Ru(III) Complexes of Phenoxy-İmine Ligands: Synthesis, Characterisation and Testing as Oxidation Catalysts

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Summary: A series of new mononuclear Ru(III) complexes bearing phenoxy-imine Schiff base tetradentate ligands (phenylimino, 4-chlore phenylimino, 3,4-dichlore phenylimino) have been prepared and characterized by elemental analysis, TGA, UV-VIS, FT-IR, ^{1}H-NMR and ^{13}C NMR spectra. The proposed structure of the ligands have a O_2N_2 core to form mononuclear Ru (III) complexes. Preliminary studies on the catalytic performances of the compounds in the cycloalkane oxydation are described. The catalytic effect of all Ru complexes results in the epoxidation reaction of cyclohexane, as shown in the substrate conversion reaction appears to be very high.

Keywords: Schiff bases, Ru(III) complexes, Oxidation reactions, Catalyst.

Introduction

Phenoxy-benzoyl-imine compounds are a versatile class of ligand which is the application area in large number. The successes of phenoxy-imines are presumably due to the availability of scope for suitable tuning of the sterics and the electronics of the ligand ancillary and also due to their easy synthetic accessibility, as the phenoxy-imines are often prepared by Schiff base condensation reactions. Interestingly enough, despite extensive use of phenoxy-imines in many important chemical transformations, their application in ring-opening polymerization (ROP) of L-lactide largely remains unexplored [1]. Phenoxy acetic acid is among the most vital moieties which are associated with potent fungicidal activities [2]. Coordination chemistry of trivalent ruthenium(III) has been developed considerably in recent years. Ruthenium complexes have been recently gaining in importance in a broad range of applications, and consequently there is a continuous endeavor to synthesize new complexes of ruthenium with different types of ligands, such as Schiff base, azo, pincer, tripodal and carbenes [3]. In particular, emphasis has been placed on ligands containing a phenolate oxygen, which is a recognized hard donor, and hence coordination by a phenolate oxygen is of importance with regard to stabilization of the higher oxidation states of ruthenium [4]. In addition, a lot of research groups are improving the synthetic chemistry associated with ruthenium complexes because of their various applications in many different scientific fields [5-7]. Ruthenium complexes are widely used as catalysts or catalyst precursors in various redox reactions and in multiple organic transformations such as transfer hydrogenation reactions, oxidation reactions epoxidation of olefins, isomerisation, polymerization, nucleophilic addition to multiple bonds and carbon–carbon bond formation [8-12].

In this study, the synthesis and characterization of Schiff base compounds (L_1, L_2 and L_3) and their Ru metal complexes are discussed using various spectroscopic methods. Ru (III) complexes have been tested as a catalyst for the oxidation of cyclohexane and cyclohexene with hydrogen peroxide as the oxidant at room temperature.

Experimental

General

Acetonitrile, n-butanol, diethylether, toluene, THF, EtOH, MeOH, DMF, $RuCl_3$ were obtained from Aldrich and Merck. All solvents were dried and purified before use. Elemental analyses were performed on a Thermo Scientific Flash 2000 elemental analyzer. Molar conductance of the Schiff base ligands and their transition metal complexes were determined in DMF at room temperature by using a Thermo Scientific electron corporation model conductivity meter. Electronic absorption spectra

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were recorded on a PG Instruments T80+UV/Vis spectrometer while infrared spectra were measured in the range of 4000-400 cm^{-1} on a Perkin-Elmer Spectrum 100 FTIR (ATR sampling accessory) spectrophotometer. The samples were dissolved in DMF and the spectra were recorded in the range of 190-1100 nm. The magnetic moments of the complexes were measured by the Gouy method on a type Sherwood Scientific model Instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker High Performance Digital FT-NMR (400 MHz) spectrometer with the samples dissolved in d_6-DMSO using TMS as an internal standard. Mass spectrum, EU Sciex QTRAP 3200 LC/MS/MS in the spectrophotometer were taken using an electro-spray method. Thermal behaviors were examined with a SetaramLabsys TGA/DTA model thermal analyzer heated from 20-870 ^0C under air. Preparations of 2-((Phenylimino)methyl)phenol, 2-(((4-chlorophenyl)imino)methyl)phenol and 2-(((3,4-dichlorophenyl)imino) methyl)phenol have been designed in keeping with the reference [13-15].

Synthesis

(Synthesis of the ligands (L_1, L_2 and L_3)

2-(2-((2-((phenylimino)methyl)phenoxy)methyl)benzyloxy)benzylidene)benzenamine (L_1):

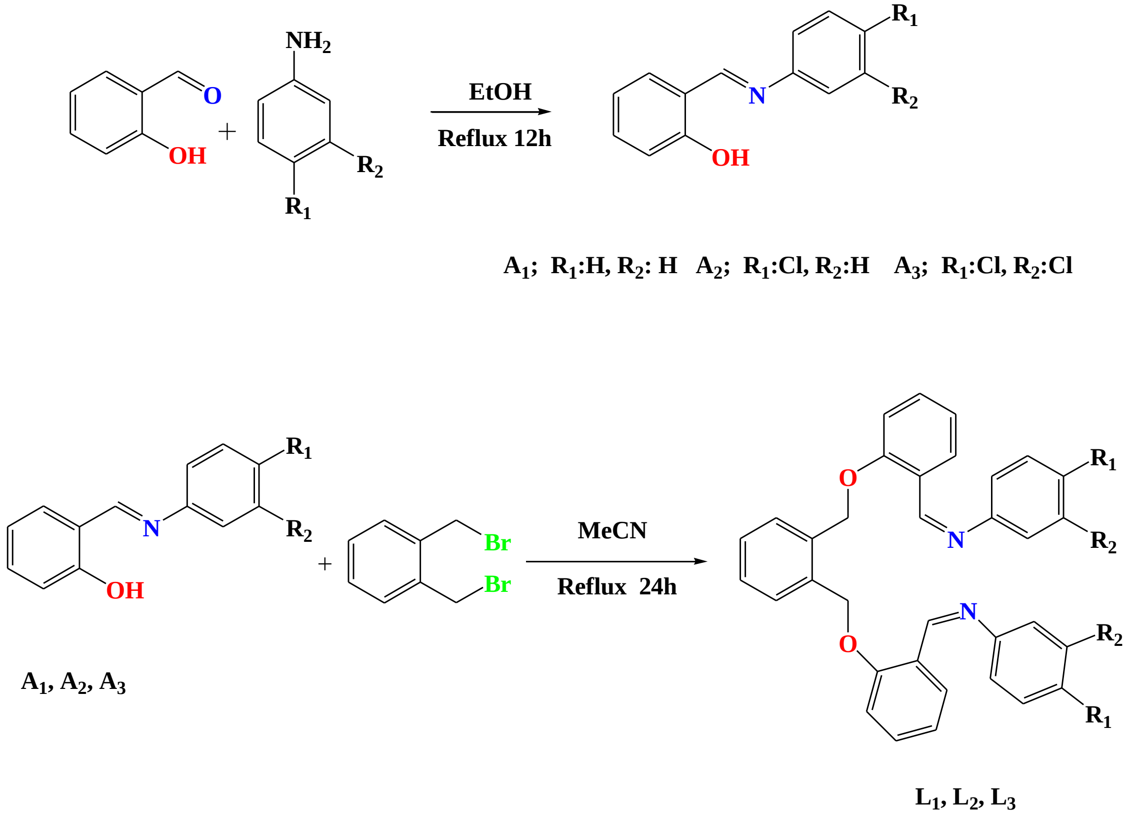
The synthetic route for the ligand L_1 is shown in Scheme 1. 2-((phenylimino)methyl)phenol (10 mmol), potassium carbonate (10 mmol) in MeCN (50 cm^3) were warmed to 100 ^0C and stirred for two hours and then 1,2-bis(bromomethyl)benzene (5 mmol) was added. The reaction mixture was stirred at 100 ^0C for 24 h. After cooling down, the mixture was poured into water (100 cm^3) and then a 0,1 N 100 mL NaOH solution was added and extracted by $CHCl_3$. The $CHCl_3$ layer was evaporated to dryness to give the crude product, which was recrystallized in MeCN to afford pure ligand L_1. Yield 76 %; color: white; m.p. 115-117 ^0C. Elemental Anal. Calc. (%): C, 82.23; H, 5.68; N, 5.64. Found: C, 81.75; H, 5.69; N, 5.91 for $C_{34}H_{28}N_2O_2$. IR ν ATR (cm^{-1}): 3054 (Ar-CH); 1615 (C=N); 1211 (C-O-C). ^1H-NMR (400 MHz, $CDCl_3$): δ, ppm 5.31 (s, 4H,-OCH_2), 6.9-8.2 (m, 22H, aryl-H), 8.94 (d, 2H, N=C-H). ^{13}C NMR (400 MHz, $CDCl_3$): δ, ppm CH_2: 68.54, Arom: 112.48, 121.04, 121.48, 125.10, 125.76, 127.90, 128.73, 129.19, 129.36, 132.78, 133.01, 134.67, 152.65, 156.00, CH=N: 158.43. UV-Vis: UV–Vis λ_{max} (nm) in DMF: 270 (1.446), 325 (1.404). LC/MS/MS, m/z: 497.3 $[L_1+H]^+$.

2-(2-((2-((4-chlorophenylimino)methyl)phenoxy)methyl)benzyloxy)benzylidene)-4-chlorobenzenamine (L_2):

The synthetic route for the ligand L_2 is shown in Scheme 1. (E)-2-(((4-chlorophenyl)imino)methyl)phenol (10 mmol), potassium carbonate (10 mmol) and MeCN (50 mL) were warmed and stirred for two hours to 100 ^0C and then 1,2-bis(bromomethyl)benzene (5 mmol) was added under similar conditions to those described above for L_1. Yield 75 %; color: white; m.p. 118-120 ^0C. Elemental Anal. Calc. (%): C, 72.21; H, 4.63; N, 4.95. Found: C, 71.92; H, 4.46; N, 5.12 for $C_{34}H_{26}Cl_2N_2O_2$. IR ν ATR (cm^{-1}): 3064 (Ar- CH); 1615 (C=N); 1217 (C-O-C). ^1H-NMR (400 MHz, $CDCl_3$): δ, ppm 5.30 (s, 4H,-OCH_2), 6.9-8.16 (m, 20H, aryl-H), 8.84 (d, 2H, N=C-H). ^{13}C NMR (400 MHz, $CDCl_3$): δ, ppm CH_2: 68.64, Arom: 112.49, 121.52, 122.32, 124.84, 127.91, 128.83, 129.16, 129.23, 131.24, 132.97, 134.63, 151.05, 156.25, CH=N: 158.46. UV-Vis: UV–Vis λ_{max} (nm) in DMF: 275 (1.942), 330 (1.961). LC/MS/MS, m/z: 565.2 $[L_2]^+$.

2-(2-((2-((3,4 dichlorophenylimino)methyl)phenoxy)methyl)benzyloxy)benzylidene)-3,4-dichlorobenzenamine (L_3):

The synthetic route for the ligand L_3 is shownin Scheme 1. 2-(((3,4-dichlorophenyl)imino)methyl)phenol (10 mmol), potassium carbonate (10 mmol) and MeCN (50 mL) were warmed and stirred for two hours to 100 ^0C and then 1,2-bis(bromomethyl)benzene (5 mmol) was added under the similar conditions as described above for L_1. Yield 70 %; color: white; m.p. 125 ^oC. Elemental Anal. Calc. (%): C, 64.37; H, 3.81; N, 4.42. Found: C, 63.94; H, 3.72; N, 4.42 for $C_{34}H_{24}Cl_4N_2O_2$. IR ν ATR (cm^{-1}): 3062 (Ar- CH); 1615 (C=N); 1210 (C-O-C). ^1H-NMR (400 MHz, $CDCl_3$): δ, ppm 5.30 (s, 4H,-OCH_2), 6.9-8.11 (m, 18H, aryl-H), 8.76 (d, 2H, N=C-H). ^{13}C NMR (400 MHz, $CDCl_3$): δ, ppm CH_2: 68.80, 112.59, 120.68, 121.55, 122.75, 124.55, 127.97, 128.95, 129.21, 129.45, 130.65, 132.75, 133.30, 134.61, 152.02, 157.07, CH=N: 158.59. UV-Vis: UV–Vis λ_{max} (nm) in DMF: 275 (1.789), 330 (1.764). LC/MS/MS, m/z: 635.0 $[L_3+H]^+$.



Scheme-1: The formation reactions of the ligands.

General procedure for preparation of ruthenium complexes

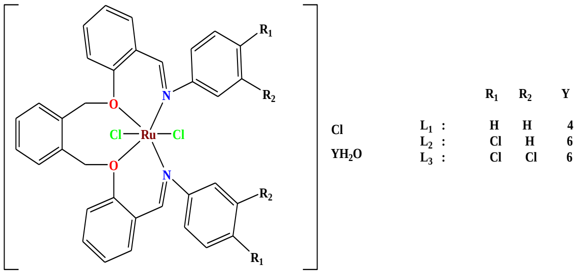
Ruthenium(III) complexes of the Schiff bases were prepared by the addition of a hot solution (40 ^{0}C) of [RuCl$_3$·nH$_2$O] (0.25 mmol) in 10 mL ethanol to the hot solution (40 ^{0}C) of Schiff base ligands (L$_1$, L$_2$ and L$_3$) (0.25 mmol) in CHCl$_3$ (30 mL) (Fig 1). The resulting mixture was stirred for 6 h under reflux. After the reaction was complete, it was evaporated to dryness to give the crude product, which was filtered off and washed with petroleum ether several times.

[Ru(L$_1$)Cl$_2$]Cl·4H$_2$O: Dark Brown solid, yield 41%, mp. 147-154 ^{0}C. $C_{34}H_{36}Cl_3N_2O_6Ru$ Elemental Anal. Calc.: C, 52.62; H, 4.68; N, 3.61. Found: C, 52.64; H, 4.08; N, 5.17%. IR ν ATR (cm^{-1}): 3075 (Ar CH); 1637 (C=N); 1227 (C-O-C), 2987 (Aliphatic CH), 548 (Ru-O); 472 (Ru-N). Meff, BM: 1.108. UV-Vis (DMF) λmax (log ε): 270 (0.543), 325 (0.352), 510 (0.22) nm. Mol. Cond (S cm^2 mol^{-1}): 20.83. LC/MS/MS, m/z: 777.2 [Ru(L$_1$)Cl$_2$]Cl·4H$_2$O+H]$^+$.

[Ru(L$_2$)Cl$_2$]Cl·6H$_2$O: Dark Burgundy solid, yield 45%, mp. 149 ^{0}C decompose. $C_{34}H_{38}Cl_5N_2O_8Ru$ Elemental Anal. Calc.: C, 46.35; H, 4.35; N, 3.18. Found: C, 45.38; H, 3.04; N, 4.82%. IR ν ATR (cm^{-1}): 3070 (Ar CH); 1641 (C=N); 1230 (C-O-C), 2989 (Aliphatic CH), 539 (Ru-O); 489 (Ru-N). Meff, BM: 1.23. UV-Vis (DMF) λmax (log ε): 270 (0.531), 315 (0.359), 515 (0.138) nm. Mol. Cond (S cm^2 mol^{-1}): 23.90. LC/MS/MS, m/z: 882.4 [Ru(L$_2$)Cl$_2$]Cl·6H$_2$O+H]$^+$.

[Ru(L$_3$)Cl$_2$]Cl·6H$_2$O: Dark Brown solid, yield 52%, mp. 163 ^{0}C decompose. $C_{34}H_{36}Cl_7N_2O_8Ru$ Elemental Anal. Calc.: C, 42.99; H, 3.82; N, 2.95. Found: C, 40.39; H, 2.70; N, 3.55%. IR ν ATR (cm^{-1}): 3068 (Ar CH); 1641 (C=N); 1236 (C-O-C), 2988 (Aliphatic CH), 530 (Ru-O); 467 (Ru-N). Meff, BM: 0.82. UV-Vis (DMF) λmax (log ε): 270 (1.111), 310 (0.768), 555 (0.149) nm. Mol. Cond

(S cm^2 mol^{-1}): 13.83. LC/MS/MS, m/z: 913.3 $[Ru(L_3)Cl_2]Cl·6H_2O]^+$.



	R_1	R_2	Y
L_1 :	H	H	4
L_2 :	Cl	H	6
L_3 :	Cl	Cl	6

Fig. 1: Proposed structures of the Ru (III) complexes.

General procedure for oxidation under microwave irradiation

The optimum conditions were obtained by catalyst: substrate: oxidant(c:s:o) ratio of 1:100:250 in acetonitrile under 300W microwave power for 30 min. The temperature and pressure were controlled at about 100 °C and 25 bar by the instrument. A blank has been run under similar conditions without any catalyst [16]. The metal complexes of ruthenium (III) have an octahedral geometry. The products formed by the effect of metal complexes in the catalytic oxidation of cyclohexane and cyclohexene under microwave irradiation are shown in Figs 2 and 3. A method of catalytic oxidation of cyclohexane and cyclohexene; 0.02 mmol catalyst: 2 mmol cyclohexane: 4 mmol hydrogene peroxide (1:100:250) and 5mL acetonitrile was used for each reaction. 300W power was applied for 30 min. The reaction temperature and pressure were held at around 100 °C and 25 bar in closed DAP60 vessels

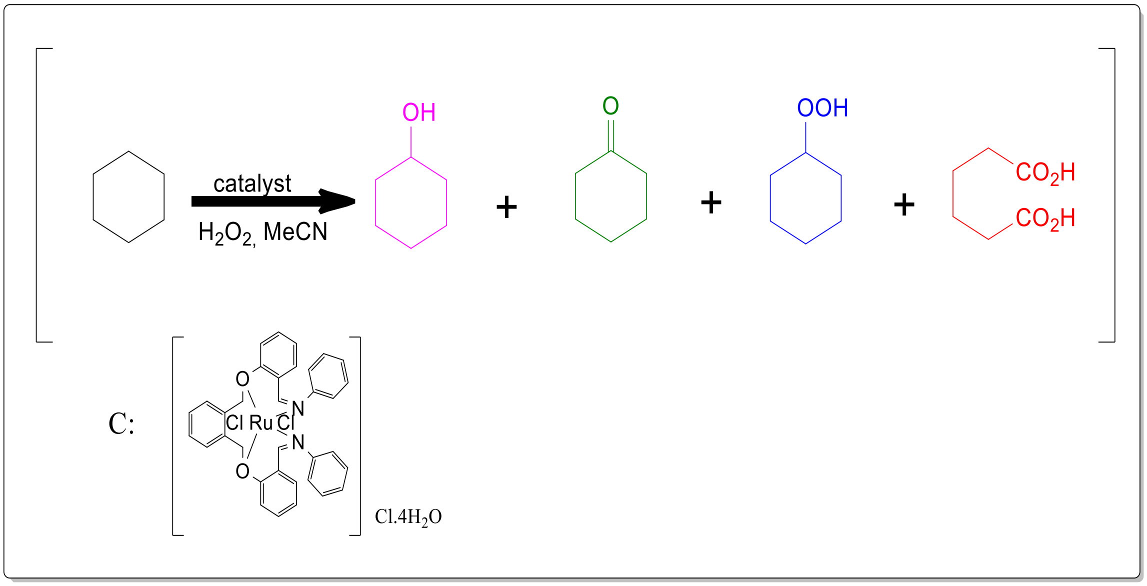


Fig. 2: Catalytic oxidation of cyclohexane under microwave irradiation.

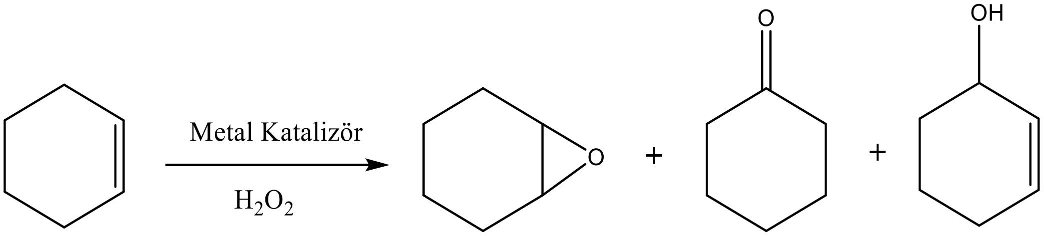


Fig. 3: Catalytic oxidation of cyclohexene under microwave irradiation.

Results and Discussion

Synthesis

A_1, A_2 and A_3 Schiff bases were easily prepared by condensation of salicylaldehyde with the appropriate substituted aniline in ethanol. These synthesized Schiff bases with 1,2-bis(bromomethyl)benzene in the reaction of new phenoxy-imine compounds to be used as ligands (L_1, L_2 and L_3) were synthesized. Metal complexes of these ligands with Ru(III) chlorine salts were obtained. The structure of ligands was characterized by using elemental analysis, ^{1}H and ^{13}C NMR, FT IR. The possible reaction is shown in Scheme 1. In the proposed structure the ligands have a O_2N_2 core to form mononuclear Ru (III) complexes. The stoichiometries of the complexes determined by mass and elemental analysis correspond to the general formula $[MLCl_2]Cl.nH_2O$ (where M is Ru(III)) and L is the Schiff base ligands (L_1, L_2 and L_3). These propositions are also in accord with IR, UV–Vis data, TGA, magnetic and molar conductivity measurements. The proposed structures of the reported complexes are shown in Fig 1. The white-coloured ligand and its complexes are insoluble in water and common organic solvents, but soluble in DMSO and DMF.

IR spectra

The FT IR spectra show marked changes of the ligands L_1, L_2 and L_3. The characteristic bands of Schiff base ligands and their Ru(III) complexes are tabulated in Table 1. The IR spectra of Schiff bases L_1, L_2 and L_3 showed a weak broad absorption band at 3054 cm^{-1} 3064 cm^{-1} and 3062 cm^{-1} assigned to the aromatic rıngs stretching vibration respectively [17-19], absorption bands at 1615 cm^{-1} assigned to the imin C=N stretching vibration, absorption band at 1211 cm^{-1} 1217 cm^{-1} and 1210 cm^{-1} assigned to the etheric oxygen C-O-C stretching vibration respectively. The FTIR spectrum of the isolated L_1, L_2 and L_3 ligands shows sharp absorption bands characteristic of ν(C=N) stretching at 1615 cm^{-1}. However in the complexes these bands were shifted higher to about 22-26 cm^{-1} wavenumbers indicating the participation of azomethine nitrogen in the coordination to the metal ion [20-22]. Aromatic C-H bands in ligands were shifted up to about 6-21 cm^{-1} in complexes respectively. Weak intensity absorption bands at 1211 cm^{-1} down to 1227 cm^{-1} in L_1, 1217 cm^{-1} up to 1230 cm^{-1} in L_2 and 1210 cm^{-1} up to 1236 cm^{-1} in L_3 are related to ν(C-O-C) etheric oxygen stretching vibration in complexes. New bands in the complexes at 548-472 cm^{-1} in L_1, 539-489 cm^{-1} in L_2 and 530-467 cm^{-1} in L_3 are attributed to the *ν*(Ru-O) and *ν*(Ru-N) vibrations [23, 24]. The IR spectra of the Schiff base ligands and a representative example of metal complexes are given in Fig S1, S2, S3 (Supplementary materials).

Table-1: Characteristic IR bands of the Schiff bases and their metal complexes (in cm^{-1}).

Compounds	**ν(Ar C-H)**	**ν(C=N)**	**ν(C-O-C)**	**ν(Ru-O)**	**ν(Ru-N)**	**ν(H_2O)**
L_1 ($C_{34}H_{28}N_2O_2$)	**3054**	**1615**	**1211**	**-**	**-**	
L_2 ($C_{34}H_{26}Cl_2N_2O_2$)	**3064**	**1615**	**1217**	**-**	**-**	
L_3 ($C_{34}H_{24}Cl_4N_2O_2$)	**3062**	**1615**	**1210**	**-**	**-**	
$[Ru(L_1)Cl_2]Cl·4H_2O$	**3075**	**1637**	**1227**	**548**	**472**	**3383**
$[Ru(L_2)Cl_2]Cl·6H_2O$	**3070**	**1641**	**1230**	**539**	**489**	**3485**
$[Ru(L_3)Cl_2]Cl·6H_2O$	**3068**	**1641**	**1236**	**530**	**467**	**3383**

NMR spectra

^{1}H and ^{13}C NMR spectra of Schiff base ligands (L_1, L_2 and L_3) were recorded in $CDCl_3$ solution. The ^{1}H-NMR and ^{13}H-NMR spectrum were recorded and are presented in Fig 4, 5 for L_1. In addition, for L_2 and L_3 they are shown in Fig S4, S5, S6, S7 (Supplementary materials). The ^{1}H-NMR spectra of L_1, L_2 and L_3 showed the singlets (2H) at 8.94 ppm, 8.84 ppm and 8.76 ppm [25-27]. The signals of Aryl-H were visible at δ: 6.9-8.2 (m, 22H) ppm, 6.9-8.16 (m, 20H) ppm and 6.9-8.11 (m, 18H) ppm for L_1, L_2 and L_3, respectively. The signals of -CH_2-O- were observed at 5.31 ppm, 5.30 ppm and 5.30 ppm for L_1, L_2 and L_3, respectively [28, 29, 18]. More detailed information about the structure of Schiff bases (L_1, L_2 and L_3) is provided by its. ^{13}C NMR spectrum. In the spectrum of Schiff bases a new signal was observed at 158.43 ppm for L_1, 158.46 ppm for L_2 and 158.59 ppm for L_3 due to imine carbon (C=N). The signals for the C-O carbons of the ligands (for L_1, L_2 and L_3) were observed at 156.00, 156.25 and 157.07 ppm, respectively, and the peaks observed at 152.65, 151.05 and 152.02 ppm, respectively, belong to the C-N carbon. Ethereal oxygen of the C is considerable and corresponds to δ 68.54 ppm for L_1, 68.64 ppm L_2 and 68.80 ppm L_3. The peaks of the other aromatic ring carbons were observed at 112.48-134.67, 112.49-134.63 and 112.59-134.61 ppm, respectively. These observations are evidence of the formation of Schiff bases [29-31, 18].

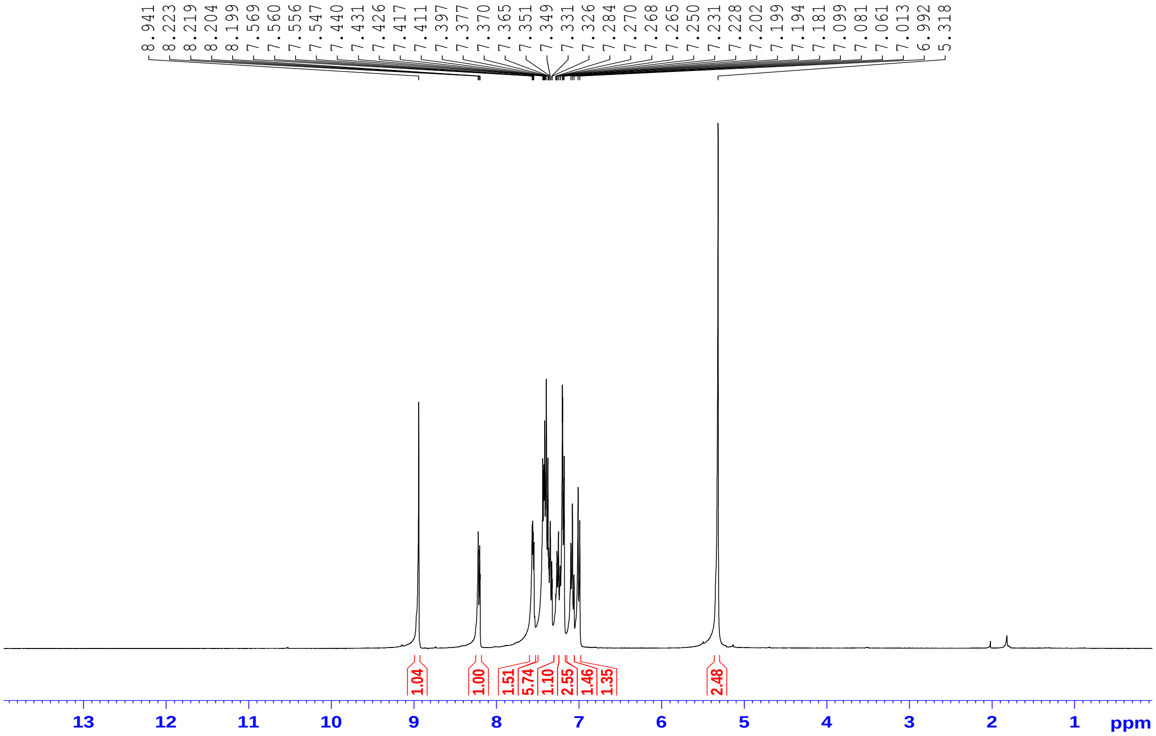


Fig. 4: ^{1}HNMR spectra of the ligand $L_{1.}$

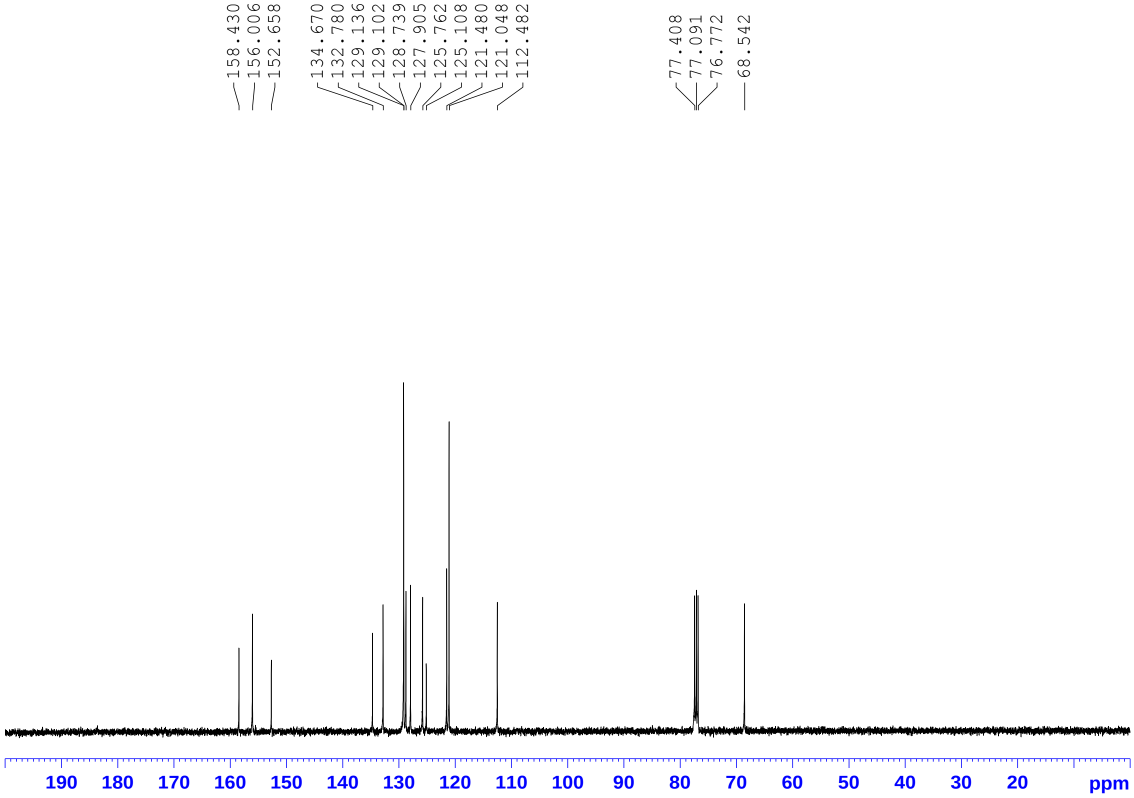


Fig. 5: ^{13}CNMR spectra of the ligand $L_{1.}$

UV–Vis absorbance and emission studies

Ultraviolet spectra analyses of L_1, L_2 and L_3 have been investigated experimentally and theoretically. The UV-*Vis* spectra of the title compounds in DMF solvent were recorded within the 190-1100 nm range and representative spectra are given in Fig S8 (Supplementary materials). The C=N system is a weak chromophor, which absorbs ultraviolet light. Conjugation with phenyl groups shifts the absorbance to the visible region. When the UV-Vis spectra of phenoxy imine ligands was examined, two peaks were observed in the range of 200-400 nm. Transitions observed in the UV-Vis spectrum between 200-270 nm are transitions originating from the aromatic rings and unshared electrons of the ligand [32]. The maximums are observed at 270-325 nm in L_1, 275-335 nm in L_2 and 275-335 nm in L_3 related to n- π^* transitions of the imine groups. Approximately 325-270 nm in L_1, 315-270 nm in L_2 and 320-270 nm in L_3 are related to n-π^* and π-π^* transitions of the imine and etheric oxygen groups in Ru (III) complexes of ligands [33, 34]. The bands at 425-510 nm in L_1, 510-615 nm in L_2 and 435-565 nm in L_3 are shown as weak and intermediate transitions of d-d. During the formation of the complexes, these bands are shifted to lower and higher wavelengths suggesting that the nitrogen atoms of the imine groups are coordinated to the metal ion [35].

Magnetic Moment and Molar Conductivity

Magnetic susceptibility measurements of the synthesized Ru complexes and standard material were taken at room temperature. The C_{BAL} value was found in the magnetic susceptibility measurements of standard material. Subsequently, magnetic susceptibility measurements were taken at 25 ° C for each sample to calculate BM values. The room temperature magnetic moment of the metal complexes is 1.108 BM for L_1-Ru, 1.23 BM for L_2-Ru and 0.82 BM for L_3-Ru [35, 36]. It is understood that the Ru complexes are paramagnetic according to the magnetic susceptibility values. The magnetic susceptibility values of the complexes are octahedral in the complexes according to data in the literature [37, 38].

The electrolytic conductivities of synthesized ligands and metal complexes were taken in DMF solvent at room temperature and 1.10^{-3} molar concentration. Molar conductivity data of synthesized metal complexes are of 20.83 S cm^2 mol^{-1} for L_1-Ru, 23.90 S cm^2 mol^{-1} for L_2-Ru and 13.83 S cm^2 mol^{-1} for L_3Ru. When looking at the molar conductivity values of metal complexes, all Ru complexes have a 1:1 metal: electrolytic ligand ratio; So, a chloride ion is outside the coordination area in these complexes [39].

Mass spectra

Mass spectral data and the most stable fragmentation values of ligands and metal complexes are shown in the experimental part. Ligands and metal complexes show marked molecular ion peaks. The mass spectra of ligands and metal complexes are in displayed molecular ion peaks at *m/z* 497.3 for $[L_1 +H]^+$ and 777.2 for $[L_1\text{-Ru+H}]^+$, 565.2 for $[L_2 +H]^+$ and 882.4 for $[L_2\text{-Ru+H}]^+$, and 635.0 for $[L_3 +H]^+$ and 913.3 for $[L_3\text{-Ru}]^+$. The mass spectral data of the Schiff bases and metal complexes strongly confirmed the best possible structures.

TGA

Thermogravimetric analysis of the complexes is used to obtain information about its thermal stability. The TGA/DTA curves of the complexes are given in Fig S9 (Supplementary materials). Thermal decomposition of the title complexes was monitored from the room temperature to 900 °C at heating rates of 10 °C/min under nitrogen atmosphere. The DTA curves of the complexes show five endothermic peaks: the first peak at lower temperatures corresponding to the melting of the complex and another comparatively broad peak at higher temperatures, which is consistent with the volatilization of the complexes. In the TGA curve, there are three mass loss stages. In the first masses loss occurs at 50-250 °C, the hydration water molecules are lost and equal 8.85% L_1Ru, 10.2% L_2Ru, and 11.5% L_3Ru of total mass, respectively. The second mass loss stage corresponds to the loss of the hydrochloric acid and organic groups in the 250–600 °C temperature range, respectively. In the last stage, the organic fragment of the residual complex decomposes [40]. Thermal analysis results of the complexes are shown in Table-2.

Table-2: Thermogravimetric characteristics of Ru complexes.

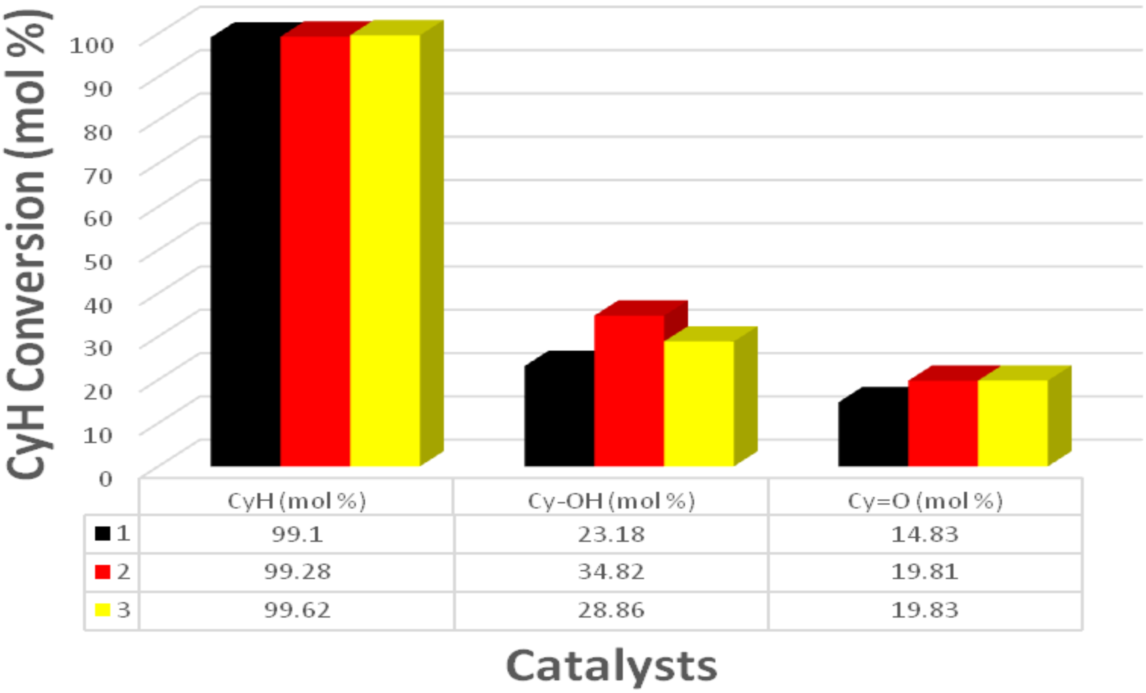
Compounds	Stages	Temp.Range (°C)	Mass Loss (%) (calc) Found	Assignment
$[Ru(L_1)Cl_2]Cl·4H_2O$	1.Stage	25-230	(9.2) 8.85	H_20
	2.Stage	230-360	(26.3) 25.35	HCl, Phenyl
	3.Stage	360-500	(12.1) 12.01	Phenyl
	4.Stage	500-800	(52.4), 53.7	Organic waste, Metal oxide
$[Ru(L_2)Cl_2]Cl·6H_2O$	1.Stage	25-250	(10.76) 10.2	H_20
	2.Stage	250-420	(24.94) 25.1	H_20, HCl, Phenyl
	3.Stage	420-560	(10.02) 9.5	Phenyl
	4.Stage	560-800	(54.1) 55.2	Organic waste, Metal oxide
$[Ru(L_3)Cl_2]Cl·6H_2O$	1.Stage	25-250	(11.8) 11.5	H_20
	2.Stage	250-380	(22.29) 21.96	HCl, Phenyl
	3.Stage	380-540	(10.29) 10.55	Phenyl
	4.Stage	540-800	(55.62), 55.99	Organic waste, Metal oxide

Cyclohexane oxidation under microwave irradiation

The Schiff base Ru (III) complexes cyclohexane oxidation mechanism, the first and longest step is the oxidation of CyH to Cy–OH and then Cy=O and other further oxidized products. If the first step is controlled, the ratio of desired products Cy–OH and Cy=O selectivity can be increased [41]. The possible reaction products are shown in Fig. 6**.** It has been shown that the microwave power and the novel ruthenium catalysts could affect the selective oxidation of CyH to Cy=O and Cy–OH. The mononuclear L_2-Ru(III) complex showed better catalytic activity than the L_1-Ru(III) and L_3-Ru(III) complexes. The Ru(III) complexes synthesized in various ways have been shown to be good catalyst in much of the literature. In this study, the Ru(III) complexes showed high catalytic activity on cyclohexane. This is due to the ligands and their mononuclear Ru(III) complex structure. In the complexes, cyclohexane is affected by the π–π electron delocalization phenomena occur throughout the ligand structure. This situation affects the oxidation reaction. The best selectivities of the desired products Cy=O and Cy–OH were obtained in the Ru(III) complex. The catalytic performance of the mononuclear Ru(III) complexes are comparable to the activity exhibited by the earlier reported different complexes [42,43]. The focus point in the conversion of cyclohexane to the oxidized products is the reduction of Ru(III)–L to Ru(II)–L (L:ligand). This reduction to Ru(I)–L is facilitated by the ligands easing around the metal cation. The formation of the oxidation products Cy–OH and Cy=O show the effect of the activated bonds. Octahedral geometry of the mononuclear Ru(III) complexes may be the reason for having high activity on cyclohexane. In the formation of the oxidation product Cy=O, mononuclear Co(II) complexes also have high activity.

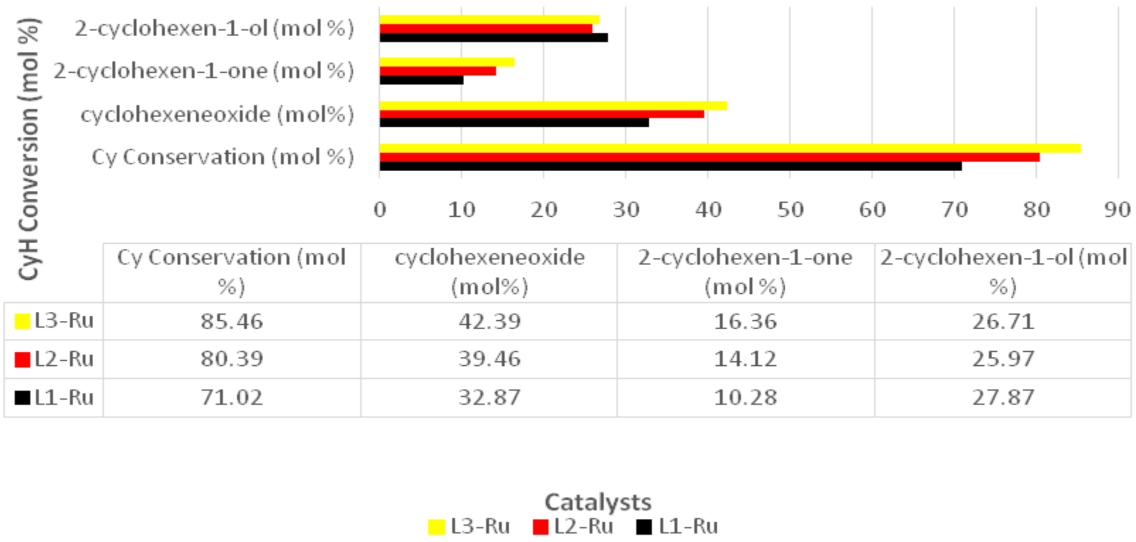
Cyclohexene oxidation under microwave irradiation

Schiff base metal complexes carried out using the oxidation reaction of cyclohexane substrate and ratios extracted using the results obtained are given in Fig. 7**.** The high selectivity and ease of separation of the heterogeneous catalysis, wherein the catalyst of the reaction from the reaction medium provide advantages of great importance. The instability of such catalysts in the oxidation atmosphere on the other hand, leads to the drawback of limited reproducibility and show low activity. H_2O_2 is an initiator in the reaction medium used and the reaction is performed at high temperatures in a microwave oven. An interesting feature of the hydrogen peroxide in the reaction medium is that it is transformed into a highly active form of peroxo mono carbonate ion. Soluble alkanes may be an epoxy with high efficiency with H_2O_2. They can be water-insoluble epoxy alcohols under similar conditions using acetonitrile as a solvent-water mixture. The catalytic effect of all transition metal complexes of Schiff base results in the epoxidation reaction of cyclohexane, as shown in the substrate conversion reaction appears to be very high. Conversion rate is over 98%. But the cyclohexane oxide conversion rate is lower. By products, 2-cyclohexen-1-one and 2-cyclohexene-1-ol compounds are also formed. Cyclohexene oxide ratio as seen from the data obtained the highest L_3-Ru (85.46%) and L_2-Ru, (80.39%) and are used as catalysts in epoxidation reactions of metal complexes.



	CyH (mol %)	Cy-OH (mol %)	Cy=O (mol %)
■ 1	99.1	23.18	14.83
🟥 2	99.28	34.82	19.81
🟨 3	99.62	28.86	19.83

Fig. 6: Influence of the complexes in cyclohexane oxidation under microwave irradiation.



	Cy Conservation (mol %)	cyclohexeneoxide (mol%)	2-cyclohexen-1-one (mol %)	2-cyclohexen-1-ol (mol %)
🟨 L3-Ru	85.46	42.39	16.36	26.71
🟥 L2-Ru	80.39	39.46	14.12	25.97
■ L1-Ru	71.02	32.87	10.28	27.87

Fig. 7: Influence of the complexes in cyclohexene oxidation under microwave irradiation.

Conclusions

The new three Schiff base ligands containing phenoxy group and their Ru(III) complexes have been synthesized and characterized by analytic and spectroscopic methods. It can be concluded from all the results given above that the Schiff base ligands act as ONNO tetradentate chelate in mononuclear complexes.

The synthesized complexes were tested as oxidative catalysts from cyclohexane and cyclohexene with their oxidation products under microwave irradiation. The catalytic effect of all Ru complexes results in the epoxidation reaction of cyclohexane, as shown in the substrate conversion reaction appears to be very high. Especially, L_3-Ru and L_2-Ru complexes showed the best catalytic activities in epoxidation reactions.

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