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

GANGA NAIK KRISHNAMURTHY^{1*} and NARASHIMAIAH SHASHIKALA²

¹Department of Chemistry, Sahyadri Science College (Autonomous), Kuvempu University, Shimoga 577 203, Karnataka and ²Department of Chemistry, Central College Campus, Bangalore University, Bangalore-560 001, Karnataka, India

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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 (L_9) in 2-methoxyethanol produces various coloured complexes of the formulae $[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L})_2] \cdot x\text{H}_2\text{O}$ ($\text{L} = 1-(o\text{-hydroxybenzyl})-2-(o\text{-hydroxyphenyl})\text{benzimidazole}$ (L_1), $1-(o\text{-hydroxyphenyl})\text{benzimidazole}$ (L_4), $1-(p\text{-hydroxyphenyl})\text{benzimidazole}$ (L_5), $1-(p\text{-chlorobenzyl})-2-p\text{-chlorophenylbenzimidazole}$ (L_7), $1-[1-(\text{dimethylamino})\text{benzyl}]-2-[1-(\text{dimethylamino})\text{phenyl}]\text{benzimidazole}$ (L_{10}), $x = 0$; $\text{L} = 2\text{-benzylbenzimidazole}$ (L_8), $1,4\text{-bis}(\text{benzimidazol-2-yl})\text{benzene}$ (L_9), $x = 2$; $\text{L} = 1-(o\text{-chlorobenzyl})-1-(o\text{-chlorophenyl})\text{benzimidazole}$ (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 $[\text{Ru}(\text{CO})_2(\text{L}_3)_4]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ ($\text{L}_2 = 1-(m\text{-hydroxybenzyl})-2-(m\text{-hydroxyphenyl})\text{benzimidazole}$; $\text{L}_3 = 1-(p\text{-hydroxybenzyl})-2-(p\text{-hydroxyphenyl})\text{benzimidazole}$). The complexes were characterized by elemental analysis, conductivity measurements, as well as infrared, electronic, ^1H - and ^{13}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,¹ hydroformylation,² isomerisation and other reactions involving organic substrates.^{3–5} Some of the complexes form adducts with dioxygen and dinitrogen and the study

* Corresponding author. E-mail: gkmmaik_sahyadri@yahoo.co.in
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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.^{6,7}

Carbonyl complexes of ruthenium are important in the homogeneous catalysis of carbonylation and oxo reactions.⁸ Much of the knowledge concerning carbonyl complexes has come from the study of metal complexes in lower oxidation states,⁹ 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.^{10,11} The synthesis of various carbonyl complexes by the passage of CO through a suspension of substituted N-heterocyclic complexes of ruthenium(II) was reported.¹² 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 $[\text{RuCl}_5(\text{CO})]^{2-}$.¹² In view of the increased interest in oxygenation and carbonylation of ruthenium(II) complexes as new catalysts,^{13,14} 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 (L_1), 1-(*m*-hydroxybenzyl)-2-(*m*-hydroxyphenyl)benzimidazole (L_2), 1-(*p*-hydroxybenzyl)-2-(*p*-hydroxyphenyl)benzimidazole (L_3), 2-(*o*-hydroxyphenyl)benzimidazole (L_4), 2-(*p*-hydroxyphenyl)benzimidazole (L_5), 1-(*o*-chlorobenzyl)-1-(*o*-chlorophenyl)benzimidazole (L_6), 1-(*p*-chlorobenzyl)-2-(*p*-chlorophenyl)benzimidazole (L_7), 2-benzylbenzimidazole (L_8), 1,4-bis-(benzimidazol-2-yl)benzene (L_9) and 1-[*p*-(dimethylamino)benzyl]-2-[*p*-(dimethylamino)phenyl]benzimidazole (L_{10}), Fig. 1.

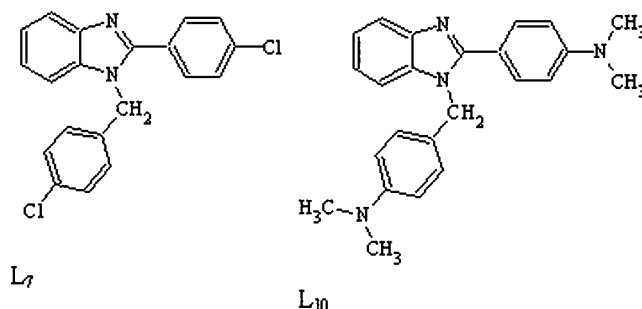


Fig. 1. Structures of the ligands 1-(*p*-chlorobenzyl)-2-(*p*-chlorophenyl)benzimidazole (L_7) and 1-[*p*-(dimethylamino)benzyl]-2-[*p*-(dimethylamino)phenyl]benzimidazole (L_{10}).

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.¹⁵

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^{-1} . The NMR spectra were recorded (in DMSO- d_6) 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.¹⁶ 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_1).

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_2 , (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_3 , (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_6 (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_7 (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_{10}), separated, which was recrystallized from ethanol to afford pale yellow crystals (yield: 80 %).

The ligand L_9 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 $[\text{Ru}(\text{CO})_2\text{Cl}_2]_x$ was prepared by reacting $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (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	Λ^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)

^aMolar 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 cm^{-1} , respectively.^{17,18} The band due to $\nu(\text{OH})$ of lattice water molecules^{19,20} was observed around 3350 cm^{-1} in the carbonyl complexes of L_2 , L_3 and L_6 . The $\nu(\text{OH})$ of the ligands containing a phenolic OH group and their complexes appeared around 3200 cm^{-1} . Bands due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ vibrations occurred around 1620 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 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.²¹ The spectra of the complexes of L_8 , L_4 , L_5 and L_9 exhibited the NH out-of-plane bending vibration at around 730 cm^{-1} . A weak band in the spectrum of $[\text{RuCl}_2(\text{CO})_2(\text{L}_{10})_2]$ at 1480 cm^{-1} is assigned to the N–CH₃ deformation mode. Another band at around 1320 cm^{-1} is attributed to C–N stretching of the N–CH₃ group.²² Medium intensity bands in the spectra of the complexes at around 1490, 1200, 1100, 720 and 540 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 cm^{-1} is assigned to the C–Cl stretching vibration.²³ Two intense bands at ≈ 1900 and ≈ 2000 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.^{19,20} 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 (cm^{-1}) of the ruthenium(II) carbonyl complexes

Compound	$\nu(\text{NH})$	$\nu(\text{O}-\text{H})$ of lat- tice H_2O	$\nu(\text{O}-\text{H})$ 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> - Disubsti- tuted benzene
L_1	–	–	–	–	1616s	1590s	1491m, 1057m, 740m, 540w
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_1)_2]$	–	–	3190br	2055s 1988s 1936s	1610s	1600s	1496m, 1052m, 748m
$[\text{Ru}(\text{CO})_2\text{Cl}(\text{L}_2)_3] \cdot \text{Cl} \cdot 3\text{H}_2\text{O}$	–	3320br	3178br	2040 1962	1624s	1590s	1310s, 1150s, 726ms
L_4	3170 br	–	3230w	–	1616s	–	1243w, 1090w, 722s

TABLE II. Continued

Compound	$\nu(\text{NH})$	$\nu(\text{O-H})$ of lat- tice H_2O	$\nu(\text{O-H})$ 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> - Disubsti- tuted benzene
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_4)_2]$	3178 <i>br</i>	—	3238w	2045s 1967s	1626s	—	1243s, 1093w, 726s
L_5	3160 <i>br</i>	—	3203w	—	1616s	—	1253s, 1010s, 736m
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_5)_2]$	3166 <i>br</i>	—	3172b	2034s 1962s	1605s	—	1233w, 1020w, 730m
L_8	3180 <i>br</i>	—	—	—	1600s	1558w	1108w, 720s, 548s
$[\text{RuCl}_2(\text{CO})_2(\text{L}_8)_2] \cdot 2\text{H}_2\text{O}$	3190 <i>br</i>	3440 <i>br</i>	—	2034s 2064s 1988	1605s	1554w	1103s, 731s, 545w
L_9	3150 <i>br</i>	—	—	—	1626s	—	1226s, 1090s, 742s, 540w
$\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_9)_2 \cdot 2\text{H}_2\text{O}$	3170 <i>br</i>	3400 <i>br</i>	—	2045s 1962s	1631s	—	1220s, 1090s, 747s, 529w

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

Compound	$\nu_{\text{Coordinated}}$ lattice H_2O	$\nu(\text{OH/NH})$	$\nu(\text{C=O})$	$\nu(\text{C=C})$ and $\nu(\text{C=N})$	$\nu(\text{N-CH}_2)$	<i>o</i> -, <i>m</i> -, <i>p</i> -Substituted benzene
L_3	—	3260	—	1610s	1594s	1468b, 1181m, 1114s, 752m
$[\text{Ru}(\text{CO})_2(\text{L}_3)_4]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$	3358 <i>br</i>	3198 <i>br</i>	2049s 1972s	1621s	1600s	1476s, 1279s, 1186m, 726s
L_{10}	—	—	—	1616s	1590s	1470s, 1180m
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_{10})_2]$	—	—	2050s 1962s	1610s	1595s	1455s, 1171s, 750s, 653s
L_6	—	—	—	1616s	1590s	1438s, 1196m, 788s
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_6)_2] \cdot 3\text{H}_2\text{O}$	3369s	—	2055s 1983s	1600s	1584s	1450s, 1190s, 780s
L_7	—	—	—	1600w	1590s	1460s, 1220s, 1192s, 780s
$[\text{Ru}(\text{CO})_2\text{Cl}_2(\text{L}_7)_2]$	—	—	2052s 1982s	1616s	1588s	1464s, 1234s, 1198s, 786s

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 cm^{-1} are assigned to the transitions $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$, respectively, based on the earlier assignments.^{24–27} A strong band observed around 34000 cm^{-1} is assigned to the charge transfer transition.

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

Compound	Electronic transitions and assignments		
	$\pi \rightarrow \pi^*$	$^1A_{1g} \rightarrow ^1T_{2g}$	$^1A_{1g} \rightarrow ^1T_{1g}$
$[\text{Ru}(\text{CO})_2(\text{L}_9)_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	28570	25640	—
$[\text{Ru}(\text{CO})_2(\text{L}_1)_2\text{Cl}_2]$	32786	27780	12500
$[\text{Ru}(\text{CO})_2\text{Cl}(\text{L}_2)_3]\text{Cl} \cdot 3\text{H}_2\text{O}$	—	27027	20000
$[\text{Ru}(\text{CO})_2(\text{L}_3)_4]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$	31250	25974	—
$[\text{Ru}(\text{CO})_2(\text{L}_4)_2\text{Cl}_2]$	30300	26310	—
$[\text{Ru}(\text{CO})_2(\text{L}_5)_2\text{Cl}_2]$	38460	29410	—
$[\text{Ru}(\text{CO})_2(\text{L}_6)_2\text{Cl}_2] \cdot 3\text{H}_2\text{O}$	—	26500	17500
$[\text{Ru}(\text{CO})_2(\text{L}_7)_2\text{Cl}_2]$	34722	31250	27780
$[\text{Ru}(\text{CO})_2(\text{L}_8)_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	—	26310	16950
$[\text{RuCl}_2(\text{CO})_2(\text{L}_{10})_2]$	26450	20490	12500

The ^1H -NMR spectra of the free ligands and their complexes were recorded in DMSO- d_6 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_4 and L_5 was observed at δ 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_1 , 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_2 and L_3 . The signal due to hydroxyl protons of the phenylene ring in the $[\text{RuCl}_2(\text{CO})_2(\text{L}_1)_2]$ complex was observed at 10.26 ppm and it appeared at around 9.72 ppm in the complexes of L_2 and L_3 . The spectra of L_9 and its complexes showed a resonance around 13.5 ppm, due to the imine proton. In the complex $[\text{RuCl}_2(\text{CO})_2(\text{L}_{10})_2]$, the signals due to the $-\text{CH}_3$ 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 $-\text{CH}_2-$ 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.²⁸ The coordination-induced shifts (c.i.s.) for various protons of the coordinated N-heterocycles were either positive or negative, which indicates that $\text{M} \rightarrow \text{L}$ (σ^-) or $\text{L} \rightarrow \text{M}$

(π -) electron transfer occurs. A similar observation was made earlier for the spectra of related complexes.^{21,29–32}

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

TABLE Vb. ^1H -NMR spectral data (δ / 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 ₂	N–H	2	Benzyl CH ₃	Phenyl CH ₃
L ₈	–	–	–	–	7.17q	7.52m	5.73s	–	7.52m	–	–
[Ru(CO) ₂ Cl ₂ (L ₈) ₂].2H ₂ O	–	–	–	–	7.44m (0.27)	7.80d (0.28)	5.64d (–0.09)	–	7.80 (–0.28)	–	–
					6'	7'	6				
L ₉	–	–	–	–	7.25m	7.69d	8.35s	13.5s	–	–	–
[Ru(CO) ₂ Cl ₂ (L ₉)].2H ₂ O	–	–	–	–	7.27m (0.02)	7.66m (–0.03)	8.38t (0.03)	13.84m (0.34)	–	–	–
L ₁₀	6.63t	6.88d	6.88d	6.63t	7.61m	7.99d	5.42s	–	2.99s	2.89s	–
[Ru(CO) ₂ Cl ₂ (L ₁₀)]	6.91d (0.28)	6.83d (–0.05)	6.83d (–0.05)	6.58 (–0.08)	7.23m (–0.38)	7.15d (–0.84)	4.70s (–0.72)	–	2.83m (–0.16)	2.77m (–0.12)	–

The ^{13}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 δ 47.20 ppm was assigned to the N–CH₃ carbon in the L₁₀ complex.

In the complexes of L_4 and L_5 , 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_1 complex was found at 110.50 ppm, while in the complexes of L_2 and L_3 , it was observed at 153.30 and 156.60 ppm, respectively. The resonance of phenylene C–OH of L_1 appeared at 161.73 ppm and in the complexes of L_2 and L_3 at 157.64 and 158.87 ppm, respectively. The resonance of the CH_2 carbon occurred near 47.00 ppm in the L_2 and L_3 complexes. In the case of the $[RuCl_2(CO)_2(L_9)_2]$ complex, the resonance signal due to the benzimidazole ring occurred in the range 112.15–150.0 ppm. In the $[RuCl_2(CO)_2(L_8)_2] \cdot 2H_2O$ 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_2 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. ^{13}C -NMR spectral data (δ / ppm) of the ruthenium(II) carbonyls with substituted benzimidazoles (the values in the parentheses are coordination induced shifts (c.i.s.) = $\delta_{complex} - \delta_{ligand}$)

Compound	CO	1''	1'	6'	4	8	9	2	CH ₂
L_1	–	120.37s	120.37s	127.86s	136.66s	140.50s	146.98	157.33d	65.04s
$[RuCl_2(CO)_2(L_1)_2]$	190.6s	120.30s	120.30s	127.16s	137.45	140.48s	146.96s	157.56s	65.04s
		(–0.07)	(–0.07)	(–0.70)	(–0.21)s	(–0.02)	(–0.02)	(–0.23)	(0.0)
L_2	–	116.97s	116.97s	122.19s	131.23s	135.90s	138.33s	142.64s	47.48s
$[Ru(CO)_2Cl(L_2)_3]Cl \cdot 3H_2O$	199.0s	116.94s	116.91s	122.13d	131.20s	135.91s	138.34s	142.6s	47.90s
		(–0.03)	(–0.06)	(–0.06)	(–0.03)	(0.01)	(–0.04)	(–0.04)	(0.42)
L_3	–	120.85	127.11s	115.53s	127.49s	135.87s	142.80s	153.50s	47.30s
$[Ru(CO)_2(L_3)_4]Cl_2 \cdot 3H_2O$	194.35d	120.87	129.27	115.56	127.59t	135.88s	142.76s	153.65s	47.12s
		(0.02)	(2.16)	(0.03)	(0.10)	(0.01)	(–0.04)	(0.05)	(–0.18)
L_4	–	112.66s	–	117.18s	126.23s	131.67s	131.67s	158.09s	–
$[Ru(CO)_2(L_4)_2Cl_2]$	190.10s	109.54s	–	114.15s	131.89s	134.56s	134.56s	157.34s	–
		(–3.12)		(–3.03)	(5.66)	(2.86)	(2.86)	(–0.75)	
L_5	–	114.63s	–	115.73s	128.21s	121.69	121.16s	159.18s	–
$[RuCl_2(CO)_2(L_5)_2]$	190.10s	114.47s	–	116.41s	129.98s	124.90s	124.90s	161.95s	–
		(–0.16)		(–0.68)	(1.77)	(3.21)	(3.74)	(2.77)	
L_6	–	123.07s	129.67s	130.33s	132.06d	131.14s	139.03s	142.54s	46.14s
$[Ru(CO)_2(L_6)_2Cl_2] \cdot 3H_2O$	199.0s	118.64s	123.79s	128.00s	132.18s	130.66s	139.02s	142.36s	47.15s
		(–4.43)	(–5.88)	(–2.33)	(0.12)	(0.48)	(–0.01)	(–0.18)	(1.01)
L_7	–	136.38s	142.94s	134.35m	147.94s	155.45s	171.79s	157.35d	54.17s
$[Ru(CO)_2(L_7)_2Cl_2]$	198.5s	133.49s	134.29s	125.58s	138.08s	149.76s	168.32s	149.76s	58.18s
		(–2.89)	(–8.65)	(–9.77)	(–9.86)	(–5.69)	(–3.47)	(–7.59)	(–4.01)
L_8	–	115.12s	121.81s	128.81d	128.00s	153.49s	137.22s	61.23	
$[Ru(CO)_2(L_8)_2Cl_2] \cdot 2H_2O$	201.0s	–	118.49s	122.18m	128.28m	128.28s	153.2s	126.52d	57.88s
			(3.38)	(0.37)	(–0.53)	(0.28)	(–0.29)	(–10.70)	(3.35)
L_9	CO	–	131.19s	126.92s	111.41s	143.91s	131.19s	143.94s	–
$[Ru(CO)_2Cl_2(L_9)_2] \cdot 2H_2O$	200.0s	–	130.58s	127.22s	112.15s	138.4m	133.69s	150.15s	–
			(–0.61)	(0.30)	(0.74)	(–5.53)	(2.50)	(6.21)	
L_{10}	–	115.84s	126.78s	125.84s	123.73s	131.83s	138.36s	154.39s	47.50s
$[Ru(CO)_2(L_{10})_2Cl_2]$	199.5s	114.50s	128.33s	129.10s	123.69s	135.06s	137.9s	152.6s	47.20s
		(–1.34)	(1.55)	(4.74)	(–0.13)	(3.17)	(–0.6)	(–1.79)	(–0.30)

Stereochemistry

As discussed above, the analytical, infrared, electronic, ^1H - and ^{13}C -NMR data indicate coordination of the ligands to the metal ion. The dicarbonyl complexes show two intense CO stretching bands around 2000 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 cm^{-1} for octahedral geometry. Similar to this, the discussed complexes also exhibited bands at around 17700 and 25000 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).

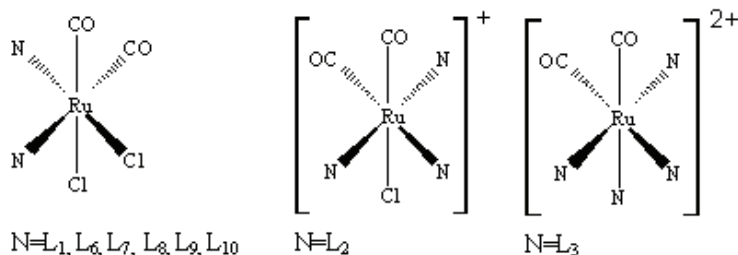


Fig. 2. The possible geometry of the complexes.

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ИЗВОД

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

GANGA NAIK KRISHNAMURTHY¹ и NARASHIMAIAH SHASHIKALA²

¹Department of Chemistry, Sahyadri Science College (Autonomous), Kuvempu University, Shimoga 577 203, Karnataka и ²Department of Chemistry, Central College Campus, Bangalore University, Bangalore-560 001, Karnataka, India

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 (L_9) 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 (L_1), 1-(*o*-хидроксифенил)бензимидазол (L_4), 1-(*p*-хидроксифенил)бензимидазол (L_5), 1-(*p*-хлоробензил)-2-(*p*-хлорофенил)бензимидазол (L_7), 1-[*p*-(диметиламино)бензил]-2-[*p*-(диметиламино)фенил]бензимидазол (L_{10}), $x = 0$; $\text{L} = 2$ -бензилбензимидазол (L_8), 1,4-бис(бензимидазол-2-ил)бензен (L_9), $x = 2$; $\text{L} = 1$ -(*o*-хлоробензил)-1-(*o*-хлорофенил)бензимидазол (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, ^1H - и ^{13}C -NMR спектралним проучавањима.

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REFERENCES

1. N. E. Leadbeater, K. A. Scott, L. J. Scott, *J. Org. Chem.* **65** (2000) 3231
2. P. Kalck, J. Frances, P. Fister, T. G. Southern, A. Thorez, *J. Chem. Soc. Chem. Commun.* (1983) 510
3. E. G. Leelamani, N. M. Nanje Gowda, V. Gayathri, G. K. N. Reddy, *Recent Advances in Catalysis and Catalytic Reaction Engineering*, RRL, CSIR, Hyderabad, 1986
4. R. Uson, J. Gimano, L. A. Oro, M. Valderrama, R. Sariego, E. Martinez, *Transition Met. Chem.* **6** (1981) 103
5. N. H. Li, J. M. J. Frenchet, *J. Chem. Soc. Chem. Commun.* **16** (1985) 1100
6. R. S. Drago, *Coord. Chem. Rev.* **117** (1992) 185
7. M. Frigerio, M. Santagostino, S. Sputore, G. Palamisano, *J. Org. Chem.* **60** (1965) 727
8. G. S. Fink, G. F. Schmidt, *J. Mol. Catal.* **42** (1987) 361
9. M. Schroder, T. A. Stephenson, *Comprehensive Coordination Chemistry*, G. Wilkinson, Ed., Pergamon Press, New York, 1987, Vol. 4, p. 277
10. M. M. Taquikhan, G. Ramachandraiah, R. S. Shukla, *Inorg. Chem.* **27** (1988) 3274
11. M. M. Taquikhan, A. Hussain, K. Venkatasubramanian, G. Ramachandraiah, V. Oomen, *J. Mol. Catal.* **44** (1988) 117
12. J. Halpen, B. R. James, A. L. W. Kemp, *J. Am. Chem. Soc.* **88** (1996) 5142
13. M. M. Taquikhan, C. Sreelatha, S. A. Mirza, G. Ramachandraiah, S. H. R. Abdi, *Inorg. Chim. Acta* **154** (1988) 103
14. I. W. Hein, R. I. Arhum, J. J. Liquitt, *J. Am. Chem. Soc.* **79** (1957) 427
15. D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1966
16. N. V. Subba Rao, C. V. Ratnam, *Curr. Sci.* **24** (1955) 174
17. K. Takahashi, Y. Nishida, S. Kida, *Polyhedron* **3** (1984) 113
18. J. Tamm, H. J. Eggers, R. Batalannian, A. P. Wanger, K. Folkers, *Nature* **223** (1969) 785
19. K. Nakanishi, P. H. Solomon, *Infrared Absorption Spectroscopy*, Holden-Day Inc., Sydney, 1977
20. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed., John Wiley, New York, 1978
21. G. Krishnamurthy, N. Shashikala, *J. Chem. Res.* **2006** (2006) 766
22. G. K. N. Reddy, B. R. Ramesh, *Indian J. Chem. A* **15** (1977) 621
23. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1975

24. T. A. Stephenson, G. Wilkinson, *J. Inorg. Nucl. Chem.* **28** (1966) 945
25. J. Chatt, G. J. Leigh, D. M. P. Mingos, R. J. Paske, *J. Chem. Soc. A* (1968) 2636
26. L. R. Ramirez, T. A. Stephenson, *J. Chem. Soc. D* (1975) 2244
27. A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, New York, 1968
28. D. M. Grant, R. J. Pugmire, *J. Am. Chem. Soc.* **93** (1971) 1880
29. a) P. G. Douglas, B. L. Shaw, *J. Chem. Soc. D* (1969) 624; b) P. G. Douglas, B. L. Shaw, *J. Chem. Soc. A* (1970) 334
30. T. A. Stephenson, *J. Chem. Soc. A* (1970) 889
31. B. S. Hammes, M. T. Kieber-Emmons, R. Sommer, A. L. Rheingold, *Inorg. Chem.* **41** (2002) 1351
32. M. Haga, M. Ishizuya, T. Kanetsugu, T. Yutaka, D. Sakiyama, J. Fees, W. Kaim, *Ind. J. Chem.* **42A** (2003) 2290.