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Original scientific paper

## Synthesis of ruthenium(II) carbonyl complexes with 2-monosubstituted and 1,2-disubstituted benzimidazoles

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**Abstract:** The reaction of the polymeric carbonyl complex  $[\text{RuCl}_2(\text{CO})_2]_x$  with 2-monosubstituted and 1,2-disubstituted benzimidazoles and 1,4-bis(benzimidazol-2-yl)benzene ( $\text{L}_9$ ) in 2-methoxyethanol produces various coloured complexes of the formulae  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L})_2] \cdot x\text{H}_2\text{O}$  ( $\text{L} = 1-(o\text{-hydroxybenzyl})\text{-}2\text{-}(o\text{-hydroxyphenyl})\text{benzimidazole}$  ( $\text{L}_1$ ),  $1-(o\text{-hydroxyphenyl})\text{benzimidazole}$  ( $\text{L}_4$ ),  $1-(p\text{-hydroxyphenyl})\text{benzimidazole}$  ( $\text{L}_5$ ),  $1-(p\text{-chlorobenzyl})\text{-}2\text{-}p\text{-chlorophenylbenzimidazole}$  ( $\text{L}_7$ ),  $1\text{-}[1\text{-}(\text{dimethylamino})\text{benzyl}]\text{-}2\text{-}[1\text{-}(\text{dimethylamino})\text{phenyl}]\text{benzimidazole}$  ( $\text{L}_{10}$ ),  $x = 0$ ;  $\text{L} = 2\text{-benzylbenzimidazole}$  ( $\text{L}_8$ ),  $1,4\text{-bis}(\text{benzimidazol-}2\text{-yl})\text{benzene}$  ( $\text{L}_9$ ),  $x = 2$ ;  $\text{L} = 1-(o\text{-chlorobenzyl})\text{-}1-(o\text{-chlorophenyl})\text{benzimidazole}$  ( $\text{L}_6$ );  $x = 3$ ),  $[\text{Ru}(\text{CO})_2\text{Cl}(\text{L}_2)_3]\text{Cl} \cdot 3\text{H}_2\text{O}$  and  $[\text{Ru}(\text{CO})_2(\text{L}_3)_4]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  ( $\text{L}_2 = 1-(m\text{-hydroxybenzyl})\text{-}2-(m\text{-hydroxyphenyl})\text{benzimidazole}$ ;  $\text{L}_3 = 1-(p\text{-hydroxybenzyl})\text{-}2-(p\text{-hydroxyphenyl})\text{benzimidazole}$ ). The complexes were characterized by elemental analysis, conductivity measurements, as well as infrared, electronic,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectral studies.

**Keywords:** carbonyl complexes; 2-mono and 1,2-disubstituted benzimidazoles; ruthenium(II) carbonyl complexes.

### INTRODUCTION

Ruthenium exhibits dissimilar behaviour in forming complexes compared to the other platinum group metals. It exhibits variable oxidation states 0, +2, +3 and +4, as well as unusual oxidation states. Furthermore, the metal also shows different coordination numbers for the same oxidation state. The complexes of ruthenium are important due to their catalytic activity towards several reactions, such as polymerisation, photo-splitting of water, solar energy conversion,<sup>1</sup> hydroformylation,<sup>2</sup> isomerisation and other reactions involving organic substrates.<sup>3–5</sup> Some of the complexes form adducts with dioxygen and dinitrogen and the study

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of the properties of such adducts was helpful in the understanding of the mechanism of oxygen metabolism and nitrogen fixation in biological systems.<sup>6,7</sup>

Carbonyl complexes of ruthenium are important in the homogeneous catalysis of carbonylation and oxo reactions.<sup>8</sup> Much of the knowledge concerning carbonyl complexes has come from the study of metal complexes in lower oxidation states,<sup>9</sup> mainly due to the stabilization of these oxidation states by CO. Studies of carbonyl complexes of higher valent ruthenium in aqueous solutions are, however, scarce because of the hydrolytic tendency of the metal ion in aqueous solution.<sup>10,11</sup> The synthesis of various carbonyl complexes by the passage of CO through a suspension of substituted N-heterocyclic complexes of ruthenium(II) was reported.<sup>12</sup> However, *in situ* reactions wherein CO generation occurs in a homogeneous medium are simpler and more effective. Reaction of  $\text{RuCl}_3 \cdot \text{H}_2\text{O}$  with CO in acidic medium yields the octahedral species  $[\text{RuCl}_5(\text{CO})]^{2-}$ .<sup>12</sup> In view of the increased interest in oxygenation and carbonylation of ruthenium(II) complexes as new catalysts,<sup>13,14</sup> the synthesis and characterization of carbonyl complexes of ruthenium(II) with various 2-monosubstituted and 1,2-disubstituted N-heterocycles are reported herein. The substituted benzimidazoles used for the synthesis of ruthenium(II) chlorocarbonyl complexes are: 1-(*o*-hydroxybenzyl)-2-(*o*-hydroxyphenyl)benzimidazole ( $\text{L}_1$ ), 1-(*m*-hydroxybenzyl)-2-(*m*-hydroxyphenyl)benzimidazole ( $\text{L}_2$ ), 1-(*p*-hydroxybenzyl)-2-(*p*-hydroxyphenyl)benzimidazole ( $\text{L}_3$ ), 2-(*o*-hydroxyphenyl)benzimidazole ( $\text{L}_4$ ), 2-(*p*-hydroxyphenyl)benzimidazole ( $\text{L}_5$ ), 1-(*o*-chlorobenzyl)-1-(*o*-chlorophenyl)benzimidazole ( $\text{L}_6$ ), 1-(*p*-chlorobenzyl)-2-(*p*-chlorophenyl)benzimidazole ( $\text{L}_7$ ), 2-benzylbenzimidazole ( $\text{L}_8$ ), 1,4-bis(benzimidazol-2-yl)benzene ( $\text{L}_9$ ) and 1-[*p*-(dimethylamino)benzyl]-2-[*p*-(dimethylamino)phenyl]benzimidazole ( $\text{L}_{10}$ ), Fig. 1.

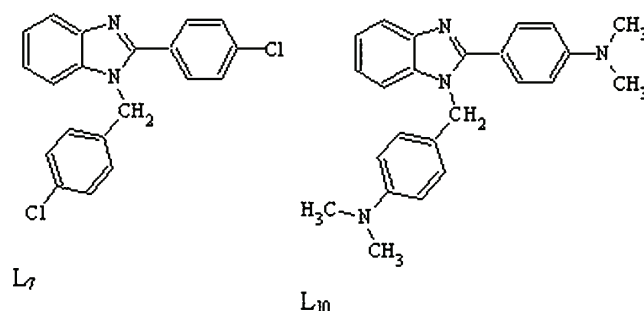


Fig. 1. Structures of the ligands 1-(*p*-chlorobenzyl)-2-(*p*-chlorophenyl)benzimidazole ( $\text{L}_7$ ) and 1-[*p*-(dimethylamino)benzyl]-2-[*p*-(dimethylamino)phenyl]benzimidazole ( $\text{L}_{10}$ ).

## EXPERIMENTAL

### Reagents

Hydrated ruthenium(II) chloride was purchased from Arora-Matthey. *o*-Phenylenediamine, salicylaldehyde, *m*-hydroxybenzaldehyde and *p*-hydroxybenzaldehyde were fine

chemicals from Merck/SD. The employed solvents were Merck chemicals, which were purified according to literature methods.<sup>15</sup>

#### Methods and instruments

The microanalyses of the carbon, hydrogen and nitrogen contents of the complexes were performed on a Carlo-Erba analyzer. The IR spectra (in nujol) were recorded on a Nicolet 4000D spectrophotometer. The molar conductivity measurements were made in dimethylformamide (DMF) using a digital conductivity meter-304 (SYSTRONICS) with a conventional dip type conductivity cell with a cell constant 1.00 cm<sup>-1</sup>. The NMR spectra were recorded (in DMSO-*d*<sub>6</sub>) on a Bruker WH-270 or AMX-400 MHz spectrometer using TMS as the internal standard. A Shimadzu UV-Vis-NIR Model UV-3101pc and a Hitachi-V3400 UV-visible-spectrophotometer were used for recording the electronic spectra of the solid samples as nujol-mull.

#### Preparation of the ligands

The ligands were prepared according to literature methods.<sup>16</sup> A mixture of salicylaldehyde (0.20 mol) and *o*-phenylenediamine (0.10 mol) in the molar ratio of 2:1 in benzene was refluxed on a water bath for 1 h. The solution was cooled and left over night. After the evaporation of the solvent, a yellow solid separated out. This was filtered to obtain 1-(*o*-hydroxybenzyl)-2-(*o*-hydroxyphenyl)benzimidazole (L<sub>1</sub>).

A similar procedure was followed for the preparation of the other ligands. A mixture of *m*-hydroxybenzaldehyde (0.20 mol) and *o*-phenylenediamine (0.10 mol) in benzene was refluxed for 1 h. After workup, a pale-yellow coloured compound, L<sub>2</sub>, (yield: 90 %) was obtained.

A solution of *p*-hydroxybenzaldehyde (0.20 mol) and *o*-phenylenediamine (0.10 mol) in benzene was refluxed for 1 h. After workup, a pale-buff coloured compound, L<sub>3</sub>, (yield: 60 %) was obtained.

To a solution of *o*-phenylenediamine (0.10 mol) in benzene (100 mL), a solution of *o*-chlorobenzaldehyde (0.20 mol) was added and the mixture was refluxed for 2 h on a steam bath. On standing over night, a yellow crystalline solid separated out, which was filtered to afford L<sub>6</sub> (yield: 80 %).

A solution of *o*-phenylenediamine (0.10 mol) and *p*-chlorobenzaldehyde (0.20 mol) in benzene (100 mL) was refluxed of 2 h on a steam bath. On standing over night, a yellow crystalline solid separated out, which was filtered to afford L<sub>7</sub> (yield: 70 %).

A mixture of *o*-phenylenediamine (0.10 mol) and *p*-(dimethylamino)benzaldehyde (0.20 mol) in benzene (100 mL) was refluxed for 2 h on a steam bath. On standing over night, a yellow crystalline solid, 1-[*p*-(dimethylamino)benzyl]-2-[*p*-(dimethylamino)phenyl]benzimidazole, (L<sub>10</sub>), separated, which was recrystallized from ethanol to afford pale yellow crystals (yield: 80 %).

The ligand L<sub>9</sub> was prepared by refluxing *o*-phenylenediamine (20 mmol) and terephthalic acid (10 mmol) in syrupy phosphoric acid at 240 °C for 4 h. The coloured melt was poured into cold water (500 mL) under stirring, whereby a blue-green coloured precipitate was obtained. The precipitate was neutralized with 10 % aqueous sodium carbonate solution. The resulting solid was recovered by filtration and then recrystallized from ethanol to afford a pale pink-coloured compound (yield: 75 %).

#### Preparation of the complexes

The polymeric compound [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>x</sub> was prepared by reacting RuCl<sub>3</sub>·3H<sub>2</sub>O (1.0 mmol) with HCOOH (2.0 mmol). This was refluxed for 4–5 h, whereby the reaction mixture

turned lemon yellow. The resultant solution was cooled and evaporated slowly to obtain a yellow-coloured solid. To this, a solution of the ligand (2.0 mmol) in 2-methoxyethanol (10 mL) was added and the solution was refluxed for 4–5 h. After the evaporation of the solvent, distilled water (5.0 mL) was added, when a coloured compound separated out. The solid was filtered and washed with water and dried under vacuum (yield: 70–80 %).

## RESULTS AND DISCUSSION

### *Synthesis and characterization*

The complexes were soluble in common organic solvents. The molar conductance values of the complexes (Table I) in nitrobenzene indicated the uni-univalent and uni-bivalent nature of the  $[\text{RuCl}(\text{CO})_2(\text{L}_2)_3]\text{Cl}\cdot 3\text{H}_2\text{O}$  and  $[\text{Ru}(\text{CO})_2(\text{L}_3)_4]\text{Cl}_2\cdot 3\text{H}_2\text{O}$  complexes, respectively. All the other complexes showed non-electrolytic behaviour.

TABLE I. Physical properties and analytical data of the ruthenium(II) carbonyl complexes with substituted benzimidazoles

Complex	Colour	M.p. °C	$\Lambda^a$ $\text{S cm}^2 \text{ mol}^{-1}$	Anal. (Calcd.), %		
				C	H	N
$[\text{RuCl}_2(\text{CO})_2(\text{L}_1)_2]$	Brown	>250	0.60	58.77 (58.60)	4.35 (3.74)	6.01 (6.51)
$[\text{RuCl}(\text{CO})_2(\text{L}_2)_3]\text{Cl}\cdot 3\text{H}_2\text{O}$	Pale-green	144	27	60.42 (60.49)	4.46 (4.42)	6.70 (6.82)
$[\text{Ru}(\text{CO})_2(\text{L}_3)_4]\text{Cl}_2\cdot 3\text{H}_2\text{O}$	Grey	174	55	63.42 (63.64)	4.77 (4.69)	7.50 (7.23)
$[\text{RuCl}_2(\text{CO})_2(\text{L}_4)_2]$	Straw	194	7.5	51.62 (51.86)	4.00 (3.10)	9.03 (8.63)
$[\text{RuCl}_2(\text{CO})_2(\text{L}_5)_2]$	Straw	216	12	51.26 (51.86)	4.02 (3.10)	9.10 (8.63)
$[\text{RuCl}_2(\text{CO})_2(\text{L}_6)_2]\cdot 3\text{H}_2\text{O}$	Grey	>250	0.20	51.05 (51.03)	3.81 (3.67)	7.07 (5.67)
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_7)_2]$	Grey	>250	0.30	54.40 (53.98)	3.34 (3.02)	6.70 (5.99)
$[\text{RuCl}_2(\text{CO})_2(\text{L}_8)_2]\cdot 2\text{H}_2\text{O}$	Dark green	128	5.0	53.18 (52.94)	4.59 (4.14)	7.45 (8.23)
$[\text{RuCl}_2(\text{CO})_2(\text{L}_9)_2]\cdot 2\text{H}_2\text{O}$	Yellow	>280	2.5	57.50 (57.05)	3.66 (3.64)	12.36 (12.66)
$[\text{RuCl}_2(\text{CO})_2(\text{L}_{10})_2]$	Grey	186	0.20	62.10 (61.97)	5.64 (5.40)	10.36 (11.56)

<sup>a</sup>Molar conductance of  $\approx 10^{-3}$  M solution in nitrobenzene

### *Spectral studies*

The infrared spectra (in nujol mull) of the complexes were similar to those of the uncoordinated ligands except for slight shifts in the positions of some of the bands and some changes in their intensities due to coordination (Tables II and III). In the spectrum of the  $[\text{RuCl}_2(\text{CO})_2(\text{L}_8)_2]\cdot 2\text{H}_2\text{O}$  complex, bands due to the

$\nu(\text{OH})$  of hydration water and  $\nu(\text{NH})$  of the ligand appeared at 3440 and 3190  $\text{cm}^{-1}$ , respectively.<sup>17,18</sup> The band due to  $\nu(\text{OH})$  of lattice water molecules<sup>19,20</sup> was observed around 3350  $\text{cm}^{-1}$  in the carbonyl complexes of  $\text{L}_2$ ,  $\text{L}_3$  and  $\text{L}_6$ . The  $\nu(\text{OH})$  of the ligands containing a phenolic OH group and their complexes appeared around 3200  $\text{cm}^{-1}$ . Bands due to  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{C})$  vibrations occurred around 1620  $\text{cm}^{-1}$ , very close to each other, as weak bands in the spectra of free heterocycles and they were shifted to lower or higher wave numbers by 5–10  $\text{cm}^{-1}$  on complexation. These shifts in the positions of  $\nu(\text{C}=\text{N})$  and  $\nu(\text{C}=\text{C})$  indicate coordination of the substituted benzimidazoles *via* the tertiary nitrogen of the imidazole moiety.<sup>21</sup> The spectra of the complexes of  $\text{L}_8$ ,  $\text{L}_4$ ,  $\text{L}_5$  and  $\text{L}_9$  exhibited the NH out-of-plane bending vibration at around 730  $\text{cm}^{-1}$ . A weak band in the spectrum of  $[\text{RuCl}_2(\text{CO})_2(\text{L}_{10})_2]$  at 1480  $\text{cm}^{-1}$  is assigned to the N–CH<sub>3</sub> deformation mode. Another band at around 1320  $\text{cm}^{-1}$  is attributed to C–N stretching of the N–CH<sub>3</sub> group.<sup>22</sup> Medium intensity bands in the spectra of the complexes at around 1490, 1200, 1100, 720 and 540  $\text{cm}^{-1}$  are assignable to the *o*-, *m*-, *p*-disubstituted benzene ring. In the spectra of the  $[\text{RuCl}_2(\text{CO})_2(\text{L}_6)_2] \cdot 2\text{H}_2\text{O}$  and  $[\text{RuCl}_2(\text{CO})_2(\text{L}_7)_2]$  complexes, a strong band around 760  $\text{cm}^{-1}$  is assigned to the C–Cl stretching vibration.<sup>23</sup> Two intense bands at  $\approx 1900$  and  $\approx 2000$   $\text{cm}^{-1}$  were observed in the spectra of all the complexes. These are attributed to  $\nu(\text{CO})$  and the data suggest that the two carbonyl groups are placed in the *cis* position.<sup>19,20</sup> In the case of the  $[\text{Ru}(\text{CO})_2(\text{L}_8)_2] \cdot 2\text{H}_2\text{O}$  and  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_1)_2]$  complexes, one of the two  $\nu(\text{CO})$  peaks splits further and to give a weak band which may be due to a mixture of two isomers.

TABLE II. IR spectral data ( $\text{cm}^{-1}$ ) of the ruthenium(II) carbonyl complexes

Compound	$\nu(\text{NH})$	$\nu(\text{O}-\text{H})$ of lattice $\text{H}_2\text{O}$	$\nu(\text{O}-\text{H})$ coordinated $\text{H}_2\text{O}/\text{ligand}$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$	$\nu(\text{N}-\text{CH}_2)$	<i>o</i> -, <i>m</i> -, <i>p</i> - Disubstituted benzene
$\text{L}_1$	–	–	–	–	1616 <sub>s</sub>	1590 <sub>s</sub>	1491 <sub>m</sub> , 1057 <sub>m</sub> , 740 <sub>m</sub> , 540 <sub>w</sub>
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_1)_2]$	–	–	3190 <sub>br</sub>	2055 <sub>s</sub> 1988 <sub>s</sub> 1936 <sub>s</sub>	1610 <sub>s</sub>	1600 <sub>s</sub>	1496 <sub>m</sub> , 1052 <sub>m</sub> , 748 <sub>m</sub>
$[\text{Ru}(\text{CO})_2\text{Cl}(\text{L}_2)_3]\text{Cl} \cdot 3\text{H}_2\text{O}$	–	3320 <sub>br</sub>	3178 <sub>br</sub>	2040 1962	1624 <sub>s</sub>	1590 <sub>s</sub>	1310 <sub>s</sub> , 1150 <sub>s</sub> , 726 <sub>ms</sub>
$\text{L}_4$	3170 <i>br</i>	–	3230 <sub>w</sub>	–	1616 <sub>s</sub>	–	1243 <sub>w</sub> , 1090 <sub>w</sub> , 722 <sub>s</sub>

TABLE II. Continued

Compound	$\nu(\text{NH})$	$\nu(\text{O-H})$ of lattice $\text{H}_2\text{O}$	$\nu(\text{O-H})$ coordinated $\text{H}_2\text{O}/\text{ligand}$	$\nu(\text{C=O})$	$\nu(\text{C=N})$ and $\nu(\text{C=C})$	$\nu(\text{N-CH}_2)$	<i>o</i> -, <i>m</i> -, <i>p</i> - Disubstituted benzene
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_4)_2]$	3178 <i>br</i>	—	3238 $w$	2045 $s$ 1967 $s$	1626 $s$	—	1243 $s$ , 1093 $w$ , 726 $s$
$\text{L}_5$	3160 <i>br</i>	—	3203 $w$	—	1616 $s$	—	1253 $s$ , 1010 $s$ , 736 $m$
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_5)_2]$	3166 <i>br</i>	—	3172 $b$	2034 $s$ 1962 $s$	1605 $s$	—	1233 $w$ , 1020 $w$ , 730 $m$
$\text{L}_8$	3180 <i>br</i>	—	—	—	1600 $s$	1558 $w$	1108 $w$ , 720 $s$ , 548 $s$
$[\text{RuCl}_2(\text{CO})_2(\text{L}_8)_2] \cdot 2\text{H}_2\text{O}$	3190 <i>br</i>	3440 $br$	—	2034 $s$ 2064 $s$ 1988	1605 $s$	1554 $w$	1103 $s$ , 731 $s$ , 545 $w$
$\text{L}_9$	3150 <i>br</i>	—	—	—	1626 $s$	—	1226 $s$ , 1090 $s$ , 742 $s$ , 540 $w$
$\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_9)_2 \cdot 2\text{H}_2\text{O}$	3170 <i>br</i>	3400 $br$	—	2045 $s$ 1962 $s$	1631 $s$	—	1220 $s$ , 1090 $s$ , 747 $s$ , 529 $w$

TABLE III. IR spectral data ( $\text{cm}^{-1}$ ) of the ruthenium(II) carbonyl complexes

Compound	$\nu^{\text{Coordinated}}$ lattice $\text{H}_2\text{O}$	$\nu(\text{OH/NH})$	$\nu(\text{C=O})$	$\nu(\text{C=C})$ and $\nu(\text{C=N})$	$\nu(\text{N-CH}_2)$	<i>o</i> -, <i>m</i> -, <i>p</i> -Substituted benzene
$\text{L}_3$	—	3260	—	1610 $s$	1594 $s$	1468 $b$ , 1181 $m$ , 1114 $s$ , 752 $m$
$[\text{Ru}(\text{CO})_2(\text{L}_3)_4]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$	3358 $br$	3198 $br$	2049 $s$ 1972 $s$	1621 $s$	1600 $s$	1476 $s$ , 1279 $s$ , 1186 $m$ , 726 $s$
$\text{L}_{10}$	—	—	—	1616 $s$	1590 $s$	1470 $s$ , 1180 $m$
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_{10})_2]$	—	—	2050 $s$ 1962 $s$	1610 $s$	1595 $s$	1455 $s$ , 1171 $s$ , 750 $s$ , 653 $s$
$\text{L}_6$	—	—	—	1616 $s$	1590 $s$	1438 $s$ , 1196 $m$ , 788 $s$
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_6)_2] \cdot 3\text{H}_2\text{O}$	3369 $s$	—	2055 $s$ 1983 $s$	1600 $s$	1584 $s$	1450 $s$ , 1190 $s$ , 780 $s$
$\text{L}_7$	—	—	—	1600 $w$	1590 $s$	1460 $s$ , 1220 $s$ , 1192 $s$ , 780 $s$
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_7)_2]$	—	—	2052 $s$ 1982 $s$	1616 $s$	1588 $s$	1464 $s$ , 1234 $s$ , 1198 $s$ , 786 $s$

The electronic spectra of the complexes (recorded as solids in nujol) were recorded and the spectral data are listed in Table IV. The bands observed around 17700 and 25000  $\text{cm}^{-1}$  are assigned to the transitions  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$ , respectively, based on the earlier assignments.<sup>24–27</sup> A strong band observed around 34000  $\text{cm}^{-1}$  is assigned to the charge transfer transition.

TABLE IV. Electronic spectral data ( $\text{cm}^{-1}$ ) of the ruthenium (II) carbonyl complexes

Compound	Electronic transitions and assignments		
	$\pi \rightarrow \pi^*$	${}^1A_{1g} \rightarrow {}^1T_{2g}$	${}^1A_{1g} \rightarrow {}^1T_{1g}$
[Ru(CO) <sub>2</sub> (L <sub>9</sub> ) <sub>2</sub> Cl <sub>2</sub> ]·2H <sub>2</sub> O	28570	25640	–
[Ru(CO) <sub>2</sub> (L <sub>1</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	32786	27780	12500
[Ru(CO) <sub>2</sub> Cl(L <sub>2</sub> ) <sub>3</sub> ]Cl·3H <sub>2</sub> O	–	27027	20000
[Ru(CO) <sub>2</sub> (L <sub>3</sub> ) <sub>4</sub> ]Cl <sub>2</sub> ·3H <sub>2</sub> O	31250	25974	–
[Ru(CO) <sub>2</sub> (L <sub>4</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	30300	26310	–
[Ru(CO) <sub>2</sub> (L <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	38460	29410	–
[Ru(CO) <sub>2</sub> (L <sub>6</sub> ) <sub>2</sub> Cl <sub>2</sub> ]·3H <sub>2</sub> O	–	26500	17500
[Ru(CO) <sub>2</sub> (L <sub>7</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	34722	31250	27780
[Ru(CO) <sub>2</sub> (L <sub>8</sub> ) <sub>2</sub> Cl <sub>2</sub> ]·2H <sub>2</sub> O	–	26310	16950
[RuCl <sub>2</sub> (CO) <sub>2</sub> (L <sub>10</sub> ) <sub>2</sub> ]	26450	20490	12500

The <sup>1</sup>H-NMR spectra of the free ligands and their complexes were recorded in DMSO-*d*<sub>6</sub> and the spectra of the complexes displayed features similar to those of the ligands (Tables Va and Vb), suggesting their close similarity with the free ligands. The resonance due to the hydroxyl proton in the complexes of L<sub>4</sub> and L<sub>5</sub> was observed at  $\delta$  7.83 and 10.00 ppm, respectively, while the resonance due to the imine proton appeared in the range 12.65–13.45 ppm. In the complexes of L<sub>1</sub>, the signal due to the OH protons of the benzyl group was found at 10.72 ppm, while it was found at around 9.7 ppm in the complexes of L<sub>2</sub> and L<sub>3</sub>. The signal due to hydroxyl protons of the phenylene ring in the [RuCl<sub>2</sub>(CO)<sub>2</sub>(L<sub>1</sub>)<sub>2</sub>] complex was observed at 10.26 ppm and it appeared at around 9.72 ppm in the complexes of L<sub>2</sub> and L<sub>3</sub>. The spectra of L<sub>9</sub> and its complexes showed a resonance around 13.5 ppm, due to the imine proton. In the complex [RuCl<sub>2</sub>(CO)<sub>2</sub>(L<sub>10</sub>)<sub>2</sub>], the signals due to the –CH<sub>3</sub> protons of the benzyl and phenylene groups were observed at around 2.90 and 2.80 ppm, respectively. The methylene proton resonances are found in the range 5.40–7.30 ppm in the carbonyl complexes of 1,2-disubstituted benzimidazoles. The proton signals of the benzyl ring in all the 1,2-disubstituted benzimidazole carbonyl complexes were found in the range 6.40–7.90 ppm, while those due to the phenylene protons were observed in the range 7.10–7.95 ppm. Furthermore, the resonances due to the –CH<sub>2</sub>– protons shifted by 0.15–0.40 ppm. The coordination induced larger shifts at positions 4 and 6' because of polarization of the electron density towards the metal ion after complexation.<sup>28</sup> The coordination-induced shifts (c.i.s.) for various protons of the coordinated N-heterocycles were either positive or negative, which indicates that M→L ( $\sigma^-$ ) or L→M

( $\pi$ -) electron transfer occurs. A similar observation was made earlier for the spectra of related complexes.<sup>21,29–32</sup>

TABLE Va. <sup>1</sup>H-NMR spectral data ( $\delta$  / ppm) of the ruthenium(II) carbonyl complexes (the values in the parentheses are coordination induced shifts (c.i.s.) =  $\delta_{\text{complex}} - \delta_{\text{ligand}}$ )

Compound	2''	6'	4	7	CH <sub>2</sub>	O–H <sub>b</sub>	O–H <sub>p</sub>	N–H
L <sub>1</sub>	–	7.39 <i>m</i>	7.71 <i>d</i>	7.39 <i>m</i>	5.42 <i>s</i>	9.90 <i>s</i>	9.90 <i>s</i>	–
[RuCl <sub>2</sub> (CO) <sub>2</sub> (L <sub>1</sub> ) <sub>2</sub> ]	–	7.44 <i>m</i> (0.05)	7.74 <i>m</i> (0.03)	1.74 <i>m</i> (0.35)	5.66 <i>m</i> (0.24)	10.72 <i>s</i> (0.82)	10.26 <i>s</i> (0.36)	–
L <sub>2</sub>	6.47 <i>s</i>	7.09 <i>m</i>	7.72 <i>m</i>	7.23 <i>m</i>	5.48 <i>s</i>	9.62 <i>s</i>	9.62 <i>s</i>	–
[Ru(CO) <sub>2</sub> Cl(L <sub>2</sub> ) <sub>3</sub> ]Cl·3H <sub>2</sub> O	7.16 <i>s</i> (0.69)	6.92 <i>d</i> (–0.17)	7.71 <i>d</i> (–0.01)	7.71 <i>d</i> (0.48)	5.48 <i>s</i> (0.0)	9.44 <i>m</i> (–0.18)	9.75 <i>s</i> (0.16)	–
L <sub>3</sub>	6.83	7.41	7.64	7.56	5.41 <i>s</i>	9.40 <i>s</i>	9.6 <i>s</i>	–
[Ru(CO) <sub>2</sub> (L <sub>3</sub> ) <sub>4</sub> ]Cl <sub>2</sub> ·3H <sub>2</sub> O	6.84 (0.01)	7.40 (–0.01)	7.65 (0.01)	7.57 (0.01)	5.44 <i>s</i>	9.72 <i>b</i> (0.32)	9.72 <i>b</i> (–0.24)	–
L <sub>4</sub>	–	7.65 <i>d</i>	8.05 <i>d</i>	8.05 <i>d</i>	–	–	7.38 <i>s</i>	13.15 <i>s</i>
[Ru(CO) <sub>2</sub> (L <sub>4</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	–	6.15 <i>d</i> (–1.50)	8.20 <i>d</i> (0.15)	7.67 <i>d</i> (–0.38)	–	–	7.83 <i>s</i> (0.45)	13.57 <i>s</i> (0.47)
L <sub>5</sub>	–	7.14 <i>m</i>	8.03 <i>d</i>	8.03 <i>d</i>	–	–	10.00 <i>s</i>	12.65
Ru(CO) <sub>2</sub> (L <sub>5</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	–	7.17 <i>m</i> (0.03)	8.01 <i>d</i> (–0.02)	8.01 <i>d</i> (–0.02)	–	–	10.00 (0.0)	13.42 <i>s</i> (0.77)
L <sub>6</sub>	–	7.52 <i>d</i>	7.92 <i>m</i>	7.42 <i>d</i>	5.43 <i>s</i>	–	–	–
[Ru(CO) <sub>2</sub> Cl <sub>2</sub> (L <sub>6</sub> ) <sub>2</sub> ]·3H <sub>2</sub> O	–	7.23 <i>d</i> (–0.29)	7.76 <i>d</i> (–0.16)	7.51 <i>d</i> (0.09)	5.42 <i>s</i> (–0.01)	–	–	–
L <sub>7</sub>	7.65 <i>m</i>	7.93 <i>m</i>	8.00 <i>d</i>	8.00 <i>d</i>	7.23 <i>d</i>	–	–	–
[Ru(CO) <sub>2</sub> (L <sub>6</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	7.27 <i>m</i> (–0.38)	7.63 <i>m</i> (–0.30)	8.19 <i>d</i> (0.19)	8.19 <i>d</i> (0.19)	7.27 <i>m</i> (0.04)	–	–	–

TABLE Vb. <sup>1</sup>H-NMR spectral data ( $\delta$  / ppm) of the ruthenium(II) carbonyl complexes (the values in the parentheses are coordination induced shifts (c.i.s.) =  $\delta_{\text{complex}} - \delta_{\text{ligand}}$ )

Compound	2''	3''	5''	6''	6'	4	CH <sub>2</sub>	N–H	2	Benzyl CH <sub>3</sub>	Phenyl CH <sub>3</sub>
L <sub>8</sub>	–	–	–	–	7.17 <i>q</i>	7.52 <i>m</i>	5.73 <i>s</i>	–	7.52 <i>m</i>	–	–
[Ru(CO) <sub>2</sub> Cl <sub>2</sub> (L <sub>8</sub> ) <sub>2</sub> ]·2H <sub>2</sub> O	–	–	–	–	7.44 <i>m</i> (0.27)	7.80 <i>d</i> (0.28)	5.64 <i>d</i> (–0.09)	–	7.80 (–0.28)	–	–
L <sub>9</sub>	–	–	–	–	7.25 <i>m</i>	7.69 <i>d</i>	8.35 <i>s</i>	13.5 <i>s</i>	–	–	–
[Ru(CO) <sub>2</sub> Cl <sub>2</sub> (L <sub>9</sub> ) <sub>2</sub> ]·2H <sub>2</sub> O	–	–	–	–	7.27 <i>m</i> (0.02)	7.66 <i>m</i> (–0.03)	8.38 <i>t</i> (0.03)	13.84 <i>m</i> (0.34)	–	–	–
L <sub>10</sub>	6.63 <i>t</i>	6.88 <i>d</i>	6.88 <i>d</i>	6.63 <i>t</i>	7.61 <i>m</i>	7.99 <i>d</i>	5.42 <i>s</i>	–	–	2.99 <i>s</i>	2.89 <i>s</i>
Ru(CO) <sub>2</sub> Cl <sub>2</sub> (L <sub>10</sub> )	6.91 <i>d</i> (0.28)	6.83 <i>d</i> (–0.05)	6.83 <i>d</i> (–0.05)	6.58 (–0.08)	7.23 <i>m</i> (–0.38)	7.15 <i>d</i> (–0.84)	4.70 <i>s</i> (–0.72)	–	–	2.83 <i>m</i> (–0.16)	2.77 <i>m</i> (–0.12)

The <sup>13</sup>C-NMR spectral data of the free ligands and their complexes are tabulated in Table VI. The spectra of the complexes show resonances in the regions that are in agreement with those expected based on the carbon environments. The resonance at  $\delta$ 47.20 ppm was assigned to the N–CH<sub>3</sub> carbon in the L<sub>10</sub> complex.



In the complexes of L<sub>4</sub> and L<sub>5</sub>, the signal due to C–OH was found at 129.00 and 118.99 ppm, respectively. The resonance due to C–OH of the benzyl group of the L<sub>1</sub> complex was found at 110.50 ppm, while in the complexes of L<sub>2</sub> and L<sub>3</sub>, it was observed at 153.30 and 156.60 ppm, respectively. The resonance of phenylene C–OH of L<sub>1</sub> appeared at 161.73 ppm and in the complexes of L<sub>2</sub> and L<sub>3</sub> at 157.64 and 158.87 ppm, respectively. The resonance of the CH<sub>2</sub> carbon occurred near 47.00 ppm in the L<sub>2</sub> and L<sub>3</sub> complexes. In the case of the [RuCl<sub>2</sub>(CO)<sub>2</sub>(L<sub>9</sub>)<sub>2</sub>] complex, the resonance signal due to the benzimidazole ring occurred in the range 112.15–150.0 ppm. In the [RuCl<sub>2</sub>(CO)<sub>2</sub>(L<sub>8</sub>)<sub>2</sub>]·2H<sub>2</sub>O complex, the signals for C-4, 8, 9 and 1' were shifted to a greater extent and, therefore, have higher c.i.s. values. The resonance due to the CH<sub>2</sub> carbon was observed at 57.88 ppm. The resonance signal in the region 190–200 ppm was observed in all the complexes, which indicates the presence of coordinated carbonyl groups.

TABLE VI. <sup>13</sup>C-NMR spectral data ( $\delta$ / ppm) of the ruthenium(II) carbonyls with substituted benzimidazoles (the values in the parentheses are coordination induced shifts (c.i.s.) =  $\delta_{\text{complex}} - \delta_{\text{ligand}}$ )

Compound	CO	1''	1'	6'	4	8	9	2	CH <sub>2</sub>
L <sub>1</sub>	–	120.37 <sub>s</sub>	120.37 <sub>s</sub>	127.86 <sub>s</sub>	136.66 <sub>s</sub>	140.50 <sub>s</sub>	146.98	157.33 <sub>d</sub>	65.04 <sub>s</sub>
[RuCl <sub>2</sub> (CO) <sub>2</sub> (L <sub>1</sub> ) <sub>2</sub> ]	190.6 <sub>s</sub>	120.30 <sub>s</sub>	120.30 <sub>s</sub>	127.16 <sub>s</sub>	137.45	140.48 <sub>s</sub>	146.96 <sub>s</sub>	157.56 <sub>s</sub>	65.04 <sub>s</sub>
		(–0.07)	(–0.07)	(–0.70)	(–0.21) <sub>s</sub>	(–0.02)	(–0.02)	(–0.23)	(0.0)
L <sub>2</sub>	–	116.97 <sub>s</sub>	116.97 <sub>s</sub>	122.19 <sub>s</sub>	131.23 <sub>s</sub>	135.90 <sub>s</sub>	138.33 <sub>s</sub>	142.64 <sub>s</sub>	47.48 <sub>s</sub>
[Ru(CO) <sub>2</sub> Cl(L <sub>2</sub> ) <sub>3</sub> ]Cl·3H <sub>2</sub> O	199.0 <sub>s</sub>	116.94 <sub>s</sub>	116.91 <sub>s</sub>	122.13 <sub>d</sub>	131.20 <sub>s</sub>	135.91 <sub>s</sub>	138.34 <sub>s</sub>	142.6 <sub>s</sub>	47.90 <sub>s</sub>
		(–0.03)	(–0.06)	(–0.06)	(–0.03)	(0.01)	(–0.04)	(–0.04)	(0.42)
L <sub>3</sub>	–	120.85	127.11 <sub>s</sub>	115.53 <sub>s</sub>	127.49 <sub>s</sub>	135.87 <sub>s</sub>	142.80 <sub>s</sub>	153.50 <sub>s</sub>	47.30 <sub>s</sub>
[Ru(CO) <sub>2</sub> (L <sub>3</sub> ) <sub>4</sub> ]Cl <sub>2</sub> ·3H <sub>2</sub> O	194.35 <sub>d</sub>	120.87	129.27	115.56	127.59 <sub>t</sub>	135.88 <sub>s</sub>	142.76 <sub>s</sub>	153.65 <sub>s</sub>	47.12 <sub>s</sub>
		(0.02)	(2.16)	(0.03)	(0.10)	(0.01)	(–0.04)	(0.05)	(–0.18)
L <sub>4</sub>	–	112.66 <sub>s</sub>	–	117.18 <sub>s</sub>	126.23 <sub>s</sub>	131.67 <sub>s</sub>	131.67 <sub>s</sub>	158.09 <sub>s</sub>	–
[Ru(CO) <sub>2</sub> (L <sub>4</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	190.10 <sub>s</sub>	109.54 <sub>s</sub>	–	114.15 <sub>s</sub>	131.89 <sub>s</sub>	134.56 <sub>s</sub>	134.56 <sub>s</sub>	157.34 <sub>s</sub>	–
		(–3.12)		(–3.03)	(5.66)	(2.86)	(2.86)	(–0.75)	
L <sub>5</sub>	–	114.63 <sub>s</sub>	–	115.73 <sub>s</sub>	128.21 <sub>s</sub>	121.69	121.16 <sub>s</sub>	159.18 <sub>s</sub>	–
[RuCl <sub>2</sub> (CO) <sub>2</sub> (L <sub>5</sub> ) <sub>2</sub> ]	190.10 <sub>s</sub>	114.47 <sub>s</sub>	–	116.41 <sub>s</sub>	129.98 <sub>s</sub>	124.90 <sub>s</sub>	124.90 <sub>s</sub>	161.95 <sub>s</sub>	–
		(–0.16)		(–0.68)	(1.77)	(3.21)	(3.74)	(2.77)	
L <sub>6</sub>	–	123.07 <sub>s</sub>	129.67 <sub>s</sub>	130.33 <sub>s</sub>	132.06 <sub>d</sub>	131.14 <sub>s</sub>	139.03 <sub>s</sub>	142.54 <sub>s</sub>	46.14 <sub>s</sub>
[Ru(CO) <sub>2</sub> (L <sub>6</sub> ) <sub>2</sub> Cl <sub>2</sub> ]·3H <sub>2</sub> O	199.0 <sub>s</sub>	118.64 <sub>s</sub>	123.79 <sub>s</sub>	128.00 <sub>s</sub>	132.18 <sub>s</sub>	130.66 <sub>s</sub>	139.02 <sub>s</sub>	142.36 <sub>s</sub>	47.15 <sub>s</sub>
		(–4.43)	(–5.88)	(–2.33)	(0.12)	(0.48)	(–0.01)	(–0.18)	(1.01)
L <sub>7</sub>	–	136.38 <sub>s</sub>	142.94 <sub>s</sub>	134.35 <sub>m</sub>	147.94 <sub>s</sub>	155.45 <sub>s</sub>	171.79 <sub>s</sub>	157.35 <sub>d</sub>	54.17 <sub>s</sub>
[Ru(CO) <sub>2</sub> (L <sub>7</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	198.5 <sub>s</sub>	133.49 <sub>s</sub>	134.29 <sub>s</sub>	125.58 <sub>s</sub>	138.08 <sub>s</sub>	149.76 <sub>s</sub>	168.32 <sub>s</sub>	149.76 <sub>s</sub>	58.18 <sub>s</sub>
		(–2.89)	(–8.65)	(–9.77)	(–9.86)	(–5.69)	(–3.47)	(–7.59)	(–4.01)
L <sub>8</sub>	–	115.12 <sub>s</sub>	121.81 <sub>s</sub>	128.81 <sub>d</sub>	128.00 <sub>s</sub>	153.49 <sub>s</sub>	137.22 <sub>s</sub>	61.23	
[[Ru(CO) <sub>2</sub> (L <sub>8</sub> ) <sub>2</sub> Cl <sub>2</sub> ]·2H <sub>2</sub> O	201.0 <sub>s</sub>	–	118.49 <sub>s</sub>	122.18 <sub>m</sub>	128.28 <sub>s</sub>	153.2 <sub>s</sub>	126.52 <sub>d</sub>	57.88 <sub>s</sub>	
			(3.38)	(0.37)	(–0.53)	(0.28)	(–0.29)	(–10.70)	(3.35)
L <sub>9</sub>	CO	–	131.19 <sub>s</sub>	126.92 <sub>s</sub>	111.41 <sub>s</sub>	143.91 <sub>s</sub>	131.19 <sub>s</sub>	143.94 <sub>s</sub>	–
[Ru(CO) <sub>2</sub> Cl <sub>2</sub> (L <sub>9</sub> ) <sub>2</sub> ]·2H <sub>2</sub> O	200.0 <sub>s</sub>	–	130.58 <sub>s</sub>	127.22 <sub>s</sub>	112.15 <sub>s</sub>	138.4 <sub>m</sub>	133.69 <sub>s</sub>	150.15 <sub>s</sub>	–
			(–0.61)	(0.30)	(0.74)	(–5.53)	(2.50)	(6.21)	
L <sub>10</sub>	–	115.84 <sub>s</sub>	126.78 <sub>s</sub>	125.84 <sub>s</sub>	123.73 <sub>s</sub>	131.83 <sub>s</sub>	138.36 <sub>s</sub>	154.39 <sub>s</sub>	47.50 <sub>s</sub>
[Ru(CO) <sub>2</sub> (L <sub>10</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	199.5 <sub>s</sub>	114.50 <sub>s</sub>	128.33 <sub>s</sub>	129.10 <sub>s</sub>	123.69 <sub>s</sub>	135.06 <sub>s</sub>	137.9 <sub>s</sub>	152.6 <sub>s</sub>	47.20 <sub>s</sub>
		(–1.34)	(1.55)	(4.74)	(–0.13)	(3.17)	(–0.6)	(–1.79)	(–0.30)

### Stereochemistry

As discussed above, the analytical, infrared, electronic,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data indicate coordination of the ligands to the metal ion. The dicarbonyl complexes show two intense CO stretching bands around  $2000\text{ cm}^{-1}$  in the infrared spectra suggesting that the two carbonyl groups are in the *cis* position. In the cases of the  $[\text{RuCl}_2(\text{CO})_2(\text{L}_8)_2] \cdot 2\text{H}_2\text{O}$  and  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_1)_2]$  complexes, the spectra showed an additional, comparatively weak band, which is due to the presence of the *cis-trans* isomer. Furthermore, as the ruthenium(II) is in the low spin  $d^6$  configuration and is diamagnetic, two bands are expected at  $21000$  and  $25000\text{ cm}^{-1}$  for octahedral geometry. Similar to this, the discussed complexes also exhibited bands at around  $17700$  and  $25000\text{ cm}^{-1}$ , which were assigned to the transitions:  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$  and  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ , respectively. In addition, the coordination environment around the metal ion in all the complexes were not symmetrical. Therefore, it is suggested they have distorted octahedral geometry, which makes *fac*-isomers impossible. The coordination of the benzimidazole ligands occurred through the tertiary nitrogen. The following are the five possible structures for the complexes and the complex may exist in one of these structures (Fig. 2).

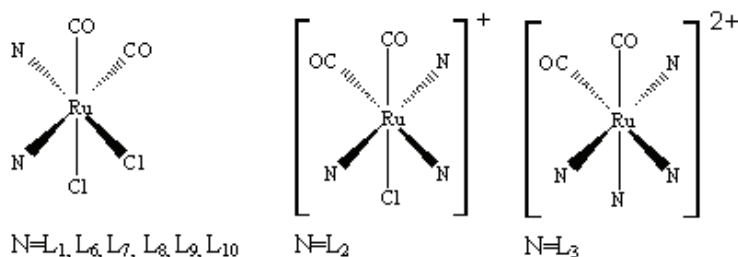


Fig. 2. The possible geometry of the complexes.

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### ИЗВОД

### СИНТЕЗА РУТЕНИЈУМ(II) КАРБОНИЛ КОМПЛЕКСА СА 2-МОНОСУПСТИТУИСАНИМ И 1,2-ДИСУПСТИТУИСАНИМ БЕНЗИМИДАЗОЛИМА

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Реакција полимерног карбонилног комплекса  $[\text{RuCl}_2(\text{CO})_2]_x$  са 2-моносупституисаним и 1,2-дисупституисаним бензимидазолима и 1,4-бис(бензимидазол-2-ил)бенzenом ( $\text{L}_6$ ) у 2-ме-

токсичности етанолу даје различито обојене комплексе формуле  $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L})_2] \cdot x\text{H}_2\text{O}$  ( $\text{L} = 1$ -(*o*-хидроксибензил)-2-(*o*-хидроксифенил)бензимидазол ( $\text{L}_1$ ), 1-(*o*-хидроксифенил)бензимидазол ( $\text{L}_4$ ), 1-(*p*-хидроксифенил)бензимидазол ( $\text{L}_5$ ), 1-(*p*-хлоробензил)-2-(*p*-хлорофенил)бензимидазол ( $\text{L}_7$ ), 1-[*p*-(диметиламино)бензил]-2-[*p*-(диметиламино)фенил]бензимидазол ( $\text{L}_{10}$ ),  $x = 0$ ;  $\text{L} = 2$ -бензилбензимидазол ( $\text{L}_8$ ), 1,4-бис(бензимидазол-2-ил)бензен ( $\text{L}_9$ ),  $x = 2$ ;  $\text{L} = 1$ -(*o*-хлоробензил)-1-(*o*-хлорофенил)бензимидазол ( $\text{L}_6$ );  $x = 3$ )  $[\text{Ru}(\text{CO})_2\text{Cl}(\text{L}_2)_3]\text{Cl} \cdot 3\text{H}_2\text{O}$  и  $[\text{Ru}(\text{CO})_2(\text{L}_3)_4]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  ( $\text{L}_2 = 1$ -(*m*-хидроксибензил)-2-(*m*-хидроксифенил)бензимидазол;  $\text{L}_3 = 1$ -(*p*-хидроксибензил)-2-(*p*-хидроксифенил)бензимидазол). Комплекси су окарактерисани елементалном анализом, мерењем проводљивости, IR, електронским,  $^1\text{H}$ - и  $^{13}\text{C}$ -NMR спектралним проучавањима.

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