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# Synthesis and Characterization of Ru(III) Complexes Containing Quinazoline Derivatives and their Biological and Catalytic Activities

RITA BHATTACHARJEE[1,*] and VIRUPAIAH GAYATHRI[2]

[1]Department of Chemistry, B.M.S. College for Women, Bengaluru-560004, India
[2]Department of Post Graduate Studies in Chemistry, Bangalore City University, Bangalore-560001, India

*Corresponding author: E-mail: rita@bmscw.edu.in

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Ruthenium trichloride trihydrate ($RuCl_3{\cdot}3H_2O$) reacted with quinazoline derivative ligands (L) in 1:1 mole ratio in acetone to yield a series of brown/green/greenish black ruthenium(III) complexes of the type $RuX_3L{\cdot}nH_2O$ where X = Cl, n = 0, 1, 2 and 3 and L is 6-R-5,6-dihydrobenzoimidazo[1,2-c]quinazoline (R = ethyl: $L^1$/*n* or *i*-propyl: $L^2$, $L^3$/*n* or *i*-butyl: $L^4$, $L^5$/phenyl: $L^6$/furyl: $L^7$/thiophenyl: $L^8$/*o* or *p*-hydroxyphenyl: $L^9$, $L^{10}$/*o* or *p*-chlorophenyl: $L^{11}$, $L^{12}$/dimethylaminophenyl: $L^{13}$). All the synthesized Ru(III) complexes were characterized by elemental analyses, conductivity measurements, infrared, electronic, ESR and mass spectral techniques, TGA, magnetic susceptibility and electrochemical studies. A square pyramidal geometry around the metal ion was proposed for all the complexes. The biological activities of the ligand and its ruthenium(III) complexes have been studied on microorganisms such as *B. subtilis*, *E. coli* and yeast by cup-plate method. The catalytic activity of the synthesized ruthenium(III) complexes towards oxidation of benzyl alcohol, cyclohexanol and hydroquinone was also carried out in acetonitrile with *tert.*-butyl hydroperoxide (*t*-BuOOH) as co-oxidant.

**Keywords: Dihydrobenzoimidazoquinazoline derivatives, Cyclic voltammetry, Ru(III) complexes, Biological activity.**

## INTRODUCTION

Quinazolines are an important class of *N*-heterocycles and the quinazoline ring systems along with many alkaloids [1-3] are widely recognized for their medicinal applications and are in the forefront of pharmaceutical research. They are effective antimicrobial agents [4] and some have been reported to show anti-HIV activities [5]. Quinazoline derivatives exhibiting anti-inflammatory and analgesic properties have been reported [6].

Transition metal complexes containing the quinazoline derivatives are gaining importance in catalysis and pharmacology because of the ability of the N-heterocycles to stabilize various oxidation states of the transition metals [7]. Ruthenium complexes containing *N*-heterocycles have been reported to be employed as industrial catalysts in epoxidation of alkenes and oxidation of alcohols [7,8]. The complexes are also being utilized as catalysts in various reactions such as oxidation, hydrogenation, carbonylation and hydroformylation due to its existence in multiple oxidation states, which are stable and interconvertible [9-11]. In view of the multifaceted applications of this class of *N*-heterocyclic compounds and ruthenium complexes, synthesis and characterization of some quinazoline derivatives (Fig. 1) and their ruthenium(III) complexes were undertaken. The biological and catalytic activities of the synthesized ruthenium(III) complexes were also investigated.

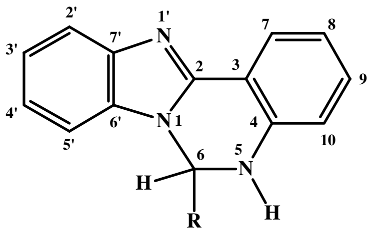


Fig. 1. Structure of 6-R-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline (**RDiq**) (R = ethyl: $\mathbf{L^1}$/*n* or *i*-propyl: $\mathbf{L^2}$, $\mathbf{L^3}$/*n* or *i*-butyl: $\mathbf{L^4}$, $\mathbf{L^5}$/ phenyl: $\mathbf{L^6}$/furyl: $\mathbf{L^7}$/thiophenyl**:** $\mathbf{L^8}$/*o* or *p*-hydroxyphenyl: $\mathbf{L^9}$, $\mathbf{L^{10}}$/ *o* or *p*-chlorophenyl: $\mathbf{L^{11}}$, $\mathbf{L^{12}}$/dimethylaminophenyl**:** $\mathbf{L^{13}}$)

## EXPERIMENTAL

AnalaR grade reagents were used as received. Standard procedures were used to purify the solvents [12] and ruthenium trichloride trihydrate was purchased from Arora Matthey, Kolkata, India. Reported procedures [13] were followed for the synthesis of quinazoline derivative ligands (L).

**Characterization:** Microanalyses were performed using a 240B elemental analyzer made by Perkin-Elmer. Shimadzu FTIR 8400s was used to record IR (nujol mull) spectra, while Bruker IFS 66v/S instrument was utilized to record far-IR spectra and Shimadzu UV 3101PC was used to record electronic spectra in DMF. AUTOLAB PGSTAT 30 supported with GPES 4.9 was utilized for cyclic voltammetric measurements. JEOL SX102 mass spectrometer at room temperature using Argon/Xenon as the FAB gas and *m*-nitrobenzyl alcohol as the matrix was used to record FAB mass spectra. Bruker ESP-300 spectrometer at X-band frequency recorded ESR spectra at 77 K and room temperature. Systronic conductivity meter 304-cell type CD-1 was utilized for molar conductivity measurements. Mettler TAHE-20 thermal analyzer with heating rate of 15 ºC min$^{-1}$ in nitrogen atmosphere was used for TGA.

## Synthesis of quinazoline derivatives and its ruthenium complexes

**Dihydrobenzo[1,2-*c*]imidaquinazoline derivatives:** Synthesis of the quinazoline derivatives and single crystal studies of L$^4$, L$^6$, L$^7$, L$^{10}$ [14-17] and L$^{13}$ [18] have been reported.

**Synthesis of Di-µ-chloro-*bis*[6-ethyl/*n* or *i*-propyl/*n* or *i*-butyl/phenyl/furyl/thiophenyl/*o* or *p*-hydroxyphenyl/*o* or *p*-chlorophenyl/dimethylaminophenyl)-5,6-dihydrobenzo imidazo(1,2-*c*)quinazoline]tetrachloro diruthenium(III) [A-M]:** Ruthenium trichloride trihydride (1 mmol) and quinazoline derivatives (1 mmol) were dissolved in 50 mL of acetone and refluxed for about 4 h during which brown/green/greenish black solid separated. It was washed with acetone and dried in vacuum (**Scheme-I**).

**Di-µ-chloro-*bis*[6-ethyl-5,6-dihydrobenzoimidazo[1,2-*c*]-quinazoline]tetrachlorodiruthenium(III), [RuCl$_3$(L$^1$)]·H$_2$O (A):** Green solid; yield: 70%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3458, 3167, 1614, 1306; Far-IR (polyethylene pellets): 341, 319 cm$^{-1}$; ESR (solid state, 77 K) $g_{\parallel}$ 2.25, $g_{\perp}$ 1.89; Magnetic moment (B.M.): 1.26; Anal. calcd. (found) % for L$^1$: C, 40.28 (40.48); H, 3.56 (3.61); N, 8.70 (8.85); Electronic transitions (DMF, cm$^{-1}$): Ligand and CT: 34247-28011, *d-d*: 22472, ε 2568, 17079, ε 827 TGA (ºC, species lost) 89: H$_2$O, 162: Cl, 286: Cl, 624: Cl+L$^1$; Molar conductance (in DMF): 22 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

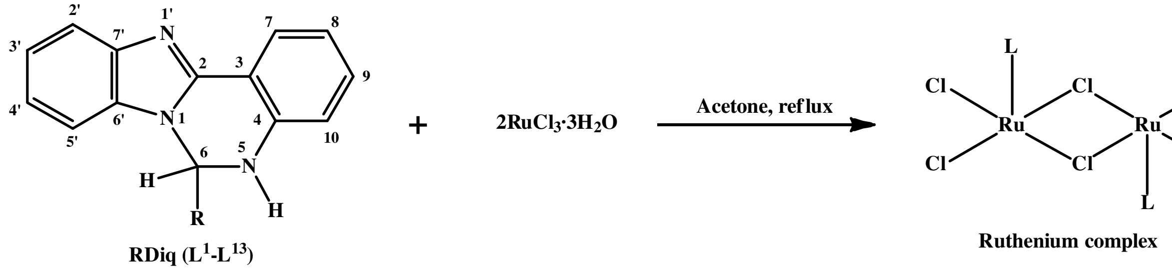
**Di-µ-chloro-*bis*[6-*n*-propyl-5,6-dihydrobenzoimidazo-[1,2-*c*]quinazoline]tetrachlorodiruthenium(III), [RuCl$_3$(L$^2$)]·H$_2$O (B):** Greenish black; yield: 70%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3485, 3140, 1626, 1306; Far-IR (polyethylene pellets): 343, 313 cm$^{-1}$; ESR (solid state, 77 K) $g_{\parallel}$ 2.39, $g_{\perp}$ 1.87; magnetic moment (B.M.): 0.92; Anal. calcd. (found) % for L$^2$: C, 41.59 (41.77); H, 3.80 (3.91); N, 8.45 (8.60); Electronic transitions (DMF, cm$^{-1}$): Ligand and CT: 36563-27435, *d-d*: 23559, ε 5794, 18975, ε 992; TGA (ºC, species lost) 77: H$_2$O, 269: Cl, 404: 2Cl, 639: L$^2$; FAB-MS (*m/z*); 941 [Ru$_2$Cl$_6$L$_2$], 926 [Ru$_2$Cl$_6$L (L-CH$_3$). Molar conductance (in DMF): 31 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Di-µ-chloro-*bis*[(6-*i*-propyl-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]tetrachlorodiruthenium(III), [RuCl$_3$(L$^3$)]·H$_2$O (C):** Greenish black solid; yield: 72%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3506, 3290, 1629, 1308; Far-IR (polyethylene pellets): 343, 317 cm$^{-1}$; ESR (solid state, 77 K) $g_{\parallel}$ 2.42, $g_{\perp}$ 1.89; magnetic moment (B.M.): 1.19; Anal. calcd. (found) % for L$^3$: C, 41.90 (41.77); H, 3.80 (3.91); N, 8.37 (8.60); Electronic transitions (DMF, cm$^{-1}$): Ligand and CT: 34423-29675, *d-d*: 22341, ε 2043, 18850, ε 1109. TGA (ºC, species lost) 75: H$_2$O, 179: Cl, 293: 2Cl, 534: L$^3$; Molar conductance (in DMF): 27 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Di-µ-chloro-*bis*[6-*n*-butyl)-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]tetrachlorodiruthenium(III), [RuCl$_3$(L$^4$)]·2H$_2$O (D):** Greenish black solid; yield: 71%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3477, 3180, 1625, 1308; Far-IR (polyethylene pellets): 340, 316 cm$^{-1}$; ESR (solid state, 77 K) $g_{\parallel}$ 2.31, $g_{\perp}$ 1.97; magnetic moment (B.M.): 1.38; Anal. calcd. (found) % for L$^4$: C, 41.33 (41.51); H, 4.38 (4.45); N, 7.92 (8.07); Electronic transitions (DMF, cm$^{-1}$): Ligand and CT: 36363-29718, *d-d*: 22624, ε 2475, 16598, ε 592; TGA (ºC, species lost) 100: 2H$_2$O, 264: Cl, 377: 2Cl, 707: L$^4$; Molar conductance (in DMF): 24 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Di-µ-chloro-*bis*[6-*i*-butyl)-5,6-dihydrobenzoimidazo-[1,2-*c*]quinazoline]tetrachlorodiruthenium(III), [RuCl$_3$(L$^5$)]·2H$_2$O (E):** Greenish black solid; yield: 70%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3477, 3180, 1625, 1315; Far-IR (polyethylene pellets): 340, 319 cm$^{-1}$; ESR (solid state, 77 K) $g_{\parallel}$ 2.31, $g_{\perp}$ 1.97; magnetic moment (B.M.): 1.28; Anal. calcd. (found) % for L$^5$: C, 41.40 (41.51); H, 4.26 (4.45); N, 8.20 (8.07); Electronic transitions (DMF, cm$^{-1}$): Ligand and CT: 34662-29586, *d-d*: 22371, ε 2043, 17036, ε 512. TGA (ºC, species lost) 100: 2H$_2$O, 250: Cl, 407: 2Cl, 774: L$^5$; Molar conductance (in DMF): 21 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Di-µ-chloro-*bis*[6-phenyl)-5,6-dihydrobenzoimidazo-[1,2-*c*]quinazoline]tetrachlorodiruthenium(III), [RuCl$_3$(L$^6$)]·2H$_2$O (F):** Green solid; yield: 70%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3506, 3175, 1625; Far-IR (polyethylene pellets): 342, 321 cm$^{-1}$; ESR (solid state, 77 K) $g_{\parallel}$ 2.38, $g_{\perp}$ 2.21; magnetic moment (B.M.): 1.05; Anal. calcd. (found) % for L$^6$: C, 44.37 (44.42); H, 3.42 (3.54); N, 7.67 (7.77); Electronic transitions (DMF, cm$^{-1}$):



**Scheme-I:** Synthesis of RuX$_3$L·nH$_2$O

Ligand and CT: 34364-27894, *d-d*: 22371, ε 3028, 17212, ε 915 TGA (ºC, species lost) 100: 2H$_2$O, 264: Cl, 305 Cl, 771: Cl+L$^6$; Molar conductance (in DMF): 24 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Di-μ-chloro-*bis*[6-furyl)-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]tetrachlorodiruthenium(III), [RuCl$_3$(L$^7$)]·H$_2$O (G):** Dark brown; yield: 69%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3485, 3180, 1608, 1303; Far-IR (polyethylene pellets): 342, 321; ESR (solid state, 77 K) $g_{\parallel}$ 2.34, $g_{\perp}$ 2.29; magnetic moment (B.M.): 1.2 9; Anal. calcd. (found) % for L$^7$: C, 42.19 (42.16); H, 2.77 (2.95); N, 8.19 (8.20); Electronic transitions (DMF, cm$^{-1}$): Ligand and CT: 35907-28409, *d-d*: 22522, ε 5071, 16142, ε 706. TGA (ºC, species lost) 64: H$_2$O, 182: Cl, 314: 2Cl, 513: L$^7$; Molar conductance (in DMF): 18 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Di-μ-chloro-*bis*[6-thiophenyl)-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]tetrachlorodiruthenium(III), [RuCl$_3$(L$^8$)] (H):** Brown solid; yield: 75%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3485, 3196, 1610, 1319; Far-IR (polyethylene pellets): 343, 318 cm$^{-1}$; ESR (solid state, 77 K) $g_{\parallel}$ 2.38, $g_{\perp}$ 2.03; magnetic moment (B.M.): 1.40; Anal. calcd. (found) % for L$^8$: C, 42.03 (42.33); H, 2.40 (2.57); N, 8.20 (8.23); Electronic transitions (DMF, cm$^{-1}$): Ligand and CT: 36363-27894, *d-d*: 22624, ε 4519, 14409, ε 288 TGA (ºC, species lost), 157:Cl, 336: 2Cl, 814: L$^8$; Molar conductance (in DMF): 18 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Di-μ-chloro-*bis*[6-*o*-hydroxyphenyl)-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]tetrachlorodiruthenium(III), [RuCl$_3$(L$^9$)]·2H$_2$O (I):** Green solid; yield: 71%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3485, 3215, 1625, 1348; Far-IR (polyethylene pellets): 343, 318 cm$^{-1}$; ESR (solid state, 77 K) $g_{\parallel}$ 1.96, $g_{\perp}$ 1.88; magnetic moment (B.M.): 0.96; Anal. calcd. (found) % for L$^9$: C, 42.97 (43.14); H, 3.23 (3.44); N, 7.39 (7.55); Electronic transitions (DMF, cm$^{-1}$): Ligand and CT: 36363-27739, *d-d*: 22701, ε 4539, 165556, ε 860. TGA (ºC, species lost) 100: 2H$_2$O, 318: 2Cl, 609: Cl + L$^9$; Molar conductance (in DMF): 23 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Di-μ-chloro-*bis*[6-*p*-hydroxyphenyl)-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]tetrachlorodiruthenium(III), [RuCl$_3$(L$^{10}$)]·3H$_2$O (J):** Greenish black solid; yield: 69%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3458, 3174, 1608, 1328; Far-IR (polyethylene pellets) 343, 319 cm$^{-1}$; ESR (solid state, 77 K) $g_{\parallel}$ 2.26, $g_{\perp}$ 1.88; magnetic moment (B.M.):1.48; Anal. calcd. (found) % for L$^{10}$: C, 41.71 (41.82); H, 3.48 (3.69); N, 7.20 (7.32); Electronic transitions (DMF, cm$^{-1}$): Ligand and CT: 36563-30487, *d-d*: 22831, ε 2931, 17079, ε 1021. TGA (ºC, species lost) 100: 3H$_2$O, 275: Cl, 286: 2Cl, 503: L$^{10}$; Molar conductance (in DMF): 26 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Di-μ-chloro-*bis*[6-*o*-chlorophenyl)-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]tetrachlorodiruthenium(III), [RuCl$_3$(L$^{11}$)]·H$_2$O (K):** Greenish black solid; yield: 70%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3493, 3180, 1627, 1329; Far-IR (polyethylene pellets): 344, 313 cm$^{-1}$; ESR (solid state, 77 K) $g_{\parallel}$ - 2.38, $g_{\perp}$ 1.88; magnetic moment (B.M.): 1.11; Anal. calcd. (found): for L$^{11}$: C, 42.98 (43.11); H, 2.90 (2.89); N, 7.50 (7.54); Electronic transitions (DMF, cm$^{-1}$): Ligand and CT: 35906-29586, *d-d*: 22371, ε 2973, 17241, ε 695. TGA (ºC, species lost) 92: H$_2$O, 267: Cl: 285: Cl, 346: Cl, 615: L$^{11}$; Molar conductance (in DMF): 28 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Di-μ-chloro-*bis*[6-*p*-chlorophenyl)-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]tetrachlorodiruthenium(III), [RuCl$_3$(L$^{12}$]·2H$_2$O (L):** Greenish black solid; yield: 71%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3477, 3172, 1625, 1328; Far-IR (polyethylene pellets): 343, 312 cm$^{-1}$; ESR (solid state, 77 K) $g_{\parallel}$ 2.10, $g_{\perp}$ 1.98; magnetic moment (B.M.): 1.11; Anal. calcd. (found) % for L$^{12}$: C, 41.60 (41.76); H, 3.25 (3.15); N, 7.24 (7.31); Electronic transitions (DMF, cm$^{-1}$): Ligand and CT: 36363-28169, *d-d*: 22272, ε 2866, 16461, ε 552. TGA (ºC, species lost) 100: 2H$_2$O, 142: Cl, 315: Cl, 683: Cl +L$^{12}$; FAB-MS (*m/z*) Ru$_2$Cl$_6$L$_2$: 1078, Ru$_2$Cl$_4$L$_2$: 1008; Molar conductance (in DMF): 28 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Di-μ-Chloro-*bis*[6-dimethylaminophenyl)-5,6-dihydrobenzoimidazo[1,2-*c*]quinazoline]tetrachlorodiruthenium (III), [RuCl$_3$(L$^{13}$)]·2H$_2$O (M):** Green solid; yield: 71%; IR (nujol, $\nu_{max}$, cm$^{-1}$): 3498, 3180, 16275, 1328; Far-IR (polyethylene pellets): 345, 314 cm$^{-1}$; ESR (solid state, 77 K) $g_{\parallel}$ 2.05, $g_{\perp}$ 1.98; magnetic moment (B.M.): 1.06; Anal. calcd. (found) % for L$^{13}$: C, 45.14 (45.25); H, 4.20 (4.14); N, 9.82 (9.60); Electronic transitions (DMF, cm$^{-1}$): Ligand and CT: 36363-25575, *d-d*: 22472, ε 2786, 16835, ε 1365; TGA (ºC, species lost) 75: 2H$_2$O, 371: 2Cl, 619: Cl + L$^{13}$; Molar conductance (in DMF): 57 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

## RESULTS AND DISCUSSION

Reactions of ruthenium trichloride with quinazoline derivatives (L$^1$ to L$^{13}$) in 1:1 molar ratio in acetone synthesized complexes of the composition RuX$_3$L·nH$_2$O. All the synthesized ruthenium(III) complexes were insoluble in common organic solvents but soluble in DMF and DMSO in which they behaved as non-electrolytes.

**Thermal studies:** The TGA of ruthenium(III) complexes were recorded in nitrogen atmosphere at a heating rate of 15 ºC/min. The TGA data indicated that water molecules were lost below 100 ºC in all the ruthenium(III) complexes (except the one containing L$^8$) implying the presence of lattice water. The chloride ions and the *N*-heterocycles were lost in the range 100-800 ºC.

**Infrared studies:** The nujol mull IR spectra of the ligands L$^1$ to L$^{13}$ are comparable with those of the complexes except for minor shifts in the position of the bands implying coordination of the N-heterocycles to the ruthenium(III) ion [19,20]. The spectra of the complexes displayed ν(NH) of quinazoline ring between 3290 to 3140 cm$^{-1}$ and peaks due to the ν(C=N) was observed around 1620 cm$^{-1}$ [21]. Bands at 1300 cm$^{-1}$ and 1320 cm$^{-1}$ are assigned to ν(CN) and δ(NH). The ν(C=N) peak shows a shift by 6-21 cm$^{-1}$ after complexation. The spectra of the complexes exhibit a peak around 3450 cm$^{-1}$ due to ν(O-H) of lattice water. The far-IR spectra of the complexes show a peak between 345 to 340 cm$^{-1}$ due to terminal ν(Ru-Cl) and a peak in the region 323 to 312 cm$^{-1}$ due to bridging ν(Ru-Cl) [22].

**Mass studies:** The FAB mass spectra for the complexes [RuCl$_3$(L$^2$)] and [RuCl$_3$(L$^{12}$)] were recorded using argon/xenon as carrier gas and the spectra exhibited molecular ion peak at *m/z* 941 and 1078, respectively corresponding to the dimeric nature of the complexes.

**Electronic studies:** The electronic spectra of the ligands and the ruthenium(III) complexes were recorded in DMF. The spectra of the ruthenium(III) complexes displayed bands due to the coordinated quinazoline derivatives between 25,600 to 36,600 $cm^{-1}$, which may be attributed to the n-π* and π-π* transitions. The metal to ligand charge transfer transitions appeared around 29,600 and 31,000 $cm^{-1}$ except for $L^7$ and $L^8$ complexes which may be obscured by the ligands transitions. The Ru(III) ion exhibited two bands due to *d-d* transitions, one of which appeared as a weak band between 14,400 and 19,000 $cm^{-1}$ and another band, which appeared as a shoulder in most cases between 22,200 and 23,600 $cm^{-1}$. These bands may be assigned as $^2B_{2g}\rightarrow{}^2B_{1g}$ and $^2B_{2g}\rightarrow{}^2E_g$ transitions, respectively and are consistent with a square pyramidal environment for $d^5$ configuration of Ru(III) [23,24]. The *N*-heterocycles behave as monodentate ligands coordinating through the *tert.*-nitrogen of the benzimidazole moiety.

**Magnetic moment measurements:** The magnetic moment of the complexes have been measured by Guoy and Faraday methods at room temperature and were in the range of 0.92 to 1.48 B.M. The values are fairly lower than the spin only value for one unpaired electron of a low spin $d^5$ configuration. The mass spectral results suggest a binuclear structure for the complexes and the far IR spectra revealed the presence of dichloro bridges. Hence, there may be weak antiferromagnetic coupling between the Ru(III) ions through the chloro bridges, which accounts for the low magnetic moment values [25].

**ESR spectral data:** The ESR spectra of Ru(III) complexes was recorded at ambient temperature and 77 K. The spectra at ambient temperature were not well-resolved. The $g_{\parallel}$ values were in the range 1.96 to 2.42 and $g_{\perp}$ values were found between 1.88 and 2.29, which are characteristic of Ru(III) complexes [21].

**Cyclic voltammetric studies:** The cyclic voltammetric (CV) studies were carried out for all the synthesized Ru(III) complexes and $RuCl_3{\cdot}3H_2O$ ($10^{-3}$ M) in acetonitrile using 0.1 M *tert.*-butylammonium perchlorate (TBAP) as supporting electrolyte and saturated calomel electrode (SCE) was taken as the reference electrode and Pt wire as the working electrode. The scan rate of 100 mV/s was set and readings recorded at 298 K. The results are tabulated in Table-1. All the Ru(II) complexes showed similar electrochemical behaviour displaying one reversible oxidation and one reversible reduction couples except $RuCl_3(L^3){\cdot}H_2O$, which displayed only one reversible redox couple. The $E^{1/2}$ values range from 0.03 V to 0.54 V and appear as well defined waves for oxidation. The reduction of Ru ion was also observed as distinct peaks and ranged from -0.1 V to -0.63 V. The redox processes are metal-centered. The peak to peak potential diffe-rence ($\Delta E_p$) for the redox processes were observed between 40-300 mV indicating single step one electron transfer process. The closely spaced couples are assigned as oxidation couple for Ru(III)→Ru(IV) and reduction couples for Ru(III)→Ru(II) [26]. The cyclic voltammogram of A is shown as representative graph in Fig. 2.

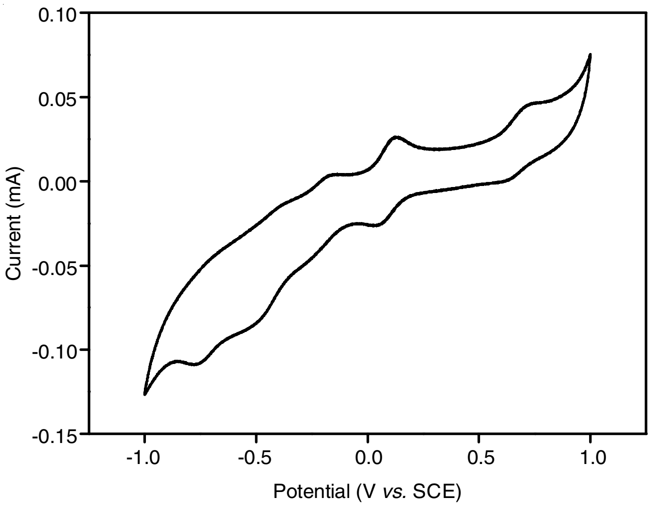


Fig. 2. Cyclicvoltammogram of **A**

**Stereochemistry:** The coordination of the *N*-heterocycles to the metal ion is evident from the analytical data and IR spectral studies. The TGA studies of the complexes revealed the presence of lattice water molecules except for $RuCl_3(L^8)$ and FAB-MS study of the complexes support binuclear nature for the complexes. The ESR and magnetic moment measurements indicate the paramagnetic nature of the complexes. Lower magnetic moments of the complexes indicate weak antiferromagnetic coupling between Ru(III) ions by a dimer form-

TABLE-1
CYCLIC VOLTAMMETRIC DATA OF Ru(III) COMPLEXES

| Complex | $E_{pa}$ (V) | $E_{pc}$ (V) | $E_f$ (V) | $\Delta E_p$ (mV) | $E_{pa}$ (V) | $E_{pc}$ (V) | $E_f$ (V) | $\Delta E_p$ (mV) |
|---|---|---|---|---|---|---|---|---|
| **A** | 0.26 | 0.22 | 0.24 | 40 | 0.12 | 0.06 | 0.09 | 60 |
| **B** | 0.20 | 0.02 | 0.11 | 180 | 0.68 | 0.60 | 0.64 | 80 |
| **C** | 0.00 | 0.30 | 0.15 | 300 | – | – | – | – |
| **D** | 0.20 | 0.00 | 0.10 | 200 | 0.40 | 0.32 | 0.36 | 80 |
| **E** | -0.02 | 0.06 | -0.20 | 40 | -0.24 | -0.20 | 0.22 | 40 |
| **F** | -0.02 | -0.10 | -0.06 | 80 | -0.22 | -0.30 | 0.26 | 80 |
| **G** | 0.70 | 0.50 | 0.60 | 200 | 0.66 | -0.60 | 0.06 | 60 |
| **H** | -0.14 | 0.04 | 0.27 | 100 | 0.56 | 0.46 | 0.51 | 100 |
| **I** | 0.00 | -0.06 | 0.03 | 60 | -0.26 | -0.22 | -0.24 | 40 |
| **J** | -0.04 | 0.06 | 0.05 | 100 | -0.16 | -0. 24 | -0.20 | 80 |
| **K** | 0.80 | 0.00 | 0.04 | 80 | -0.10 | -0.16 | -0.13 | 60 |
| **L** | -0.04 | -0.12 | -0.08 | 80 | -0.24 | -0.30 | -0.27 | 60 |
| **M** | -0.02 | -0.10 | 0.06 | 80 | -0.24 | -0.30 | -0.27 | 60 |
| $RuCl_3{\cdot}3H_2O$ | 0.60 | 0.48 | 0.54 | 120 | 0.32 | 0.20 | 0.26 | 120 |

$E_f = 0.5\ (E_{pa} + E_{pc})$, $\Delta E_p = (E_{pc} - E_{pa}) \times 100$ Mv, $E_{pc}$ and $E_{pa}$ are potential for cathodic and anodic peaks, respectively.

ation through chloride bridges. The far-IR spectra confirmed the presence of terminal and bridging chloride ions. The electrochemical studies of the complexes display an oxidation peak, which indicate the presence of chloro bridges between the two Ru(III) ions. The dihydrobenzoimidazoquinazoline derivatives behave as monodentate ligands coordinating through the *tert.*-nitrogen(1′) of benzimidazole moiety and hence ruthenium(III) is suggested to be pentacoordinate and may have a trigonal bipyramidal or square pyramidal geometry. The electronic and ESR spectral data support a square pyramidal geometry for the complexes. Based on these results a dinuclear structure with a square pyramidal geometry for ruthenium(III) complexes has been suggested.

**Biological activity:** Few quinazoline derivatives and their ruthenium(III) complexes were tested for *in vitro* growth inhibitory activity against *Bacillus subtilis*, *E. coli* and yeast by cup-plate method (Table-2). Test solution of quinazoline derivatives (50 ppm), RuCl$_3$ and the ruthenium(III) complexes of the quinazoline derivatives were prepared in DMSO for evaluating the biological activity. Septran and ampicillin was used as the standard antibiotics for *Bacillus subtilis* and *E. coli*, respectively while grissoflumin was used as the standard antifungal agent.

The toxicity of the quinazoline derivatives and its Ru(III) complexes against the microbes were found to be effective at 50 ppm concentration. It was observed that Ru(III) complexes exhibit lower inhibitory activity as compared to those of the quinazoline derivatives. Though the Ru(III) complexes and quinazoline derivatives proved to be toxic against the studied microorganisms, the standard drugs were found to be more toxic except for L$^{10}$ and L$^{13}$, which showed higher toxicity than the standard antifungal agent grissoflumin.

**Catalytic activity:** Complexes of Ru(III) and Ru(II) are effective as stereospecific catalysts for oxidation and reduction. Various reactions of ruthenium catalyzed oxidation of alcohols have been reported [25,27]. Catalytic activity of the synthesized ruthenium(III) complexes towards the oxidation of benzyl alcohol, cyclohexanol and hydroquinone was carried out in acetonitrile with *tert.*-butyl hydroperoxide (*t*-BuOOH) as co-oxidant. The progress of the reaction was monitored by TLC and UV-Vis spectroscopic methods at 5 min interval. Benzyl alcohol was converted to benzaldehyde, which was further oxidized to benzoic acid. Cyclohexanol and hydroquinone were converted to cyclohexanone and quinone, respectively.

Blank reactions were also carried out in absence of the catalyst and the co-oxidant and formation of the product did not occur. The concentration of the catalyst and substrate were maintained in the ratio 1:100 (10$^{-5}$ mol:10$^{-3}$ mol) in the case of benzyl alcohol and cyclohexanol and 1:10 (10$^{-5}$ mol:10$^{-4}$ mol) in the case of hydroquinone. All the synthesized Ru(III) complexes oxidized benzyl alcohol to benzoic acid and hydroquinone to benzoquinone at room temperature in 30 min. Conversion of cyclohexanol to cyclohexanone was carried out at 60 ºC and it was observed that for ruthenium(III) complexes containing L$^1$ to L$^5$ conversion took place in 4 h, while for the others it took 6 h. In all the cases, the complete conversion was achieved.

## Conclusion

Synthesis of ruthenium(III) complexes with quinazoline derivatives have been carried out and characterized by various physico-chemical techniques. Based on these studies, a binuclear structure with square pyramidal geometry around ruthenium(III) ion has been proposed. The ruthenium(III) complexes were investigated for their catalytic activity towards oxidation of benzyl alcohol, cyclohexanol and hydroquinone. The ligands and its ruthenium(III) complexes have the potential for application as strong antimicrobial agents and catalysts for a variety of reactions.

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TABLE-2
BIOLOGICAL ACTIVITY OF THE LIGANDS AND THEIR Ru(III) COMPLEXES

| Compound* | Inhibition (%) | | | Ru(III) complex* | Inhibition (%) | | |
|---|---|---|---|---|---|---|---|
| | *B. subtilis* | *E. coli* | Yeast | | *B. subtilis* | *E. coli* | Yeast |
| **L$^1$** | 46 | - | 40 | **A** | 14 | 50 | 63 |
| **L$^4$** | 57 | 50 | 50 | **D** | 50 | 72 | 61 |
| **L$^6$** | 46 | 45 | 40 | **F** | 50 | 71 | 63 |
| **L$^7$** | 46 | Nd | 50 | **G** | 40 | 67 | 57 |
| **L$^8$** | 50 | 75 | 50 | **H** | 25 | 67 | 40 |
| **L$^9$** | 40 | 76 | 65 | **I** | 57 | 76 | 25 |
| **L$^{10}$** | - | 50 | 70 | **J** | 40 | 60 | 40 |
| **L$^{13}$** | - | - | 70 | **M** | - | 64 | 40 |
| Standard | 76 | 76 | 67 | RuCl$_3$·3H$_2$O | - | - | 69 |

Standard antibiotic: Septran and ampicillin, Standard antifungal: Grissoflumin; *: 50 ppm

## CONFLICT OF INTEREST

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

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