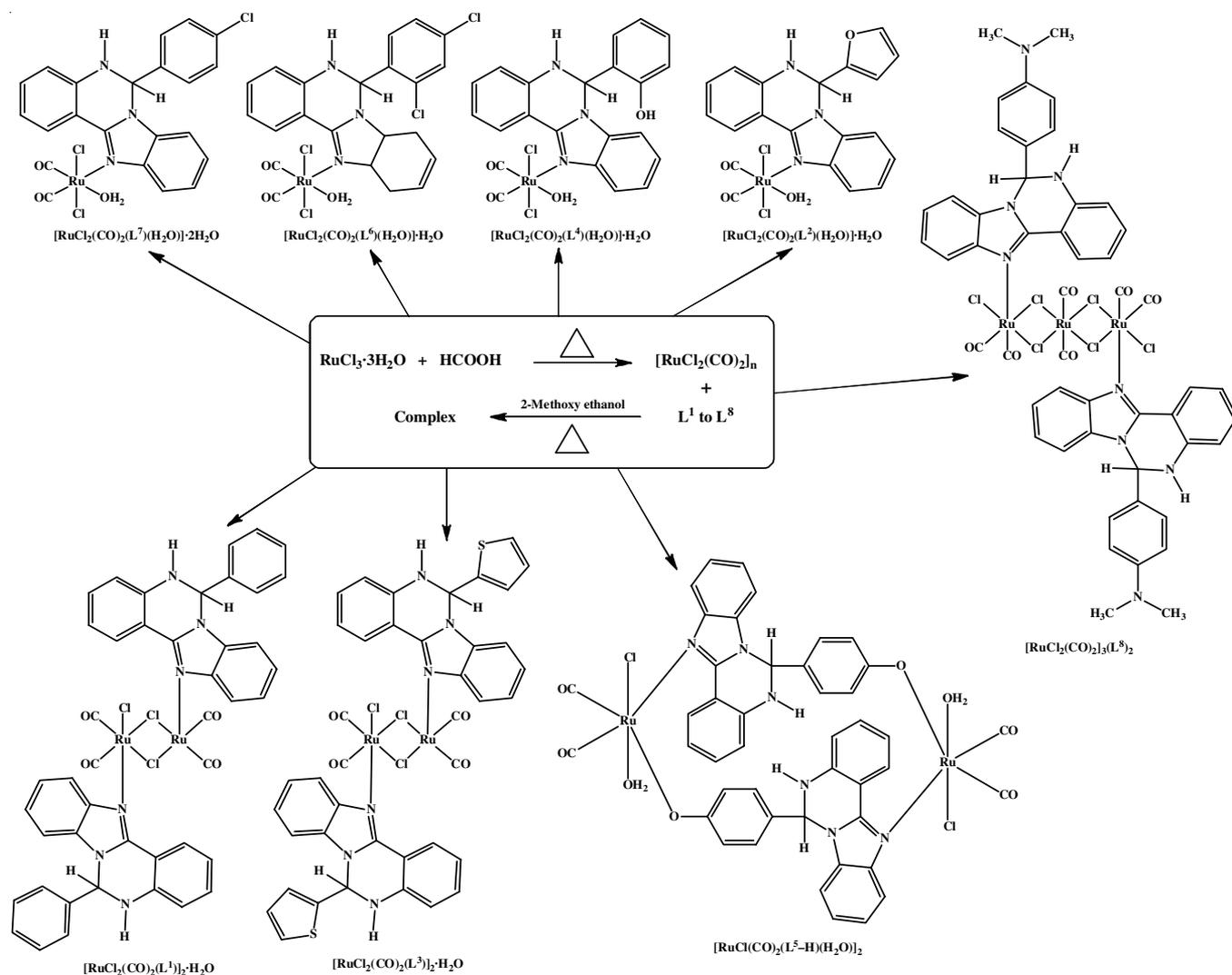
trichloride trihydrate was obtained from Arora Matthey Ltd., Kolkata, India. Carbon, hydrogen and nitrogen were determined on a 240B Perkin-Elmer elemental analyzer. IR (nujol mull) spectra were recorded on Shimadzu FTIR 8400s and Far-IR spectra were recorded on a Bruker IFS 66v/S instrument. Electronic spectra were recorded in DMF on Shimadzu UV 3101PC. FAB mass spectra were recorded on a JEOL SX102 Mass spectrometer using argon/xenon as the FAB gas and *m*-nitrobenzyl alcohol as matrix. The ^1H NMR spectra were recorded on a Bruker AMX 400 MHz (equipped with Aspect 2000 computers) NMR Spectrometer. Molar conductivity measurements were made on a Systronic conductivity meter 304-cell type CD-10. TGA were recorded on Mettler TAHE-20 thermal analyzer at heating rate of $15\text{ }^\circ\text{C min}^{-1}$ in nitrogen atmosphere.

Synthesis of 6*R*-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline derivatives: Synthesis and characterization of the quinazoline derivatives were performed as per reported method [29-32].

Synthesis of ruthenium(II) carbonyl complexes ($\text{L}^1\text{-L}^8$): Ruthenium carbonylated solution was prepared according to reported procedure [33], in brief, ruthenium trichloride trihydrate (1.0 mmol) dissolved in 2-methoxy ethanol (5 mL) was

added to formic acid (2.0 mmol) and refluxed for 4 h. The quinazoline derivatives ($\text{L}^1\text{-L}^8$) (2 mmol) dissolved in 2-methoxy ethanol (10 mL) was added to the metal solution and again refluxed for about 5 h, concentrated to small volume under vacuum, 5 (mL) of water was added it to get the carbonyl complexes as yellow solids, which correspond to the formulae $[\text{RuCl}_2(\text{CO})_2\text{L}]_2 \cdot n\text{H}_2\text{O}$ $\{n = 1, \text{L} = \text{L}^1, \text{L}^3\}$; $[\text{RuCl}_2(\text{CO})_2(\text{L})(\text{H}_2\text{O})] \cdot n\text{H}_2\text{O}$ $\{n = 1, \text{L} = \text{L}^2, \text{L}^4, \text{L}^6 \text{ and } n = 2, \text{L} = \text{L}^7\}$; $[\text{RuCl}(\text{CO})_2(\text{L}-\text{H})(\text{H}_2\text{O})]_2$ $\{\text{L} = \text{L}^5\}$ and $[\text{RuCl}_2(\text{CO})_2]_3(\text{L})_2$ $\{\text{L} = \text{L}^8\}$ (abbreviated as **R1-R8**). They were filtered, washed with dry ether followed by distilled water and finally dried in vacuum (yield: 60-65%) (**Scheme-I**).

$[\text{RuCl}_2(\text{CO})_2\text{L}^1]_2 \cdot n\text{H}_2\text{O}$ (R1): Yellow solid; m.p.: $270\text{ }^\circ\text{C}$; molar conductance (DMF): $17\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$; Anal. calcd. (found) % of $[\text{RuCl}_2(\text{CO})_2(\text{C}_{20}\text{H}_{15}\text{N}_3)]_2 \cdot \text{H}_2\text{O}$: C, 48.36 (48.63); H, 3.15 (2.93); N, 7.74 (7.87); IR (nujol, ν_{max} , cm^{-1}): 2060, 1988, 3480, 3201, 1624, Far-IR (poly-ethylene pellets, cm^{-1}): 343, 315; ^1H NMR (DMSO- d_6 , 400 MHz, δ ppm) quinazoline: 7.83-6.86, benzimidazole: 7.89-7.32, R-Group: 7.49-7.42; ^{13}C NMR (DMSO- d_6 , 400 MHz, δ ppm) CO: 196.90, 196.40, quinazoline: 149.50-62.78, benzimidazole: 141.79-111.98, R-Group: 134.23 -124.95; Electronic transitions (DMF, cm^{-1}) Ligand and CT:



Scheme-I: Synthetic route of some ruthenium(II) carbonyl complexes of substituted quinazoline derivatives (R1-R8)

37481-27012, *d-d*: 22124 (ϵ 77); TGA ($^{\circ}\text{C}$, species lost) 88: lattice H_2O , 238-256; CO, 331-400: Cl.

[RuCl₂(CO)₂(L²)(H₂O)]·H₂O (R2): Pale yellow solid, m.p.: 195 $^{\circ}\text{C}$; molar conductance (DMF): 20 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; Anal. calcd. (found) % of [RuCl₂(CO)₂(C₁₈H₁₃N₃O)(H₂O)]·H₂O: C, 43.65 (44.05); H, 2.93 (2.73); N, 7.64 (7.70); IR (nujol, ν_{max} , cm^{-1}): 2062, 1988, 3430, 3207, 3119, 1619, Far-IR (polyethylene pellets, cm^{-1}): 428, 460, 341; ¹H NMR (DMSO-*d*₆, 400 MHz, δ ppm) quinazoline: 14.12-7.38, benzimidazole: 7.95-7.3.8, R-Group: 7.75-7.10; ¹³C NMR (DMSO-*d*₆, 400 MHz, δ ppm) CO: 197.3, 191.8, quinazoline: 143.83-59.73, benzimidazole: 143.83-112.47, R-Group: 149.56-118.84; Electronic transitions (DMF, cm^{-1}) Ligand and CT: 37481-26954, *d-d*: 21844 (ϵ 134); TGA ($^{\circ}\text{C}$, species lost): 91: lattice H_2O , 144: coordinated H_2O , 275-325: CO, 400-457: Cl.

[RuCl₂(CO)₂L³]₂·nH₂O (R3): Yellow solid, m.p.: 270 $^{\circ}\text{C}$; molar conductance (DMF): 21 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; Anal. calcd. (found) % of [RuCl₂(CO)₂(C₁₈H₁₃N₃S)]₂·H₂O: C, 43.73 (43.81); H, 3.31 (3.16); N, 7.61 (7.39); IR (nujol, ν_{max} , cm^{-1}): 2056, 1987, 3485, 3217, 1624, Far-IR (polyethylene pellets, cm^{-1}): 343, 3211; ¹H NMR (DMSO-*d*₆, 400 MHz, δ ppm) quinazoline: 14.12-7.45, benzimidazole: 7.84-7.53, R-Group: 7.73-6.97; ¹³C NMR (DMSO-*d*₆, 400 MHz, δ ppm) CO: 197.40, 196.40, quinazoline: 149.65-56.36, benzimidazole: 146.32-112.40, R-Group: 144.04-118.91; Electronic transitions (DMF, cm^{-1}) Ligand and CT: 37594-37594, *d-d*: 20653 (ϵ 188); TGA ($^{\circ}\text{C}$, species lost) 94: lattice H_2O , 274-306: CO, 291-447: Cl; FAB-MS (*m/z*) [RuCl₂(CO)₂(L³)₂]: 1062, [RuCl₃(CO)₃(L³)₂] + 2H: 1001.

[RuCl₂(CO)₂(L⁴)(H₂O)]·H₂O (R4): Yellow solid, m.p.: 260 $^{\circ}\text{C}$, molar conductance (DMF): 25 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; Anal. calcd. (found) % of [RuCl₂(CO)₂(C₂₀H₁₅N₃O)(H₂O)]·H₂O: C, 45.73 (45.86); H, 3.31 (3.89); N, 8.27 (8.81); IR (nujol, ν_{max} , cm^{-1}): 2060, 1988, 3492, 3203, 3133, 1622, Far-IR (polyethylene pellets, cm^{-1}): 439, 469, 339; ¹H NMR (DMSO-*d*₆, 400 MHz, δ ppm) quinazoline: 13.89-6.95, benzimidazole: 7.39-7.34, R-Group: OH: 10.35, 7.85-7.41; ¹³C NMR (DMSO-*d*₆, 400 MHz, δ ppm) CO: 197.40-191.90, quinazoline: 144.02-57.99, benzimidazole: 144.2-112.59, R-Group: 130.05-118.92; Electronic transitions (DMF, cm^{-1}) Ligand and CT: 38432-27979, *d-d*: 21881 (ϵ 261); TGA ($^{\circ}\text{C}$, species lost) 84: lattice H_2O , 228: coordinated H_2O , 313-338: CO, 416-484: Cl.

[RuCl(CO)₂(L⁵-H)(H₂O)]₂ (R5): Dark yellow solid, m.p.: 270 $^{\circ}\text{C}$; molar conductance (DMF): 24 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; Anal. calcd. (found) % of [RuCl(CO)₂(C₂₀H₁₄N₃O)(H₂O)]₂: C, 50.40 (50.82); H, 3.27 (4.00); N, 8.02 (8.29); IR (nujol, ν_{max} , cm^{-1}): 2056, 1988, 3353, 3221, 3110, 1620, Far-IR (polyethylene pellets, cm^{-1}): 436, 484, 339; ¹H NMR (DMSO-*d*₆, 400 MHz, δ ppm) quinazoline: 13.98-7.32, benzimidazole: 7.82-7.40, R-Group: OH: 9.66, 7.20-6.74; ¹³C NMR (DMSO-*d*₆, 400 MHz, δ ppm) CO: 196.90, 196.50, quinazoline: 141.81-63.40, benzimidazole: 141.81-112.38, R-Group: 163.04-123.42; Electronic transitions (DMF, cm^{-1}) Ligand and CT: 37850-26553, *d-d*: 22321 (ϵ 64); TGA ($^{\circ}\text{C}$, species lost) 213: coordinated H_2O , 266-303: CO, 372: Cl; FAB-MS (*m/z*) [RuCl(CO)₂(L⁵-H)(H₂O)]₂: 1046, [Ru₂Cl₂(CO)₂(L⁵)(H₂O)₂] + 2H: 962.

[RuCl₂(CO)₂(L⁶)(H₂O)]·H₂O (R6): Dark Yellow solid; m.p.: 186 $^{\circ}\text{C}$; molar conductance (DMF): 45 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$;

Anal. calcd. (found) % of [RuCl₂(CO)₂(C₂₀H₁₄N₃Cl)(H₂O)]·H₂O: C, 45.73 (45.21); H, 2.97 (3.73); N, 7.27 (7.22); IR (nujol, ν_{max} , cm^{-1}): 2060, 1991, 3476, 3187, 3117, 1626, Far-IR (polyethylene pellets, cm^{-1}): 439, 493, 326; ¹H NMR (DMSO-*d*₆, 400 MHz, δ ppm) quinazoline: 14.05-7.07, benzimidazole: 7.73-7.44, R-Group: 7.86-7.47; ¹³C NMR (DMSO-*d*₆, 400 MHz, δ ppm) CO: 196.90-196.50, quinazoline: 148.8-58.09, benzimidazole: 133.57-111.76, R-Group: 141.80-128.24; Electronic transitions (DMF, cm^{-1}) Ligand and CT: 37850-26666, *d-d*: 23809 (ϵ 91); TGA ($^{\circ}\text{C}$, species lost) 51: lattice H_2O , 138: coordinated H_2O , 216-294: Cl.

[RuCl₂(CO)₂(L⁷)(H₂O)]·2H₂O (R7): Yellow solid; m.p.: 255 $^{\circ}\text{C}$; molar conductance (DMF): 18 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; Anal. calcd. (found) % of [RuCl₂(CO)₂(C₂₀H₁₄N₃Cl)(H₂O)]·2H₂O: C, 43.05 (42.71); H, 3.28 (3.91); N, 8.85 (9.54); IR (nujol, ν_{max} , cm^{-1}): 2061, 1983, 3441, 3195, 3126, 1626, Far-IR (polyethylene pellets, cm^{-1}): 439, 466, 346; ¹H NMR (DMSO-*d*₆, 400 MHz, δ ppm) quinazoline: 7.69-6.86, benzimidazole: 7.71-7.14, R-Group: 7.42-7.31; ¹³C NMR (DMSO-*d*₆, 400 MHz, δ ppm) CO: 194.40, 196.40, quinazoline: 144.02-64.39, benzimidazole: 141.99-111.92, R-Group: 149.82, 128.28; Electronic transitions (DMF, cm^{-1}) Ligand and CT: 37850-26553, *d-d*: 22768 (ϵ 78); TGA ($^{\circ}\text{C}$, species lost) 99: lattice H_2O , 141: coordinated H_2O , 216-294: CO, 347-411: Cl.

[RuCl₂(CO)₂]₃(L⁸)(R8): Yellow solid; m.p.: 265 $^{\circ}\text{C}$; molar conductance (DMF): 22 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$; Anal. calcd. (found) % of {[RuCl₂(CO)₂]₃(C₂₂H₂₀N₄)₂}: C, 44.00 (43.49); H, 2.95 (3.48); N, 8.21 (8.70); IR (nujol, ν_{max} , cm^{-1}): 2061, 1996, 3381, 3180, 1618, Far-IR (polyethylene pellets, cm^{-1}): 362, 322; ¹H NMR (DMSO-*d*₆, 400 MHz, δ ppm) quinazoline: 14.20-7.50, benzimidazole: 7.90-7.51, R-Group: N (CH₃) 3.42, 7.42-7.10; ¹³C NMR (DMSO-*d*₆, 400 MHz, δ ppm) CO: 197.40, 196.80, 191.9, 191.0, quinazoline: 149.58-68.80, benzimidazole: 143.89-112.57, R-Group: (CH₃) 149.82, 129.31-118.9; Electronic transitions (DMF, cm^{-1}) Ligand and CT: 37764-26001, *d-d*: 23753 (ϵ 702); FAB-MS (*m/z*) [RuCl₂(CO)₂]₃(L⁸)₂: 1364, [Ru₃Cl₄(CO)₄L]₃(L⁸C₂H₆) + H: 1209.

Procedure for oxidation reaction: The catalyst (10⁻⁵ mol) and substrate {(10⁻³ mol) for benzyl alcohol and hydroquinone and (10⁻⁴ mol) for cyclohexanol} were dissolved in acetonitrile (10 mL) and oxidant *t*-BuOOH (10⁻² mol, 1.3 mL) was added to it and the reaction mixture was stirred on a magnetic stirrer cum heater. The progress of the reaction was tracked at every 5 min interval using TLC and UV-Vis spectroscopy. It was observed that as the reaction progressed, the substrate peak (258 nm and 294 nm, respectively for benzyl alcohol and hydroquinone) diminished and finally disappeared whereas the product peak (246 nm and 243 nm, respectively for benzoic acid and benzoquinone) grew and attained maximum intensity marking the complete conversion of the substrate to the product [34].

RESULTS AND DISCUSSION

All the synthesized ruthenium(II) carbonyl complexes are diamagnetic and insoluble in common organic solvents but soluble in DMF and DMSO in which they behaved as non-electrolytes.

Infrared studies: The IR spectra of Ru(II) carbonyl complexes were comparable with those of the *N*-heterocycles apart from minor shifts in the position of the bands and all the complexes exhibited intense twin peaks at about 2060 and 1988 cm^{-1} , which were attributed to the stretching frequencies of the carbonyl groups present in *cis*- or *trans*-positions [35,36]. All the complexes, except complex **R3** exhibited $\nu(\text{O-H})$ of lattice water in the range 3562 to 3360 cm^{-1} , while complex **R2** revealed a broad peak in the range 3207-3181 cm^{-1} assigned to the $\nu(\text{O-H})$ of coordinated water. A peak around 1616 to 1612 cm^{-1} is assigned to $\nu(\text{C=N})$ of benzimidazole moiety and $\nu(\text{C=C})$ of benzimidazole and quinazoline ring of ligand which on complexation was shifted to 1631-1618 cm^{-1} indicating the coordination of the quinazoline derivative to the ruthenium(II) ion *via* the *tertiary* nitrogen of the benzimidazole moiety [37].

Far-IR spectra of Ru(II) complexes **R1-R7** exhibited a peak in the region 346-326 cm^{-1} attributed to terminal Ru(II)-Cl stretching vibration and two peaks in the range 435-425 cm^{-1} and 493-463 cm^{-1} are assigned to the Ru-OH₂ stretching frequencies of coordinated water [36]. Complex **R5** exhibited a peak at 339 cm^{-1} due to terminal Ru(II)-Cl bond and peaks at 484 and 436 cm^{-1} are attributed due to the $\nu(\text{Ru-O})$ of deprotonated hydroxyl group of ligand and $\nu(\text{Ru-OH}_2)$. The complexes **R1**, **R3** and **R8** showed the peaks due to bridging and terminal Ru(II)-Cl in the ranges 330-311 cm^{-1} and 364-343 cm^{-1} , respectively [38].

Electronic spectral studies: The electronic spectra of the ligands and their Ru(II) carbonyl complexes were recorded in DMF. The quinazoline derivatives displayed intense bands between 31,000 to 38,700 cm^{-1} , which is attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. The metal to ligand charge transfer transitions were observed in the region 25,000 to 28,000 cm^{-1} . The Ru(II) complexes exhibited *d-d* transitions as weak bands in the range 21,800 to 23,810 cm^{-1} are assignable to the $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ transition of octahedral spin paired d^6 system [39,40].

Mass spectral studies: The FAB mass spectra for the complexes **R3** and **R5** exhibited molecular ion peaks at m/z 1062 and 1046, respectively indicating their binuclear nature. The spectrum of complex **R8** exhibited a molecular ion peak at m/z 1364 correspond to the trimeric nature of the complex.

Thermal studies: Thermogravimetric analysis of **R1** and **R3** complexes exhibited loss of water below 100 °C indicating the presence of lattice water and **R5** showed the loss of water above 200 °C indicating the presence of coordinated water. The **R2**, **R4**, **R6** and **R7** complexes lost water in both the regions indicating the presence of both lattice and coordinated water. The carbonyl groups were lost within 340 °C followed by chloride ions. The loss of heterocycles was observed above 485 °C.

NMR studies: The ^1H & ^{13}C NMR spectra of the synthesized Ru(II) carbonyl complexes and *N*-heterocycles were recorded in DMSO-*d*₆ solvent. The protons and carbons of the *N*-heterocycles exhibited positive and negative coordination induced shifts (c.i.s.) on complexation. The positive c.i.s. values for the carbon resonances can be attributed to ligand-to-metal σ -donation and negative c.i.s. values are due to greater metal-to-ligand π -back donation [41].

The protons belonging to the quinazoline moiety H-7, 8, 9 and 10 appeared between δ 8.70 and 6.90 ppm and exhibited positive and negative c.i.s. in the range δ 0.16-1.19 ppm. The benzimidazole ring protons H-2', 3', 4' and 5' were found to resonate as multiplets between δ 8.03 and 7.32 ppm and shifted by δ 0.01 to 0.73 ppm when compared to the corresponding free ligand. The R groups of the ligands **L¹-L⁸** were found to resonate between δ 6.97 and 7.86 ppm. The proton bound to the carbon adjacent to oxygen and sulphur atoms in furyl and thiophenyl group of **L²** and **L³**, respectively were found to be more deshielded and shifted downfield appearing around δ 7.75 ppm as compared to the other protons of the group. The OH proton of the ligands **L⁴** and **L⁵** exhibited signals in the downfield region at δ 10.2 and 9.66 ppm, respectively. Complex **R4** showed a singlet at δ 10.35 ppm due to OH proton but was missing in the spectrum of complex **R5** implying deprotonation of the hydroxyl group on complexation. The proton bound to the carbon C-3'' adjacent to the carbon with chlorine atom in the complex **R6** was more deshielded and observed at δ 7.86 ppm when compared to other protons of the R groups. The spectrum of the complex **R8** exhibited H-2'' and H-6'' at δ 7.72 ppm and these protons shifted more downfield as compared to H-3'' and 5'' at δ 7.10 ppm, which are adjacent to the carbon atom bound to dimethylamino group. Additional peaks due to the methyl protons of **L⁸** observed at δ 3.42 ppm were shifted upfield by δ 0.60 ppm on complexation.

The ^{13}C NMR spectra of the complexes containing substituted quinazolines have exhibited a peak in the region δ 144-150 ppm due to the most deshielded carbon-2 of the quinazoline moiety which is directly linked to two nitrogens. The signals around δ 144 and 133 ppm are assigned to the carbons 6' and 7', respectively and each of these carbons is linked to one nitrogen. Among the two carbons, more deshielding effect was observed for 6' whose signal was shifted downfield by nearly 11 ppm as compared to that of 7' as it is linked to *tert.*-nitrogen. Carbon-4 bound to imine nitrogen appeared in the downfield region of δ 141-145 ppm. In complexes **R4** and **R5**, the 2'' (δ 150 ppm) and 4'' (δ 163 ppm) carbons, which are bound to hydroxyl group experienced downfield shift. The complexes **R6** and **R7** containing R-group with Cl in the 2'' and 4'' positions, respectively showed dissimilar pattern wherein the quaternary carbon 1'' of **L⁶** appeared downfield at δ 135.70 ppm when compared to C-2'', whereas in complex **R7** the C-4'' with Cl was seen at most downfield region of δ 149.80 ppm as against the quaternary carbon 1'' at δ 131.90 ppm. Similar pattern was seen in the spectrum of complex **R8** with a signal at δ 149.80 ppm assignable to the C-4'' of R-group having a dimethyl amino group attached in that position. This implies that more deshielding effect is felt by carbon carrying an electron withdrawing species like Cl or N(CH₃)₂ in *para* position as compared to *ortho* position. The resonance peak due to methyl groups were found at δ 43.90 ppm. A significant feature of the spectra of all the complexes was the appearance of twin peaks in the downfield region δ 197.40-191.00 ppm assigned to the terminal carbonyl carbons present in the *cis* position of the complex. The spectrum of complex **R8** exhibited two sets of peaks at δ 197.40, 196.80 and δ 191.90, 191.00 ppm due to *cis* and *trans* CO groups.

Stereochemistry: The analytical data, IR and ^1H & ^{13}C NMR spectral results indicate that the heterocycles are coordinated to the metal ion. Based on the various studies monomeric, dimeric and trimeric structure was assigned to these complexes.

Aquadicarbonyldichloro[6-furyl, *o*-hydroxy, *o*-chloro-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]ruthenium(II), $[\text{RuCl}_2(\text{CO})_2(\text{H}_2\text{O})] \cdot n\text{H}_2\text{O}$ {where $n = 1, L = L^2, L^4, L^6$ and $n = 2, L = L^7$ } (**R2, R4, R6** and **R7**, Fig. 2-I): The complexes are monomers as the ligands show negative inductive effect.

Tetracarbonyldichlorodi- μ -chloro bis[6-phenyl, thio-phenyl-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]-diruthenium(II), $[\text{RuCl}_2(\text{CO})_2\text{L}]_2 \cdot n\text{H}_2\text{O}$ { $n = 1, L = L^1, L^3$ } (**R1** and **R3**, Fig. 2-II): These complexes are dimers as the ligands show greater positive inductive effect and causes a build-up of electrons on the metal ion. In order to stabilize this there is a dimer formation with metal ion donation of electrons *via* the chloride ions bridges.

Bis[chlorodicarbonylaqua[μ -phenoxy-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]di-ruthenium(II), $[\text{RuCl}(\text{CO})_2(\text{L-H})(\text{H}_2\text{O})]_2$ { $L = L^5$ } (**R5**, Fig. 2-III): The complex of ligand L^5 has a hydroxyl group in the *para*-position and on complexation it undergoes deprotonation and oxygen of the hydroxyl group and *tert.*-nitrogen of the ligand coordinates to the ruthenium ions behaving like a bridging ligand resulting in dimer formation.

Hexacarbonyl dichloro tetra- μ -chloro bis[6-dimethyl-amino-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]tri-ruthenium(II), $\text{RuCl}_2(\text{CO})_2\text{L}_3$ { $L = L^8$ } (**R8**, Fig. 2-IV): The complex of the ligand L^8 forms a trimer as this ligand has dimethylammonium group, which shows a greater positive inductive effect causing more build-up of charge resulting in trimer formation with chloride bridges between the ruthenium ions.

Catalytic oxidation of benzyl alcohol, hydroquinone and cyclohexanol: The synthesized ruthenium(II) carbonyl complexes containing, L^2, L^4 and L^7 were evaluated for their catalytic activity towards oxidation of substrates like benzyl

alcohol, cyclohexanol and hydroquinone using *tert.*-butyl hydroperoxide (*t*-BuOOH) as co-oxidant. Benzyl alcohol was converted to benzaldehyde, which was further oxidized to benzoic acid. Cyclohexanol and hydroquinone were converted to cyclohexanone and benzoquinone, respectively. The reactions were carried out in acetonitrile by varying the catalysts-substrate concentrations (1:10, 1:100 and 1:1000). The optimum concentration of catalysts to substrate ratio was found to be 1:100 for benzyl alcohol and hydroquinone and 1:10 for cyclohexanol. It was found that the reactions were completed within 25 to 40 min at room temperature in the case of oxidation of benzyl alcohol and hydroquinone and time required for cyclohexanol was 6 h at 60 °C. The results are presented in Table-1.

Conclusion

Synthesis of ruthenium(II) carbonyl complexes with dihydrobenzoimidazo quinazoline derivatives has been carried out and characterized by various physico-chemical techniques. Based on these studies, monomeric/dimeric/trimeric structures with octahedral geometry around ruthenium(II) ion have been proposed. The complexes were found to be active towards catalytic oxidation of benzyl alcohol, cyclohexanol and hydroquinone using *t*-BuOOH as co-oxidant.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

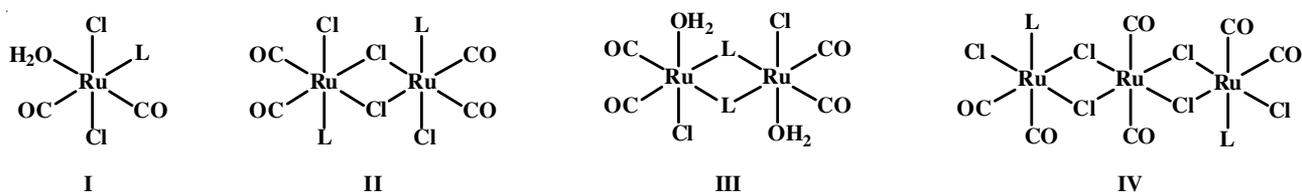


Fig. 2. Proposed structure of the complexes

TABLE-1
OXIDATION OF THE SUBSTRATES USING *t*-BuOOH AS CO-OXIDANT IN ACETONITRILE[†]

Complex	Temp. (°C) [†]	Substrate	Product	Time	Yield (%)
R2	RT	Benzyl alcohol	Benzoic acid	30 min	100
	RT	Hydroquinone	Benzoquinone	30 min	
	60	Cyclohexanol	Cyclohexanone	6 h	
R4	RT	Benzyl alcohol	Benzoic acid	30 min	100
	RT	Hydroquinone	Benzoquinone	35 min	
	60	Cyclohexanol	Cyclohexanone	6 h	
R7	RT	Benzyl alcohol	Benzoic acid	35 min	100
	RT	Hydroquinone	Benzoquinone	25 min	
	60	Cyclohexanol	Cyclohexanone	6 h	

[†]Catalyst: substrate :: 1: 100 for benzyl alcohol and hydroquinone and 1: 10 for cyclohexanol, [†]RT: room temperature

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