

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

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### **ABSTRACT**

Several ruthenium(II) carbonyl complexes, of the type  $[\text{RuCl}_2(\text{CO})_2\text{L}] \cdot n\text{H}_2\text{O}$   $\{n = 1, \text{L} = \text{L}^1, \text{L}^2, \text{L}^4, [\text{RuCl}_2(\text{CO})_2(\text{L})(\text{H}_2\text{O})] \cdot n\text{H}_2\text{O}$   $\{n = 1, \text{L} = \text{L}^3, \text{L}^5, \text{L}^5\}$ , were prepared where L is 6-R-5,6-dihydrobenzoimidazo[1,2-c]quinazoline (R-Diq; R = ethyl:  $\text{L}^1$ / n or i-propyl:  $\text{L}^2, \text{L}^3$ / n or i-butyl:  $\text{L}^4, \text{L}^5$ . The techniques used to identify them included elemental analysis, conductivity tests, TGA, infrared, electronic, NMR, and mass spectrometry. For all of the complexes, an octahedral geometry around the Ruthenium ion with monomeric and dimeric stereochemistry was proposed. Investigation of the catalytic activity of the complexes towards the oxidation of hydroquinone, cyclohexanol, and benzyl alcohol was investigated

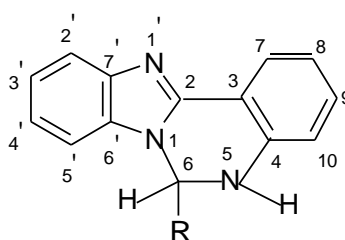
**KEYWORDS:** quinazoline derivatives, NMR studies, Ru(II) carbonyl complexes

### **INTRODUCTION**

Quinazolines are a significant group of N-heterocycles and many of its associated alkaloids<sup>1-3</sup> are well known for their therapeutic uses. Organometallic complexes of ruthenium(II) has generated a lot of interest among researchers as they can be used as model materials for optical and electronic devices<sup>4-6</sup> because 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.

Carbonyl complexes of ruthenium (II) have also proved to be good anti-microbial agents<sup>7-8</sup>.

Due to the wide range of uses for this particular class of N-heterocyclic compounds and ruthenium complexes, efforts were made to synthesise and characterise ruthenium (II) carbonyl complexes with quinazoline derivatives (figure 1). Catalytic activity of the compounds and complexes in oxidation of hydroquinone, benzyl alcohol, and cyclohexanol was studied.



**Figure 1:** Structure of the quinazoline derivative

(R = ethyl: L<sup>1</sup>/ n or i-propyl: L<sup>2</sup>, L<sup>3</sup>/ n or i-butyl: L<sup>4</sup>, L<sup>5</sup>)

## EXPERIMENTAL

### REAGENTS and MEASUREMENTS

Every reagent was of analytical grade. The utilised solvents were purified in accordance with protocol<sup>9</sup>. The company Arora Matthey Limited in Kolkata, India provided the ruthenium trichloride trihydrate.

A 240B Perkin Elmer elemental analyzer was used to determine the amounts of carbon, hydrogen, and nitrogen. Shimadzu FTIR 8400s and Bruker IFS 66v/S instruments were used to record IR (nujol mull) spectra and far-IR spectra, respectively. On the Shimadzu UV 3101PC, electronic spectra were recorded in DMF. m-nitrobenzyl alcohol was used as the matrix and Argon/Xenon was used as the FAB gas to record FAB mass spectra on a JEOL SX102 mass spectrometer. On a Bruker AMX 400 MHz NMR Spectrometer with Aspect

2000 processors, NMR spectra were captured. A Systronic conductivity metre of the 304-cell kind was used to measure molar conductivity.

## SYNTHETIC ASPECTS

### Synthesis of dihydrobenzo[1,2-c]imidaquinazoline derivatives

Synthesis of the quinazoline derivatives and single crystal studies of (**L**<sup>4</sup>) have been reported earlier<sup>10-14</sup>.

### Synthesis of Ru(II) complexes

Ruthenium carbonylated solution was reacted with **L**<sup>1</sup> to **L**<sup>5</sup> in 1:1 mole ratio at refluxing temperature in 2-methoxy ethanol to afford yellow carbonyl complexes whose elemental analyses corresponds to the formulae  $[\text{RuCl}_2(\text{CO})_2\text{L}]\cdot n\text{H}_2\text{O}$  {n = 1, L = **L**<sup>1</sup>, **L**<sup>2</sup>, **L**<sup>4</sup>,  $[\text{RuCl}_2(\text{CO})_2(\text{L})(\text{H}_2\text{O})]\cdot n\text{H}_2\text{O}$  {n = 1, L = **L**<sup>3</sup>, **L**<sup>5</sup>}. They were filtered, washed with ether and water and dried in vacuum (yield: 60-65%).

## RESULTS AND DISCUSSION

The complexes were diamagnetic and insoluble in common organic solvents but soluble in DMF and DMSO in which they behaved as non-electrolytes. The analytical data of the complexes are tabulated in **Table 1**.

**Table 1:** The analytical data of the complexes

Complex	Colour	M.Pt/ (°C)	Λ <sup>#</sup>	Analytical data (%)*		
				C	H	N
[RuCl <sub>2</sub> (CO) <sub>2</sub> ( <b>L</b> <sup>1</sup> )]·H <sub>2</sub> O	Pale	214	38	43.91	3.46	8.09
	Yellow			(43.73)	(3.47)	(8.50)

[RuCl <sub>2</sub> (CO) <sub>2</sub> (L <sup>2</sup> )].H <sub>2</sub> O	Pale Yellow	238	24	44.66 (44.80)	3.80 (3.76)	8.33 (8.25)
[RuCl <sub>2</sub> (CO) <sub>2</sub> (L <sup>3</sup> )(H <sub>2</sub> O)].H <sub>2</sub> O	Yellow	250	20	43.72 (43.29)	3.18 (4.02)	9.91 (8.97)
[RuCl <sub>2</sub> (CO) <sub>2</sub> (L <sup>4</sup> )].H <sub>2</sub> O	Yellow	167	29	45.96 (45.88)	4.12 (4.04)	8.36 (8.03)
[RuCl <sub>2</sub> (CO) <sub>2</sub> (L <sup>5</sup> )(H <sub>2</sub> O)].H <sub>2</sub> O	Yellow	234	28	44.74 (44.35)	3.59 (4.28)	8.39 (7.76)

\*: calculated values are

in parentheses; #: solvent used: DMF,  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ .

The IR spectra of the N-heterocycles and their Ru(II) complexes were recorded as nujol mull and the far-IR spectra of the complexes were recorded as polyethylene pellets (**Table 2**). The IR spectra of the 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  $\text{cm}^{-1}$  which were attributed to the stretching frequencies of the carbonyl groups present in cis position except for complex containing L<sup>3</sup> which exhibited an additional peak at 2127  $\text{cm}^{-1}$  indicating the presence of a mixture of both trans and cis carbonyls.<sup>15</sup> All the complexes exhibited  $\nu_{\text{O-H}}$  of lattice water in the range 3360 to 3562  $\text{cm}^{-1}$  and complexes of L<sup>3</sup>, L<sup>5</sup> revealed a broad peak in the range 3207 - 3181  $\text{cm}^{-1}$  is assigned to the  $\nu_{\text{O-H}}$  of coordinated water in these complexes. A peak around 1612 to 1616  $\text{cm}^{-1}$  is assigned to  $\nu_{\text{C=N}}$  of benzimidazole moiety and  $\nu_{\text{C=C}}$  of benzimidazole and quinazoline ring. This peak shifted to 1618 - 1631  $\text{cm}^{-1}$  indicating the coordination of the dihydrobenzoimidazoquinazoline derivative to the ruthenium(II) ion via the tertiary nitrogen of the benzimidazole moiety.<sup>16</sup>

The Far – IR spectra of the Ru(II) complexes containing L<sup>3</sup>, L<sup>5</sup> ligands exhibited a peak in the

region 326 to 346  $\text{cm}^{-1}$  attributable to terminal Ru(II) – Cl stretching vibration and two peaks in the range 425 – 435  $\text{cm}^{-1}$  and 463 – 493  $\text{cm}^{-1}$  which are assignable to the Ru-OH<sub>2</sub>

Stretching frequencies of coordinated water molecule.<sup>17</sup> The complexes containing the

heterocycles L<sup>1</sup>, L<sup>2</sup>, L<sup>4</sup> showed peaks due to bridging and terminal Ru(II) – Cl in the ranges

311 - 330  $\text{cm}^{-1}$  and 343 – 364  $\text{cm}^{-1}$  respectively.<sup>18</sup>

**Table 2:** IR\* and Far-IR<sup>†</sup> spectral data ( $\text{cm}^{-1}$ ) of Ru(II) carbonyl complexes with L = L<sup>1</sup> - L<sup>5</sup>.

Complex with L <sup>1</sup>	Complex with L <sup>2</sup>	Complex with L <sup>3</sup>	Complex with L <sup>4</sup>	Complex with L <sup>5</sup>	Assignments
2062, 1988	2059, 2001	2127,2052, 1986	2057,1988	2060, 1988	$\nu_{\text{CO}}$ of carbonyl group
3360	3562	3450	3455	3480	$\nu_{\text{O-H}}$ of lattice water.
–	–	3181	–	–	$\nu_{\text{O-H}}$ of coordinated water
3110	3128	3124	3217	3201	$\nu_{\text{N-H}}$ of quinazoline ring.
1620	1628	1629	1622	1624	$\nu_{\text{C=N}}$ of benzimidazole and $\nu_{\text{C=C}}$ of benzimidazole and quinazoline.
1568	1585	1568	1556	1595	N-H in-plane bending vibration.
1531	1529	1529	1537	1531	$\nu_{\text{C=C}}$ and $\delta_{\text{CH}}$
1323	1323	1323	1323	1323	$\nu_{\text{C-N}}$ and $\delta_{\text{NH}}$
1284,1012, 931,	1284,1012, 929	1284,1020, 933, 841	1282,1008, 945, 840	1284,1012, 937,880	Benzimidazole ring vibrations.

1230	1230	1231	1282	1231	In-plane CH deformation and ring breathing modes.
1151	1151	1132	1188	1155	CH out - of - plane deformation of quinazoline ring vibrations.
746	742	748	742	742	NH out-of- plane deformation.
841	841	800	841	840	CH out-of- plane bending.
628	665	669	629	675	Skeletal frequency of quinazoline.
–	–	425, 472	–	432, 468	$\nu(\text{Ru-OH}_2)$
364	343	343	353	343	$\nu_{\text{Ru-Cl(t)}}$
328	322		330		$\nu_{\text{Ru-Cl(b)}}$

\*: Spectra recorded as nujol mull, †: Spectra recorded as polyethylene pellets.

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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ . The complexes exhibited d-d transitions as weak bands in the range 21,800 to 23,810  $\text{cm}^{-1}$  assignable to the  $^1A_{1g} \rightarrow ^1T_{1g}$  transition of octahedral spin paired  $d^6$  system.<sup>19,20</sup>

**Table 3:** Electronic spectral data of the Ru(II) carbonyl complexes ( $\text{cm}^{-1}$ ) of  $L^1$  to  $L^5$ .

Complex	Electronic Spectral Data*		
	Ligand transitions	MLCT	$^1A_{1g} \rightarrow ^1T_{1g}$
$[\text{RuCl}_2(\text{CO})_2(L^1)].\text{H}_2\text{O}$	37481(13004) 34270(20726) 33244(25370) 32950(25716)	27337(4266)	22873(288)
$[\text{RuCl}_2(\text{CO})_2(L^2)].\text{H}_2\text{O}$	38699(5423) 37830(9283)	27548(2526)	23674(106)

	34199(14018) 32895(18082) 31368(14950)		
[RuCl <sub>2</sub> (CO) <sub>2</sub> (L <sup>3</sup> )(H <sub>2</sub> O)].H <sub>2</sub> O	37679(12984) 34293(17584) 33223(20871) 31526(11840)	27518(6273) 24975(338)	21929(70)
[RuCl <sub>2</sub> (CO) <sub>2</sub> (L <sup>4</sup> )].H <sub>2</sub> O	37679(9821) 34341(13455) 33113(17212) 31250(11366)	27100(3023)	21805(70)
[RuCl <sub>2</sub> (CO) <sub>2</sub> (L <sup>5</sup> )(H <sub>2</sub> O)].H <sub>2</sub> O	38610(4081) 37764(7990) 34340(10620) 33113(14130) 31056(9202)	27488(2820)	22522(114)

\*:  $\epsilon$  values are in parentheses, spectra recorded in DMF.

The FAB mass spectra for the complex containing the ligands L<sup>1</sup>, exhibited molecular ion peaks at 954 indicating its binuclear nature.

Thermogravimetric analysis of ruthenium carbonyl complexes of L<sup>1</sup>, L<sup>2</sup>, L<sup>4</sup>, exhibited loss of water below 100 °C indicating the presence of lattice water in these complexes. The complexes of L<sup>3</sup>, L<sup>5</sup> 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 SPECTRAL STUDIES

### <sup>1</sup>H NMR SPECTRAL STUDIES

The <sup>1</sup>H NMR (**Table 4**) and <sup>13</sup>C NMR (**Table 5**) spectra of the complexes and N-heterocycles were recorded in dmsd-d<sub>6</sub>. Positive and negative coordination induced shifts {c.i.s. =  $\delta$  (complex) –  $\delta$  (ligand)} were observed in the protons and carbons of the N-heterocycles on complexation. The positive c.i.s. values for the carbon resonances can be attributed to ligand – to – metal  $\sigma$  – donation and negative c.i.s. values are due to greater metal-to-ligand  $\pi$  – back donation.<sup>21</sup>

The  $^1\text{H}$  NMR spectra of the complexes of  $\text{L}^1$  to  $\text{L}^5$  with alkyl substituents were similar when compared with the spectra of the free ligands. The signal due to resonance of the NH proton of quinazoline moiety appeared around  $7\delta$  as a singlet in the ligands exhibited a downfield shift of about 0.47 to 3.74 ppm on complexation and a singlet due to the CH proton between 6.08 to 5.88 ppm in the heterocycles showed a downfield shift of 0.12 to 0.46 ppm. The protons of the quinazoline moiety H – 7, 8, 9, and 10 were observed in the region 7.88 – 6.73 ppm and have exhibited positive and negative c.i.s on complexation. Benzimidazole protons H – 2', 3', 4' and 5' appeared as multiplets between  $\delta$  8.03 and 7.18 have undergone downfield shift. The alkyl protons of  $\text{L}^1$  to  $\text{L}^5$  were seen in the upfield region of 1.84 to 0.70 ppm as a triplet for the  $\text{CH}_3$  groups and as multiplets for the  $\text{CH}_2$  and CH groups. They displayed positive and negative shifts in the range - 0.78 – 0.01 ppm on complexation.

### **$^{13}\text{C}$ NMR SPECTRAL STUDIES**

Complexes with  $\text{L}^1$  –  $\text{L}^5$  exhibited a peak in the region  $\delta$  150 – 142 ppm due to the most deshielded carbon-2 of the quinazoline moiety which is directly linked to two nitrogens. The signals of the carbons 6' and 7' appeared around  $\delta$  133 and 144 respectively and each of these carbons is linked to a single nitrogen. Among the two carbons more deshielding effect was observed for 7' whose signal was shifted downfield by nearly 11 ppm as compared to that of 6' as it is linked to a tertiary nitrogen. Carbon-4 also being linked to a single nitrogen is shifted downfield to  $\sim$  143 ppm. The carbon resonance observed in the region 55 – 74 ppm in the aliphatic region is due to CH carbon at position 6. The carbons 3 and 5' are least deshielded and appear around 112 ppm. The alkyl carbons in the complexes with  $\text{L}^1$  to  $\text{L}^5$  are observed in the aliphatic region of 39.2 - 8.34 ppm.



**Table 4: <sup>1</sup>H NMR spectral data of Ru(II) complexes with L<sup>1</sup> to L<sup>5</sup> (δ in ppm)\*.**

Compound/ Complex	Quinazoline										Benzimidazole					R-Group			
	NH	CH	7	8	9	10	2'	3'	4'	5'	1"	2"	3"	4"					
etDiq (L <sup>1</sup> )	7.18s	6.03s	7.86d	7.62t	6.78t	6.88d	7.64m	7.24m	7.23m	7.21m	1.80m	0.82t	-	-					
Complex	10.92s	6.15s	7.85d	7.63m	7.30t	7.08d	7.66m	7.56m	7.50m	7.66m	1.78m	0.85t	-	-					
c.i.s	3.74	0.12	-0.01	0.01	0.52	0.20	0.02	0.32	0.27	0.45	-0.02	0.03	-	-					
n-prDiq (L <sup>2</sup> )	7.05s	6.00s	7.87d	7.50t	6.77t	6.85d	7.61d	7.23m	7.20m	7.18m	1.68m	1.20m	0.70t	-					
Complex	7.92s	6.46s	8.00d	7.82m	6.94t	7.02m	7.98d	7.55m	7.49m	7.53m	1.84m	1.36m	0.86t	-					
c.i.s	0.87	0.46	0.13	0.32	0.17	0.17	0.37	0.32	0.29	0.35	0.16	0.16	0.16	-					
i-prDiq (L <sup>3</sup> )	7.18s	5.88m	7.85d	7.59m	6.73t	6.92d	7.62d	7.22m	7.21m	7.19m	2.20m	0.85d	0.71t	-					
Complex	7.79m	6.28s	7.91d	7.79m	6.90t	6.98d	7.63m	7.50m	7.46m	7.42m	1.42m	0.98t	0.84t	-					
c.i.s	0.61	0.40	0.06	0.20	0.17	0.06	0.01	0.28	0.25	0.23	-0.78	0.13	0.13	-					
n-buDiq (L <sup>4</sup> )	7.13s	6.06m	7.86d	7.58m	6.77t	6.87d	7.62d	7.23m	7.21m	7.19m	1.79m	1.66m	1.28m	0.79t					
Complex	7.60s	6.51s	8.10d	8.04m	6.94t	7.03d	8.03m	7.83t	7.50t	7.60m	1.80m	1.34m	1.25m	0.80t					
c.i.s	0.47	0.45	0.24	0.46	0.17	0.16	0.41	0.60	0.29	0.41	0.01	-0.32	-0.03	0.01					
i-buDiq (L <sup>5</sup> )	7.19s	6.08m	7.88d	7.51m	6.80t	6.90m	7.62d	7.28m	7.26m	7.20m	1.73m	1.41m	0.95d	0.82d					
Complex	10.90s	6.28s	7.72d	8.70t	7.31t	7.08d	7.63m	7.55t	7.49t	7.63m	1.76m	1.39m	0.99t	0.84t					
c.i.s	3.71	0.20	-0.16	1.19	0.51	0.18	0.01	0.27	0.23	0.43	0.03	-0.02	0.04	0.02					

c.i.s. = δ (complex) - δ (ligand), s = singlet, d = doublet, t = triplet, m = multiplet; \*: spectra recorded in dms<sub>o</sub>-d<sub>6</sub>.

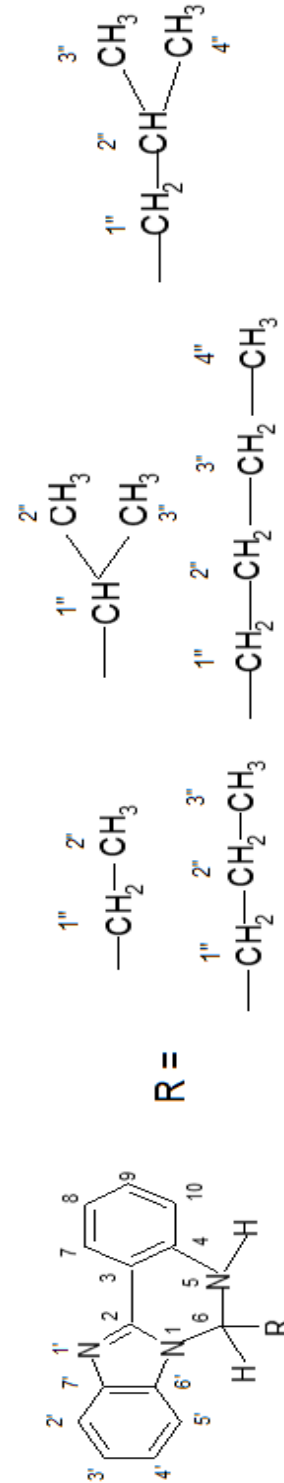
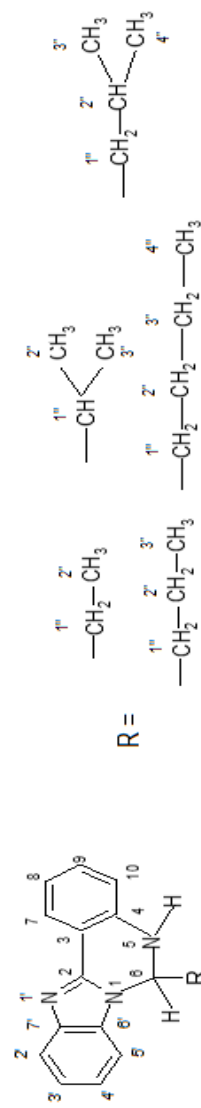


Table 5: <sup>13</sup>C NMR spectral data of Ru(II) complexes with L<sup>1</sup> to L<sup>5</sup> (δ in ppm)\*.

Ligand/ Complex	Carbonyl group	Quinazoline										Benzimidazole										R-Group			
		2	3	4	7	8	9	10	CH	2'	3'	4'	5'	6'	7'	1'	2'	3'	4'						
etDiq	-	146.55	111.92	143.33	124.46	131.46	117.66	114.74	66.47	118.49	121.86	121.81	110.03	132.64	143.68	28.84	8.50								
complex	196.9,196.4	149.77	112.33	143.92	124.92	130.87	118.86	114.21	66.59	119.02	122.85	122.22	112.09	131.88	144.82	26.65	8.34								
c.i.s	-	3.22	0.41	0.59	0.46	-0.59	1.20	-0.53	0.12	0.53	0.99	0.41	2.06	-0.76	1.14	2.19	-0.16								
n-prDiq	-	147.56	112.26	143.46	126.20	132.50	118.66	115.56	65.99	118.81	122.91	122.91	110.54	132.84	143.79	38.46	17.62	13.94							
Complex	197.4,192.0	149.67	112.60	142.01	125.59	131.96	122.19	118.94	73.88	122.27	124.46	123.61	112.60	133.82	144.02	25.60	14.30	12.80							
c.i.s	-	2.11	0.34	-1.45	-0.61	-0.54	3.53	3.38	7.89	3.465	1.55	0.70	2.06	0.98	0.23	-12.86	-3.32	-1.14							
i-prDiq	-	146.75	112.13	143.58	124.38	131.44	117.32	114.20	69.82	118.46	121.78	121.68	110.43	133.05	143.95	34.79	18.13	16.49							
Complex	197.2,191.7	149.44	113.42	143.40	124.21	131.68	118.36	113.79	64.61	118.71	123.35	122.20	112.13	133.42	144.10	37.68	19.40	14.89							
c.i.s	-	2.69	1.29	-0.18	-0.17	-0.24	1.04	-0.41	-5.21	0.25	1.57	0.52	1.70	0.37	0.15	2.89	1.27	1.60							
n-buDiq	-	146.49	112.03	143.22	128.21	131.46	117.73	114.88	65.32	118.56	121.21	121.83	109.93	132.59	143.67	37.92	37.92	17.10	13.43						
Complex	196.9,196.4	149.16	112.34	143.91	129.20	131.88	118.83	115.74	64.84	119.01	123.53	123.34	112.50	133.55	145.59	28.45	25.341	21.88	13.86						
c.i.s	-	2.67	0.31	0.69	0.99	0.42	1.10	0.86	-0.48	0.45	2.32	1.51	2.20	0.96	1.92	-9.47	-12.58	4.78	0.43						
i-buDiq	-	146.43	112.21	142.82	124.47	131.56	117.88	115.23	64.02	118.55	121.87	121.87	109.66	132.35	143.70	43.85	23.14	23.12	21.79						
Complex	197.4, 196.9	149.62	112.34	141.96	124.40	131.61	118.88	115.67	60.98	118.88	125.55	122.30	110.61	133.80	143.94	39.20	36.50	31.12	19.08						
c.i.s	-	3.19	0.13	-0.86	-0.07	0.05	1.00	0.44	-3.04	0.33	3.68	0.43	0.95	1.45	0.24	-4.65	13.36	8.00	-2.71						

c.i.s. = δ (complex) - δ (ligand), \*: spectra recorded in dimso-d.



## STEREOCHEMISTRY

The analytical data, IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral results indicate that the heterocycles are coordinated to the metal ion. The electronic spectral data of the complexes revealed the presence of an octahedral geometry around the metal ion. Thermograms of Ru(II) carbonyl complexes of  $\text{L}^3$ ,  $\text{L}^5$  confer the presence of one coordinated water molecule. Far-IR spectra of these complexes indicated the presence of terminal chlorides and coordinated water and the IR spectra of the complexes of  $\text{L}^5$  revealed the presence of cis carbonyl groups. Based on the above results, mononuclear structure (figure II) has been proposed for these complexes with the substituted benzoimidazoquinazolines acting as monodentate ligands coordinating through the tertiary nitrogen and has cis carbonyl groups around the metal ion. The complex  $[\text{RuCl}_2(\text{CO})_2(\text{L}^3)(\text{H}_2\text{O})]$  exhibited three carbonyl peaks implying the presence of cis and trans carbonyls.

The TGA of the carbonyl complexes of  $\text{L}^1$ ,  $\text{L}^2$ ,  $\text{L}^4$ , showed the absence of lattice and coordinated water. IR spectra and from far-IR spectral studies confirm the presence of cis CO groups and both terminal and bridge chlorides. FAB-MS for the complex of  $\text{L}^1$  supports the binuclear structure of these complexes with the N-heterocycles acting as monodentate ligands with bridge chlorides (figure III).

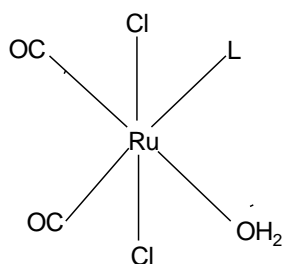


Figure II:  $\text{L} = \text{L}^3, \text{L}^5$

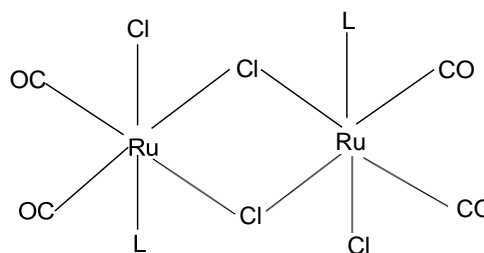


Figure III:  $\text{L} = \text{L}^1, \text{L}^2, \text{L}^4$

### **Catalytic oxidation of benzyl alcohol, hydroquinone and cyclohexanol**

The catalytic activity of the ruthenium(II) complexes including L<sup>1</sup>, L<sup>3</sup>, and L<sup>5</sup> towards the oxidation of substrates such as benzyl alcohol, cyclohexanol, and hydroquinone utilising tertiary-butyl hydroperoxide (t-BuOOH) as co-oxidant was assessed.<sup>22</sup> The transformation of benzyl alcohol into benzaldehyde and subsequent oxidation to benzoic acid. Benzoquinone and cyclohexanone were produced via the conversion of hydroquinone and cyclohexanol, respectively. In order to carry out the reactions, several catalyst-substrate concentrations (1:10, 1:100, and 1:1000) were used in acetonitrile. For benzyl alcohol, hydroquinone, and cyclohexanol, the ideal ratio of catalyst to substrate concentration was determined to be 1:100 and 1:10, respectively.

#### **Procedure for oxidation reaction.**

Acetonitrile (10 mL) was used as solvent, and the catalyst ( $10^{-5}$  mol), substrate ( $10^{-3}$  mol) for benzyl alcohol and hydroquinone, and ( $10^{-4}$  mol for cyclohexanol), and oxidant (t-BuOOH,  $10^{-2}$  mol, 1.3 mL) were all added. The reaction mixture was then agitated on a magnetic stirrer cum heater. The reaction was monitored using TLC and UV-Vis spectroscopy every five minutes. 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, while the substrate peak (258 nm and 294 nm respectively for benzyl alcohol and hydroquinone) diminished and eventually disappeared as the reaction progressed. In the case of the oxidation of benzyl alcohol and hydroquinone, the reactions were finished in 20 to 35 minutes at room temperature, but the cyclohexanol reaction took 5 hours at 60 °C. Because the maximum values of the substrate and product were so close to being identical, UV-Vis spectroscopy was not used to monitor the reaction.

A mixture of 60:40 ethyl acetate and n-hexane was employed as the eluent, and TLC was also utilised to monitor the reaction. Table 5 compiles the findings.

**Table 6:** Oxidation of the substrates using t-BuOOH as co-oxidant in acetonitrile\*

Complex	Temp. (°C) †	Substrate	Product	Time	Yield (%)
[RuCl <sub>2</sub> (CO) <sub>2</sub> L <sup>1</sup> ] <sub>2</sub> ·H <sub>2</sub> O	RT	Benzyl alcohol	Benzoic acid	20 min	100
	RT	Hydroquinone	Benzoquinone	30 min	
	60	Cyclohexanol	Cyclohexanone	5hrs	
[RuCl <sub>2</sub> (CO) <sub>2</sub> (H <sub>2</sub> O) L <sup>3</sup> ]. H <sub>2</sub> O	RT	Benzyl alcohol	Benzoic acid	25min	100
	RT	Hydroquinone	Benzoquinone	35min	
	60	Cyclohexanol	Cyclohexanone	5 hrs	
[RuCl <sub>2</sub> (CO) <sub>2</sub> (H <sub>2</sub> O) L <sup>5</sup> ]. H <sub>2</sub> O	RT	Benzyl alcohol	Benzoic acid	35min	100
	RT	Hydroquinone	Benzoquinone	25min	
	60	Cyclohexanol	Cyclohexanone	5 hrs	

\*: Catalyst: substrate:: 1:100 for benzyl alcohol and hydroquinone and 1:10 for cyclohexanol,

†: RT: room temperature

## CONCLUSION

The ligands and complexes have exhibited diverse characteristic behaviour during the their analyses using various techniques like IR, Far – IR, Electronic, TGA, FAB-MS and NMR studies. Inferences drawn from the studies suggested showed that the ligands coordinated to the ruthenium ion in different ways leading to monomeric and dimeric stereochemistry. Catalytic studies proved them to be good catalysts and further fine tuning could produce better results.

## ACKNOWLEDGEMENTS

The authors thank UGC for a SAP and DST for FIST Programme, CDRI, Lucknow for FAB-mass spectra and elemental analysis, Department of Chemistry, Pondicherry

University, Pondicherry for Far-IR spectra and NMR Center, IISc, Bangalore for recording the NMR spectra. Rita B wishes to thank UGC for a Faculty Improvement Program.

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