

Synthesis, spectral characterization, catalytic and biological studies of new Ru(II) carbonyl Schiff base complexes of active amines

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ABSTRACT

The synthesis and characterization of several hexa-coordinated Ru(II) complexes of the type [Ru(CO)(B)(L)] (B = PPh₃/AsPh₃/py/pip; L = di-basic tetradentate ligand derived from the condensation of isatin with diamines) were reported. IR, electronic, ¹H-NMR, ³¹P-NMR of the complexes are discussed. An octahedral geometry has been tentatively proposed for all these complexes. The new complexes have been tested for the catalytic activity in the reaction of oxidation of alcohols in the presence of *N*-methylmorpholine-*N*-oxide as co-oxidant. The new complexes were also exhibited antimicrobial investigations.

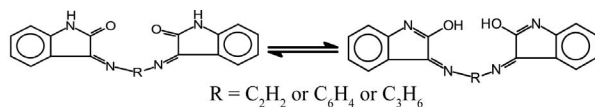
Keywords: Ruthenium(II) Complexes; Tetradentate N₂O₂ Schiff Base; Characterization; Catalytic Oxidation; Antimicrobial Activity

1. INTRODUCTION

Transition metal complexes with tetradentate Schiff base ligands have been studied as catalyst for a number of organic oxidation and reduction reactions and electrochemical reduction processes [1,2]. The accessibility of ruthenium higher oxidation states [3,4] converts them into excellent catalyst for redox reactions. Particularly, metal complexes of ruthenium have demonstrated to be useful laboratory and industrial homogeneous catalysts in the epoxidation of alkenes and oxidation of alcohols using iodobenzene, sodium hypochlorite hydrogen peroxide and *N*-methylmorpholine-*N*-oxide as oxygen sources [5-8]. Further the oxidation of organic substrates mediated by high valent ruthenium-oxo species evokes

much interest in modeling of cytochrome p.450 [9]. Sharpless *et al.* [10] carried out a yield oriented study of oxidation of cholesterol, geranial etc. catalyzed by ruthenium complexes in the presence of *N*-methylmorpholine-*N*-oxide and *N*, *N*-dimethylaniline-*N*-oxide. Furthermore, the catalytic activities of ruthenium complexes containing tertiaryphosphine or arsine ligands are well established [11,12]. Tetradentate Schiff base complexes have been employed as catalysts for many reactions and as biological models in understanding the structure of bio molecules and biological process [13,14].

In addition, the chemistry of chelating tetradentate Schiff base ligands with ruthenium has also been extensively studied [15]. This is due to the fact that Schiff bases offer opportunities for inducing substrate chirality, tuning metal centered electronic factors, enhancing solubility and stability and their use as either homogeneous or heterogeneous catalysis [16-18]. The oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones respectively, plays a central role in organic synthesis [19,20]. In continuation of our research interest [21] to understand the role of these simple and inexpensive N₂O₂ donor Schiff base ligands towards ruthenium, the reaction of Schiff bases derived from isatin and diamines with ruthenium(II) precursors containing PPh₃/AsPh₃/py/pip has been carried out. Thus, the present work describes the results of synthesis, characterization and properties of hexa coordinated Ru(II) complexes exhibiting a N₂O₂ ligating core with their catalytic activity towards oxidation of alcohols in the presence of NMO. Further, the antibacterial activity of the Schiff bases and their ruthenium complexes were examined. The following Schiff bases, derived from the condensation of isatin with ethylenediamine/o-phenylenediamine/propylene diamine (**Scheme 1**), were used to prepare the new ruthenium (II) complexes.



Scheme 1. Keto-enol tautomerism.

2. EXPERIMENTAL

2.1. Materials

The Schiff bases were prepared by the reported procedure [21,22]. All the reagents used were analytical reagent grade. Solvents were purified and dried according to standard procedures. RuCl₃·3H₂O, triphenylphosphine, propylenediamine, ethylenediamine, *o*-phenylenediamine and isatin were purchased from Loba Chemie Pvt Ltd., Bombay, India and were used as such without further purification. [RuHCl(CO)(PPh₃)₃] [23], [RuHCl(CO)(B)(PPh₃)₂] [24] (where B = py/pip) and [RuHCl(CO)(AsPh₃)₃] [25] were prepared by reported literature methods.

2.2. Physical Measurements

The analysis of C, H and N were performed on a Carlo Erba 1160 model 240 Perkin Elmer CHN analyzer, IR spectra were recorded in KBr pellets in the 4000 - 400 cm⁻¹ region in a Jasco 400 plus spectrophotometer. Electronic spectra were recorded in CH₂Cl₂ solution with a Hitachi U - 3210 spectrophotometer in the range of 800 - 200 nm. ¹H-NMR and ³¹P-NMR spectra were recorded on a Burker 400 MHz instrument using TMS as an internal reference. Melting points were recorded with Raaga apparatus and were uncorrected.

2.3. Synthesis of New Carbonyl Complexes of RU(II)

To a solution of [RuHCl(CO)(EPh₃)₂(B)] [where E = P or As; B = PPh₃/py/pip/AsPh₃] (0.1 g, 0.1 - 0.13 mmol) in benzene (25 cm³), was added the appropriate Schiff base (0.039 - 0.053 g, 0.1 - 0.13 mmol). The solution was heated under reflux for 6 hrs. Then, it was concentrated to ca. 3 cm³, cooled and new complexes were separated upon addition of small quantity (6 cm³) of light petroleum (60 - 80°C). The products were filtered, washed with light petroleum, recrystallised from CH₂Cl₂/light petroleum mixture and dried in vacuo (yield: 65% - 70%). The purity of the complexes was checked by TLC.

2.4. Catalytic Oxidation

Catalytic oxidation of alcohols to the corresponding carbonyl compounds by ruthenium(II) carbonyl Schiff base complexes was studied in the presence of NMO as co-oxidant by a typical reaction using the complex [Ru(CO)(B)L] as catalyst, and the alcohol as substrate at

a 1:100 molar ratio. For this purpose, a solution of ruthenium complex (0.01 mmol) in 20 cm³ CH₂Cl₂ was added to the solution of the substrate (1mmol) and NMO (3 mmol) and the mixture was stirred for 3 - 7 hrs at room temperature. The solvent was evaporated from the mother liquor under reduced pressure and the residue was then extracted with petroleum ether (60°C - 80°C).

2.5. Antibacterial Activity Studies

Pathogenic microbials namely *Escherichia Coli*, *Aeromonas hydrophila* and *Salmonella typhi* were used to test the biological potential of the isatin diimine and their carbonyl complexes of ruthenium (II). The antibacterial activities of the complexes were determined by disc diffusion method [26]. The bacteria were cultured in nutrient agar medium in petriplates and used inoculums for the study. The complexes to be tested were dissolved in DMSO to a final concentration of 0.25%, 0.5% and 1% and soaked in filter paper disc of 5 mm diameter and of 1 mm thickness. The disc were placed on the previously seeded plates and incubated at 35 ± 2°C for 24 hrs. The diameter of inhibitory zone around each disc was measured after 24 hrs. *Streptomycin* was used as a standard.

3. RESULTS AND DISCUSSIONS

3.1. Analytical Studies

Complexes of general formula [Ru(CO)(B)(L)] (where B = PPh₃/AsPh₃/py/pip; L= dibasic tetradentate Schiff bases) were synthesized by the reactions of [RuHCl(CO)(PPh₃)₃], [RuHCl(CO)(AsPh₃)₃] and [RuHCl(CO)(PPh₃)₂(B)] (where B = py/pip) with the respective tetradentate Schiff bases (Scheme 2) in a 1:1 molar ratio in benzene.

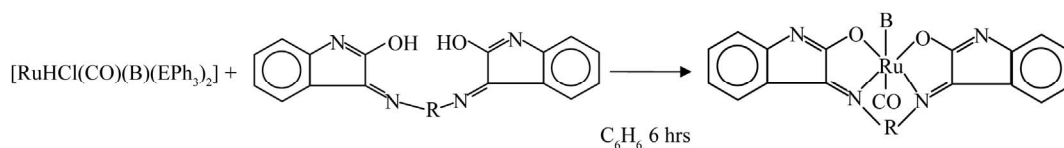
The analytical data for the new complexes agree well with the proposed molecular formula as given in Table 1. In all the reactions it has been observed that the Schiff bases behave as a dibasic tetradentate ligands by substituting the chloride ion, hydride ion and two triphenylphosphine/arsine groups from each mole of the starting complexes to form the mono nuclear complexes. These observations indicate a more labile nature for the Ru-P bond compared to the Ru-N bond of the heterocyclic nitrogen bases in these complexes. The difference in the strength of Ru-P/As and Ru-N bonds may be explained as due to the better σ donation ability of the nitrogen bases compared to that of triphenylphosphine/arsine. The Schiff base ruthenium(II) complexes are highly colored, stable to air and light and soluble in chloroform, methylene chloride, benzene and DMSO.

3.2. I.R. Spectra

The most important IR bands are presented and as-

signed in **Table 2**. The bands appearing at 1740 - 1715 cm^{-1} and 1652 - 1619 cm^{-1} in the ligand spectra were assigned to stretching vibration modes of C = O and C = N respectively. All the bands assigned to stretching vibration modes in the free ligands changed in the spectra of metal complexes. New bands recorded at 1599 - 1583

cm^{-1} and 1637 - 1600 cm^{-1} vibration modes respectively suggest the enolisation of the NH group of isatin and coordination through the oxygen of the C-O group [21, 27]. The formation of the Ru-O and Ru-N bands is further supported by the appearance of $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$ band in the regions 576 - 541 cm^{-1} and 492 - 475 cm^{-1} respec-



Scheme 2. Preparation of new Ru(II) Schiff base complexes.

Table 1. Analytical data of new Ru(II) complexes.

Complex	Mp ($^{\circ}\text{C}$)	Yield (%)	Calculated(found)%		
			C	H	N
[Ru(CO)(PPh ₃)(L ¹)]	168	80	62.80(62.61)	3.81(3.76)	7.92(8.05)
[Ru(CO)(AsPh ₃)(L ¹)]	158	78	59.12(59.25)	3.59(3.67)	7.46(7.52)
[Ru(CO)(py)(L ¹)]	143	75	54.95(55.37)	3.24(3.10)	13.35(12.50)
[Ru(CO)(pip)(L ¹)]	125	78	54.33(53.57)	4.34(4.01)	13.40(12.67)
[Ru(CO)(PPh ₃)(L ²)]	172	75	63.24(64.61)	4.02(3.85)	7.77(7.21)
[Ru(CO)(AsPh ₃)(L ²)]	160	80	59.61(62.01)	3.79(3.51)	7.32(6.56)
[Ru(CO)(py)(L ²)]	145	70	55.76(57.75)	3.53(3.87)	13.01(12.58)
[Ru(CO)(pip)(L ²)]	130	78	55.15(55.75)	4.64(4.38)	12.86(11.96)
[Ru(CO)(PPh ₃)(L ³)]	157	80	65.16(66.18)	3.58(3.85)	7.41(7.58)
[Ru(CO)(AsPh ₃)(L ³)]	142	76	61.57(62.75)	3.38(3.15)	7.00(6.91)
[Ru(CO)(py)(L ³)]	137	75	58.74(59.62)	2.97(3.03)	12.24(11.56)
[Ru(CO)(pip)(L ³)]	125	75	58.13(57.67)	3.98(3.87)	12.11(11.91)

Table 2. IR and UV - Visible Spectral data for the ligands and new Ru(II) complexes.

Complex	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	λ_{max}
HL ¹	1619	1720	-			
[Ru(CO)(PPh ₃)(L ¹)]	1620	-	1585	475	541	246, 320, 360, 600
[Ru(CO)(AsPh ₃)(L ¹)]	1628	-	1583	480	547	250, 320, 362, 590
[Ru(CO)(py)(L ¹)]	1600	-	1590	482	562	248, 316, 368, 593
[Ru(CO)(pip)(L ¹)]	1637	-	1583	488	576	246, 315, 368, 598
HL ²	1652	1715	-			
[Ru(CO)(PPh ₃)(L ²)]	1636	-	1589	487	560	246, 315, 568
[Ru(CO)(AsPh ₃)(L ²)]	1622	-	1597	490	570	248, 368, 408
[Ru(CO)(py)(L ²)]	1628	-	1599	492	575	248, 316, 463, 590
[Ru(CO)(pip)(L ²)]	1630	-	1585	479	547	250, 350, 403
HL ³	1630	1740	-			
[Ru(CO)(PPh ₃)(L ³)]	1607	-	1587	476	550	248, 318, 550
[Ru(CO)(AsPh ₃)(L ³)]	1615	-	1592	490	570	248, 325, 563
[Ru(CO)(py)(L ³)]	1603	-	1590	486	568	246, 313, 569, 600
[Ru(CO)(pip)(L ³)]	1600	-	1588	482	571	246, 320, 350, 596

tively in the spectra of the chelates [21,28,29]. The most important conclusion drawn from the infrared spectral evidence is that the diamine bis(isatin) Schiff base ligand is acting as chelating agent towards the central metal ion as dibasic ONNO tetradentate ligand, via the two coordinating sites of nitrogen atoms and two negatively charged oxygen atoms of isatin residues forming five-membered chelating rings [30]. In addition, other characteristic bands due to PPh₃ and AsPh₃ are also present around 1438 cm⁻¹ [31], in the spectra of Schiff base complexes. A medium intensity band is observed in the 1020 cm⁻¹ region, characteristics of the coordinated pyridine or piperidine [21,32]. In all the ruthenium complexes the band due to terminally coordinated C \equiv O group appeared at 1900 - 1944 cm⁻¹ [33].

3.3. Electronic Spectra

The electronic spectra of all the complexes in dichloromethane showed three to four bands in the region 246 - 600 nm. All the Schiff base ruthenium complexes are diamagnetic, indicating the presence of ruthenium in the +2 oxidation state. The ground state of ruthenium(II) in an octahedral environment is ¹A_{1g} from the t_{2g}⁶ configuration and excited states corresponding to the t_{2g}⁵ e_g¹ configurations are ³T_{1g}, ³T_{2g}, ¹T_{1g} and ¹T_{2g}. Hence four bands corresponding to the transition ¹A_{1g} \rightarrow ³T_{1g}, ¹A_{1g} \rightarrow ³T_{2g}, ¹A_{1g} \rightarrow ¹T_{1g} and ¹A_{1g} \rightarrow ¹T_{2g} are possible in the order of increasing energy. The bands around 600 - 550 nm and 463 - 403 nm are assigned to ¹A_{1g} \rightarrow ¹T_{1g} [34,35] and the charge transfer reactions respectively are listed in **Table 2**. The charge transfer bands observed in all the complexes due to M \rightarrow L transitions are possible in the visible region [36-38]. Moreover the presence of carbonyl, triphenylphosphine/arsine and heterocyclic bases as ligands, which are capable of producing strong ligand field in e_g^{*} which is relatively higher energy levels. This band has been assigned to the charge-transfer transition arising from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbital's derived from the e_g^{*} level of the ligands should appear in the relatively high energy region compared to those due to t_{2g} \rightarrow e_g^{*} transitions [34-36]. The other high energy bands have been designated as π - π^* and n- π^* transitions for the electrons localized on the azomethine group of Schiff bases [32]. The pattern of the electronic spectra of all the complexes indicated the presence of an octahedral environment around the ruthenium(II) ion, similar to that of other octahedral ruthenium(II) complexes [37].

3.4. ¹H-NMR Spectra

The ¹H NMR spectra of some complexes were recorded to confirm the bonding of the Schiff base to the ruthenium ion and given in the **Table 3**. Multiplets are

observed around 7.2 - 7.8 ppm in all the complexes and have been assigned to the aromatic protons of triphenylphosphine, triphenylarsine, pyridine, piperidine and isatin Schiff base ligands [29]. A singlet appears in the region 1.36 - 1.4 ppm for the methylene protons [39]. In the complexes [Ru(CO)(PPh₃)(L³)] and [Ru(CO)(AsPh₃)(L³)] an extra singlet was found in the region at 2.05 ppm, which has been assigned to the extra methylene group present in the Schiff base. The ¹H NMR spectra of the neutral diamagnetic chelates of the type [Ru(CO)(B)(L)] are similar to those of the ligands, excepting that the signal due to NH proton of isatin disappears. This proves the deprotonation of NH group upon complexation and supports the above NMR spectral data suggesting that the ligand acts as dibasic tetra dentate chelating agent.

3.5. ³¹P-NMR Spectra

The ³¹P-NMR spectra for a few of the complexes have been recorded in order to confirm the presence of triphenylphosphine group and to determine the geometry of the complexes (**Table 3**). The appearance of singlet at 28.78, 28.75 and 28.70 ppm for the complexes [Ru(CO)(PPh₃)(L¹)], [Ru(CO)(PPh₃)(L²)] and [Ru(CO)(PPh₃)(L³)] respectively indicates the presence of one triphenylphosphine group in these complexes.

3.6. Catalytic Activity of the Complexes

Catalytic oxidation of primary alcohols and secondary alcohols by the synthesized ruthenium(II) carbonyl Schiff base complex [Ru(CO)(B)(L)] was carried out in CH₂Cl₂ in the presence of NMO. Results of the present investigation suggest that the complex is able to react efficiently with NMO to yield a high valent ruthenium-oxo species [15,40] capable of transferring oxygen atom to alcohols. The oxidation of benzylalcohol to benzaldehyde resulted in 89% yield. Further, the complex effectively catalyzes the oxidation of aliphatic alcohols such as butane-2-ol, to the corresponding ketones effectively and is evident from **Table 4**. Moreover, the complex effectively catalyzes the oxidation of five and six membered cyclic alcohols to the corresponding ketones with the conversion rates to the extent of 90% and 82% respectively. The reaction provides a new environment friendly route to the conversion of alcoholic functions to carbonyl group and water is the only byproduct during the course of the reaction. It has been concluded that the complexes have a better catalytic efficiency in the case of oxidation of primary and secondary alcohols in the presence of NMO.

3.7. Antibacterial Studies

The *in vitro* antibacterial screening of the ligands and

Table 3. NMR Spectral data of new Ru(II) complexes.

S. No.	Complex	¹ H-NMR data (ppm)	³¹ P-NMR data (ppm)
1.	[Ru(CO)(PPh ₃)(L ¹)]	7.2 - 7.6 (Ph, m), 1.36 (N-(CH ₂) ₂ , s)	28.78
2.	[Ru(CO)(AsPh ₃)(L ¹)]	7.3 - 7.6 (Ph, m), 1.36 (N-(CH ₂) ₂ , s)	-
3.	[Ru(CO)(py)(L ¹)]	7.2 - 7.6 (Ph, m), 1.4 (N-(CH ₂) ₂ , s)	-
4.	[Ru(CO)(PPh ₃)(L ²)]	7.3 - 7.8 (Ph, m)	28.75
5.	[Ru(CO)(AsPh ₃)(L ²)]	7.2 - 7.7 (Ph, m)	-
6.	[Ru(CO)(pip)(L ²)]	7.2 - 7.6 (Ph, m)	-
7.	[Ru(CO)(PPh ₃)(L ³)]	7.3 - 7.6 (Ph, m), 1.36 (N-(CH ₂) ₂ , s), 2.05 (CH ₂ , s)	28.70
8.	[Ru(CO)(AsPh ₃)(L ³)]	7.2 - 7.6 (Ph, m), 1.36 (N-(CH ₂) ₂ , s), 2.05 (CH ₂ , s)	-

Table 4. Catalytic oxidation of alcohols by Ru(II) complexes.

Complex	Substrate	Product	Yield ^a	Turnover ^b
[Ru(CO)(PPh ₃)(L ¹)]	Benzylalcohol	Benzaldehyde	76	75
	Cyclohexanol	Cyclohexanone	82	80
	Butane-2-ol	Butanone	84	88
	Cyclopentanol	Cyclopentanone	90	92
[Ru(CO)(AsPh ₃)(L ¹)]	Benzylalcohol	Benzaldehyde	80	81
	Cyclohexanol	Cyclohexanone	82	80
	Butane-2-ol	Butanone	73	78
	Cyclopentanol	Cyclopentanone	89	88
[Ru(CO)(py)(L ¹)]	Benzylalcohol	Benzaldehyde	76	78
	Cyclohexanol	Cyclohexanone	83	86
	Butane-2-ol	Butanone	74	79
	Cyclopentanol	Cyclopentanone	90	92
[Ru(CO)(pip)(L ¹)]	Benzylalcohol	Benzaldehyde	77	79
	Cyclohexanol	Cyclohexanone	85	87
	Butane-2-ol	Butanone	80	84
	Cyclopentanol	Cyclopentanone	91	95
[Ru(CO)(PPh ₃)(L ²)]	Benzylalcohol	Benzaldehyde	81	85
	Cyclohexanol	Cyclohexanone	80	83
	Butane-2-ol	Butanone	78	87
	Cyclopentanol	Cyclopentanone	90	91
[Ru(CO)(AsPh ₃)(L ²)]	Benzylalcohol	Benzaldehyde	82	81
	Cyclohexanol	Cyclohexanone	81	85
	Butane-2-ol	Butanone	72	76
	Cyclopentanol	Cyclopentanone	89	86

[Ru(CO)(py)(L ²)]	Benzylalcohol	Benzaldehyde	82	84
	Cyclohexanol	Cyclohexanone	80	84
	Butane-2-ol	Butanone	71	74
	Cyclopentanol	Cyclopentanone	90	87
[Ru(CO)(pip)(L ²)]	Benzylalcohol	Benzaldehyde	76	79
	Cyclohexanol	Cyclohexanone	83	78
	Butane-2-ol	Butanone	72	75
	Cyclopentanol	Cyclopentanone	90	93
[Ru(CO)(PPh ₃)(L ³)]	Benzylalcohol	Benzaldehyde	75	78
	Cyclohexanol	Cyclohexanone	86	82
	Butane-2-ol	Butanone	76	80
	Cyclopentanol	Cyclopentanone	93	90
[Ru(CO)(AsPh ₃)(L ³)]	Benzylalcohol	Benzaldehyde	73	77
	Cyclohexanol	Cyclohexanone	79	80
	Butane-2-ol	Butanone	70	73
	Cyclopentanol	Cyclopentanone	91	86
[Ru(CO)(py)(L ³)]	Benzylalcohol	Benzaldehyde	75	78
	Cyclohexanol	Cyclohexanone	75	79
	Butane-2-ol	Butanone	72	75
	Cyclopentanol	Cyclopentanone	93	80
[Ru(CO)(pip)(L ³)]	Benzylalcohol	Benzaldehyde	67	70
	Cyclohexanol	Cyclohexanone	81	80
	Butane-2-ol	Butanone	78	81
	Cyclopentanol	Cyclopentanone	91	86

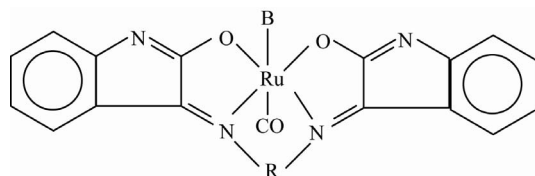
their ruthenium complexes have been carried out against *Escherichia Coli*, *Aeromonas hydrophila* and *Salmonella typhi* using a nutrient agar medium by disc diffusion method. The results (**Table 5**) showed the complexes exhibit moderate activity against *Escherichia Coli*, *Aeromonas hydrophila* and *Salmonella typhi*. The toxicity of ruthenium chelates increases on increasing the concentration [41]. The increase in the antibacterial activity of metal chelates may be due to the effect of the metal ion on the normal cell process. A possible mode of the toxicity increase may be considered in light of Tweeds chelation theory [42]. Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and possible π -electron delocalization over the whole chelate ring. Such chelation could enhance the lipophilic character of the central metal atom, which subsequently favors its per-

meation through the lipid layers of cell membrane. Furthermore, the mode of action of the compounds may involve in the formation of a hydrogen bond through the azomethine ($>C = N$) group with the active centers of cell constituents, resulting in interference with the normal cell processes [42]. Though the complexes possess activity, it could not reach the effectiveness of the standard drug *streptomycin*. The variation in the effectiveness of the different compounds against different organisms depend either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells [40,41].

Based on the analytical, spectral (IR, electronic, ¹H NMR and ³¹P-NMR) data, **Scheme 3** octahedral structure has been tentatively proposed for all the new carbonyl Schiff base complexes of ruthenium (II).

Table 5. Antibacterial activity of ligands and Ru(II) complexes (diameter of inhibition zones-mm).

Ligand/Complex	<i>Escherichia coli</i>			<i>Aeromonas hydrophila</i>			<i>Salmonella typhi</i>		
	0.25%	0.5%	1.0%	0.25%	0.5%	1.0%	0.25%	0.5%	1.0%
L ¹	10	11	13	11	12	13	9	12	13
[Ru(CO)(PPh ₃)(L ¹)]	12	14	16	14	17	18	13	16	20
[Ru(CO)(AsPh ₃)(L ¹)]	11	15	17	12	16	20	14	17	21
[Ru(CO)(py)(L ¹)]	14	16	20	13	17	19	15	17	20
[Ru(CO)(pip)(L ¹)]	16	18	20	13	17	19	15	18	20
L ²	10	12	14	9	12	15	10	11	14
[Ru(CO)(PPh ₃)(L ²)]	12	15	19	11	16	18	12	18	20
[Ru(CO)(AsPh ₃)(L ²)]	15	18	21	12	18	21	14	15	18
[Ru(CO)(py)(L ²)]	14	16	19	14	19	20	18	20	21
[Ru(CO)(pip)(L ²)]	15	20	21	16	18	21	19	20	21
L ³	10	11	13	12	14	15	10	11	14
[Ru(CO)(PPh ₃)(L ³)]	12	14	17	14	16	18	15	18	20
[Ru(CO)(AsPh ₃)(L ³)]	14	18	20	15	18	20	17	18	21
[Ru(CO)(py)(L ³)]	16	17	21	14	17	19	19	22	23
[Ru(CO)(pip)(L ³)]	17	18	22	16	18	22	17	19	22
Streptomycin	22	23	28	21	37	29	29	21	25

**Scheme 3.** Structure of New Ru(II) complexes.

4. CONCLUSIONS

A new family of carbonyl complexes of ruthenium(II) containing N₂O₂ donor Schiff bases incorporating triphenylphosphine/triphenylarsine/pyridine/piperidine ligands were synthesized and characterized. The new complexes were tested as a new and efficient catalyst for the oxidation of primary and secondary alcohols to their corresponding aldehydes and ketones with excellent yields in the presence of *N*-methylmorpholine-*N*-oxide. Further the possible explanations for the mode of action of these complexes against three different microbes are described.

REFERENCES

- [1] Canali, L. and Sherrington, D.C. (1999) Utilization of homogeneous and supported chiral metal (salen) complexes in asymmetric catalysis. *Chemical Society Reviews*, **28**, 85-93. [doi:10.1039/a806483k](https://doi.org/10.1039/a806483k)
- [2] Isse, A.A., Gennara A. and Viane, E. (1998) Mechanism of the electrochemical reduction of benzylchlorides catalyzed by Co(salen). *Journal of Electroanalytical Chemistry*, **444**, 241-245. [doi:10.1016/S0022-0728\(97\)00572-X](https://doi.org/10.1016/S0022-0728(97)00572-X)
- [3] Liobet, A., Hodgson D.J. and Meyer, T.J. (1990) Synthesis, structure and redox properties of triaqua (tris (1- pyrazolyl) methan) ruthenium(II) cation. *Inorganic Chemistry*, **29**, 3760-3766. [doi:10.1021/ic00344a023](https://doi.org/10.1021/ic00344a023)
- [4] Liobet, A. (1994) Synthesis, spectral and redox properties of a new series of aqua complexes of Ruthenium (II). *Inorganica Chimica Acta*, **221**, 125-131. [doi:10.1016/0020-1693\(94\)03963-1](https://doi.org/10.1016/0020-1693(94)03963-1)
- [5] Thron, J.R. and Wilkinson, G. (1978) Schiff base complexes of ruthenium(II). *Journal of the Chemical Society, Dalton Transactions*, **2**, 110-115. [doi:10.1039/DT9780000110](https://doi.org/10.1039/DT9780000110)
- [6] Katsuki, T. (1995) Catalytic asymmetry oxidation using optically active (salen) Manganese (III) complexes as catalysts. *Coordination Chemistry Reviews*, **140**, 189-214. [doi:10.1016/0010-8545\(94\)01124-T](https://doi.org/10.1016/0010-8545(94)01124-T)
- [7] Claustro, I., G. Abate, Sanchez, E. and Acquaye, J.H. (2003) Synthesis spectroscopic and electrochemical properties of ruthenium-2-(2'-hydroxyphenyl)-benzo-azole complexes. Crystal structure of [Ru(ter-py)HPBCl]. *Inorganica Chimica Acta*, **342**, 29-36. [doi:10.1016/S0020-1693\(02\)01068-X](https://doi.org/10.1016/S0020-1693(02)01068-X)
- [8] Silva, A.R., Freire, C. and Castro, B. (2004) Modulation of the catalytic activity of manganese(III) salen complexes in the epoxidation of styrene: Influence of the oxygen source. *New Journal of Chemistry*, **28**, 253-260. [doi:10.1039/b309125b](https://doi.org/10.1039/b309125b)

- [9] Meunier, B. (1992) Metalloporphyrins as versatile catalysts for oxidation reactions and oxidative DNA cleavage. *Chemical Review*, **92**, 1411-1456. doi:10.1021/cr00014a008
- [10] Sharpless, K.B., Akashi, K. and Osima, K. (1976) Ruthenium catalyzed oxidation of alcohols to aldehydes and ketones by amine-n-oxide. *Tetrahedron Letters*, **17**, 2503-2506. doi:10.1016/S0040-4039(00)78130-5
- [11] Leung, W.H. and Che, C.M. (1989) Oxidation chemistry of Ruthenium-Saloon Complexes. *Inorganic Chemistry*, **28**, pp. 4619-4622. doi:10.1021/ic00325a016
- [12] Wong, W.K., Chen, X.P., Gao, J.P., Chi, Y.G., Pan, W.X. and Wang, W.Y. (2002) Studies on electronic structures and related properties of complexes $M(\text{tap})_3^{2+}$ (M=Fe, Ru, Os) by the DFT method. *Journal of the Chemical Society, Dalton Transactions*, **1**, 113-119. doi:10.1039/b105266g
- [13] Bhowon, M.G., Wah, L.K. and Narain, R. (1998) Schiff base complexes of Ru (II) and their uses as catalytic oxidants. *Polyhydron*, **18**, 3341-3345.
- [14] R. Atkins, G. Brewer, E. Kokot. (1985) Copper (II) and Ni(II) complexes of unsymmetrical tetra dentate Schiff base ligands. *Inorganic Chemistry*, **24**, 128-134. doi:10.1021/ic00196a003
- [15] Khan, M.M.T., Sreelatha, C.H., Mizra, S.A., Ramachandriah, G. and Abdi, S.H.R. (1998) Synthesis and characterization of Ru(V)oxo compounds of Schiff base: bis(salicylaldehyde)-o-phenylenediamine, with appended Cl⁻, imidazole and 2-methylimidazole: the first complexes of stable oxo-complexes via direct oxygenation. *Inorganica Chimica Acta*, **154**, 103-108. doi:10.1016/S0020-1693(00)85173-7
- [16] Clercq, B.D. and Verpoort, F. (2002) Atom transfer radical polymerization of vinyl monomers mediated by Schiff base-Ruthenium-alkylidene catalysts and the adventitious effects of water in polymerization with analogous cationic complexes. *Macromolecules*, **35**, 8943-8947. doi:10.1021/ma020307d
- [17] Opstal, T. and Verpoort, F. (2002) Ruthenium indenylidene and vinylidene complexes bearing Schiff bases: Potential catalysts in Enol-Ester Synthesis. *Synlett*, **6**, 935-941. doi:10.1055/s-2002-31892
- [18] Opstal, T. and Verpoort, F. (2003) Synthesis of highly active Ruthenium indenylidene complexes for atom transfer radical polymerization and ring opening metathesis polymerization. *Angewandte Chemie International Edition*, **42**, 2876-2879. doi:10.1002/anie.200250840
- [19] Sherrington, D.C., Dijkstra, A., Arends, I.W.C.E. and Sheldon, R.A. (2001) Polymer immobilized Tempo (PIPO): An efficient catalytic system for environmentally benign oxidation of alcohols. *Supported Catalyst and Their Applications*, 118-124. doi:10.1039/9781847551962-00118
- [20] Venkatachalam, G. and Ramesh, R. (2005) Catalytic transfer hydrogenation of ketones catalysed by ortho metalated ruthenium(III) 2-(aryl azo) phenolate complexes containing triphenylarsine. *Tetrahedron Letters*, **46**, 5215-5218. doi:10.1016/j.tetlet.2005.05.116
- [21] Balasubramanian, K.P., Raju, V.V. and Chinnusamy, V. (2009) Synthesis, characteristic, catalytic and antimicrobial activities of imidazolo substituted benzilidene imines with ruthenium(II) complexes. *Journal of Indian chemistry Society*, **86**, 570-576.
- [22] Manivannan, S., Prabhakaran, R., Balasubramanian, K.P., Danabal, V., Karvembu, R., Chinnusamy, V. and Natarajan, K. (2007) Synthesis, spectral, electrochemical and catalytic studies of new Ru(III) tetra dentate Schiff base complexes. *Organic Chemistry*, **21**, 952-957. doi:10.1002/aoc.1318
- [23] Parnav, C., Kriza, A., Pop, V. and Udrea, S. (2005) Complexes of tin(IV) and Zirconium(IV) with Schiff bases derived from isatin and diamines. *Journal of Indian chemistry Society*, **82**, 7173.
- [24] Kanchanadevi, S., Balasubramanian, K.P. and Chinnusamy, V. (2005) Synthesis, characterisation and catalytic studies of ruthenium(II) Schiff base complexes. *Transition Metal Chemistry*, **30**, 330-333. doi:10.1007/s11243-004-5853-2
- [25] Raberto, A., Delgade, S., Lee, W.Y., Choi, S.R. and Jun, M.-J. (1991) The chemistry and catalytic properties of ruthenium and osmium complexes. Part 5. Synthesis of new compounds containing arsine ligands and catalytic activity in the homogeneous hydrogenation of aldehydes. *Transition Metal Chemistry*, **16**, 241-244. doi:10.1007/BF01032844
- [26] Raman, N., Kulandaisamy, A. and Jeyasubramanian, K. (2002) Synthesis, spectral, redox and biological studies of some Schiff base copper(II), Nickel(II), cobalt(II), Manganese(II), Zinc(II) and oxovanadium complexes derived from 1-phenyl-2,3dimethyl-4(4 iminopentan-2-one)pyrazole-5-one and 2-amino phenol/ 2-amino-thio-phenol. *Indian Journal of Chemistry*, **41**, 942-949.
- [27] Karvembu, R., Hemalatha, S., Prabhakaran, R. and Natarajan, K. (2003) Synthesis, characterization and catalytic activities of ruthenium complexes containing triphenylphosphine/triphenylarsine and tetra dentate Schiff bases. *Inorganic Chemistry Communications*, **6**, 486-490. doi:10.1016/S1387-7003(03)00021-2
- [28] Nakamoto, K. (1971) Infrared and Raman Spectra of Inorganic and coordination compounds. Wiley Interscience, New York.
- [29] Dyer, J.R. (1978) Application of absorption spectroscopy of organic compounds. Prentice-Hall, Upper Saddle River.
- [30] Hassaan, A.M.A. and Shehat, A.K. (1993) Metal chelates of o-phenylenediamines-bis-isatin Schiff base with La(III), Ce(III), Th(IV), UO₂(II), Ag(I) and Hg(II). *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **23**, 815-823. doi:10.1080/15533179308016863
- [31] Danialthangadurai, T., Gowri, M. and Natarajan, K. (2002) Synthesis and characterization of Ru(III) complexes containing monobasic bidentate Schiff bases and their biological activities. *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **32**, 329-343. doi:10.1081/SIM-120003211
- [32] El-Shahawi, M.S. and Shoair, A.F. (2004) Synthesis, spectroscopic characterization, redox properties and catalytic activities of some ruthenium(II) complexes containing aromatic aldehyde and triphenylphosphine or triphenylarsine. *Spectrochimica acta Part A Molecular and biomolecular spectroscopy*, **60**, 121-127.
- [33] Balasubramanian, K.P., Karvembu, R., Prabhakaran, R., Chinnusamy, V. and Natarajan, K. (2007) Synthesis, spectral, catalytic and antimicrobial studies of PPh₃/

- AsPh₃ complexes of Ru(III) with dibasic tridentate O,N,S donor ligands. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **68**, 50-54.
[doi:10.1016/j.saa.2006.10.049](https://doi.org/10.1016/j.saa.2006.10.049)
- [34] Remesh, R. and Sivagamasundari, M. (2003) Synthesis, spectral and anti-fungal activity of Ru(II) mixed ligand complexes. *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, **33**, 899-910.
[doi:10.1081/SIM-120021656](https://doi.org/10.1081/SIM-120021656)
- [35] Natarajan, K., Poddar, R.K. and Agarwala, C.U. (1977) Mixed complexes of Ruthenium (III) and Ruthenium(II) with triphenylphosphine or triphenylarsine and other ligands. *Journal of Inorganic and Nuclear Chemistry*, **39**, 431-435. [doi:10.1016/0022-1902\(77\)80056-0](https://doi.org/10.1016/0022-1902(77)80056-0)
- [36] Lever, A.B.P. (1984) *Inorganic Electronic Spectroscopy*. 2nd Edition, Elsevier, New York.
- [37] Chichak, K., Jacquenard, U. and Branda, N.R. (2002) The construction of (Salophen) Ruthenium(II) assemblies using axial coordination. *European Journal of Inorganic Chemistry*, **2002**, 357-368.
[doi:10.1002/1099-0682\(20022\)2002:2<357::AID-EJIC357>3.0.CO;2-T](https://doi.org/10.1002/1099-0682(20022)2002:2<357::AID-EJIC357>3.0.CO;2-T)
- [38] Nareshkumar, K. and Ramesh, R. (2004) Synthesis, characterization, redox property and biological activity of ruthenium(II) carbonyl complexes containing O, N – donor ligands and heterocyclic bases. *Spectrochim Acta A Mol Biomol Spectrosc*, **60**, 2913-2918.
- [39] Jayabalakrisnan, C. and Natarajan, K. (2002) Ruthenium(II) carbonyl complexes with tridentate Schiff bases and their catalytic activity. *Transition Metal Chemistry*, **27**, 75-79. [doi:10.1023/A:1013437203247](https://doi.org/10.1023/A:1013437203247)
- [40] Prabhakaran, R., Geetha, A., Thilagavathi, M., Karve-mbu, R., Krishnan, V., Bertagnolli, H. and Natarajan, K. (2004) Synthesis, characterization, EXAFS investigation and antibacterial activities of new ruthenium (III) complexes containing tetra dentate Schiff base. *Journal of Inorganic Biochemistry*, **98**, 2131-2140.
[doi:10.1016/j.jinorgbio.2004.09.020](https://doi.org/10.1016/j.jinorgbio.2004.09.020)
- [41] Padmapriya, N., Arunachalam, S.V., Sathya, N., Chinnusamy V. and Jayabalakrishnan, C. (2009) Catalytic and antimicrobial studies of binuclear ruthenium (III) complexes containing bis-β diketones. *Transition Metal Chemistry*, **34**, 437-445.
[doi:10.1007/s11243-009-9214-z](https://doi.org/10.1007/s11243-009-9214-z)
- [42] Periasamy, M., Balasubramanian, K.P. and Chinnusamy, V. (2004) Synthesis, characterization and biological activities of Ruthenium(II) Schiff base complexes. *Indian Journal of Chemistry*, **43**, 2132-2136.