J. Indian Chem. Soc.,
Vol. 87, November 2010, pp. 1305-1311

Synthesis, characterization, catalytic and antimicrobial activities of Ru^{II} complexes of Schiff bases derived from 2-substituted benzoicacid (2-oxo-1,2-dihydro-indol-3-ylidene) hydrazides

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Manuscript received 10 August 2009, revised 22 April 2010, accepted 5 May 2010

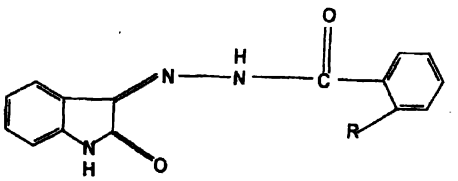
Abstract : A new ruthenium(II) Schiff base complexes of the type $[RuX(CO)(EPh_3)(B)(L)]$ (where X = H or Cl; B = EPh_3, py; E = P/As; L = monobasic bidentate ligand) have been synthesized. All the complexes were characterized by physicochemical and spectroscopic methods. An octahedral geometry has been proposed for all the complexes. The new complexes have been tested to find out their catalytic activity for the oxidation of alcohols to corresponding carbonyl compounds. Further the ligands and complexes were subjected to antimicrobial activity studies.

Keywords : Monobasic bidentate Schiff bases, ruthenium(II) complexes, spectral studies, catalytic activities and antimicrobial activities.

Introduction

The chemistry of Schiff base metal complexes is undergoing a rapid development and engaging the attention of researchers of many disciplines both experimental and theoretical. Studies of metal complexes with therapeutic compounds attains significant interest[1,2] due to its wide application in chemical, industrial, agricultural and biological field[3]. Recently, complexation has often be used to influence biological processes that are metal dependant[4,5]. At the same time many drugs behave as ligands coordinating to metal which affect their homoeostasis, it can be assumed therefore that action of some of the drugs used in the treatment of metal dependant diseases can be explained on these grounds[6,7]. There has been considerable current interest in the chemistry of ruthenium, primarily because of the fascinating electron-transfer, photochemical, catalytic and biological properties[8] exhibited by the complexes of this metal. Complexation of ruthenium by ligands of different types has been of significant importance. Ruthenium-Schiff base complexes, particularly those containing oxygen and nitrogen as donor atoms were found to be very efficient catalyst in the oxidation of alcohols using *N*-methylmorpholine-*N*-oxide as co-oxidant[9-12]. Schiff bases can accommodate different metal centers involving various coordination modes allowing successful synthesis of homo and hetero metallic complexes with varied stereochemistry[13]. Ruthenium-Schiff base complexes have been used as catalysts for the oxygenation reactions, oxygen carriers and oxygen activators[14-18].

As a part of our continuing efforts to synthesis and characterize the ruthenium chelates using simple and inexpensive Schiff base ligand, in this paper, we describe the synthesis, characterization, catalytic and antimicrobial activities of stable ruthenium(II) complexes containing bidentate Schiff bases. The general structure of the Schiff base ligands used in this paper is shown in the Fig. 1.



R	Abbreviation
H	HL_1
Cl	HL_2
NH_2	HL_3

Fig. 1. Structure of the Schiff base ligands.

Results and discussion

New ruthenium(II) complexes of the type [Ru(X)(CO)(EPh_3)(B)(L)] (X = H or Cl; B = EPh_3 or py; E = P or As; L = Schiff base anion) have been prepared from the reaction between [RuH(X)(CO)(EPh_3)$_2$(B)] and the respective Schiff bases (molar ratio 1 : 1) in benzene as shown in the equation.

$$[RuHCl(CO)(EPh_3)_2(B)] \text{ (or) } [RuH_2(CO)(PPh_3)_3] + HL \xrightarrow[6\ h]{\text{Benzene, reflux}} [RuX(CO)(EPh_3)(B)(L)]$$

(X = H or Cl; B = EPh_3 or py; E = P or As)

Formation of new Ru^{II} complexes

All of the complexes are brown colored and soluble in common organic solvents. The analytical data of the new complexes agree very well with the proposed molecular formula. In all of the above reactions, the Schiff base behave as mononegative bidentate ligand.

IR spectra :

The IR spectra of the free ligands were compared with those of the new complexes in order to confirm the coordination of ligands to the ruthenium metal. The IR spectra of the free ligands showed a band in the absorption due to ν(C=N) appears in the 1604–1624 cm^{-1} region undergoes reduction in frequency due to lowering of electron density upon coordination. In the spectra of all the new complexes, this band is shifted to the region of 1591–1579 cm^{-1} indicating the coordination through nitrogen atom[19]. A strong band which appeared in the spectra of ligands around 1248–1273 cm^{-1} due to ν(C–O) completely disappeared and a new band was observed around 1334–1345 cm^{-1}. This may be due to the enolisation and subsequent coordination through deprotonated oxygen atom[20]. The frequency of carbonyl group in indole nucleus of ligand (cm^{-1}) does not undergo any shift in complexes. This indicates non involvement of this carbonyl group in coordination. The frequence of free carbonyl group was present in region of 1910–1945 cm^{-1}. In addition to above, the characteristic bands due to PPh_3 or $AsPh_3$ were also present in the expected region[21].

Electronic spectra :

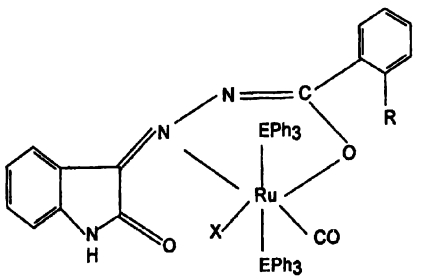
The ground state of ruthenium(II) in an octahedral environment is $^1A_{1g}$ from the t^6_{2g} configuration and excited states corresponding to the $t^6_{2g}e^1_g$ configurations are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. Hence four bands corresponding to the transition $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^3T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ are possible in the order of increasing energy. All the new ruthenium(II) Schiff base complexes were diamagnetic, indicating the presence of ruthenium in the +2 oxidation state in all the complexes. In the electronic spectra of all the complexes in CH_2Cl_2 three to four bands are appeared in the region 640–243 nm. The bands around 640–580 nm and 485–406 nm are assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ and the charge transfer reactions respectively[21,22]. The charge transfer bands observed in all the complexes due to M → L transitions are possible in the visible region[22–24]. 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 level. 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 orbitals derived from the π* level of the ligands, in accordance with the assignments made for other similar octahedral ruthenium(II) complexes[25,26].

^1H NMR spectra :

Coordination of Schiff bases in the new ruthenium complexes is further confirmed by ^1H NMR spectra. All complexes showed multiplets in the 6.9–8.2 ppm region due to the aromatic protons of the ligand, and PPh_3/$AsPh_3$[27]. -NH proton of indole appeared in the 2.2–5.0 ppm region.

^{31}P NMR spectra of the complexes {[RuCl(CO)(PPh_3)$_2$(L_1)], [RuCl(CO)($AsPh_3$)$_2$(L_1)], [RuH(CO)(PPh_3)$_2$(L_2)]} were recorded in order to confirm the presence of PPh_3 groups and to determine the geometry of the complexes. Appearance of only one signal around 28.63–29.42 (Fig. 3) in the spectrum of the complexes confirmed the presence of magnetically equivalent phosphorous atoms suggesting that the two PPh_3 groups are *trans* to each otheer[28].

On the basis of the elemental analysis, IR, electronic, ^1H NMR and ^{31}P NMR spectral data the following octahedral structure (Fig. 2) has been proposed for all the new ruthenium(II) complexes.



R= H, Cl or NH_2; B = EPh_3 or py; E= P or As; X = H or Cl

Fig. 2. Proposed structure of new Ru^{II} complexes.

uct yield obtained for the oxidation of benzyl alcohol than for cyclohexanol is due to the fact that the α-CH moiety of benzyl alcohol is more acidic compared to that of cyclohexanol[21,29]. It has been found that PPh_3 complexes posses higher catalytic activity than $AsPh_3$ complexes[28]. The catalytic oxidation is expected to proceed via Ru^{IV}, intermediate as reported earlier[1].

Antimicrobial study :

The *in vitro* antimicrobial screening of the new ruthenium complexes have been carried out against *Bacillus subtilis, Pseudomonas aeruginosa, Staphylococcus aureus,*

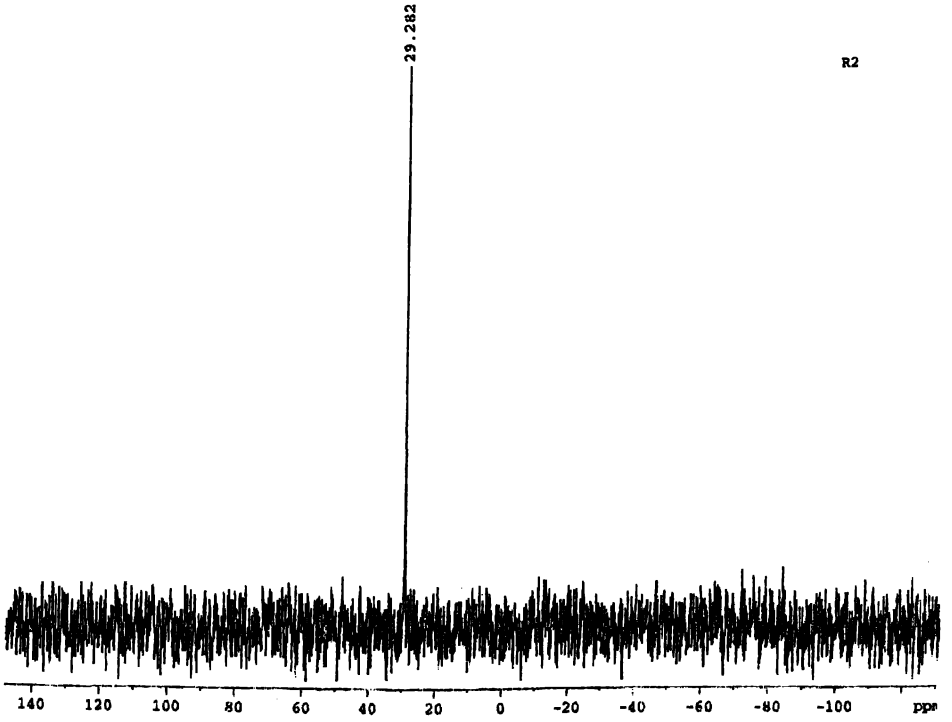


Fig. 3. ^{31}P NMR spectra of $[RuCl(CO)(PPh_3)_2(L_1)]$.

Catalytic activity :

The oxidation of alcohols was carried out with ruthenium complexes as catalyst in the presence of *N*-methyl morpholine-*N*-oxide as co-oxidant in chloroform (Table 3). The ruthenium(II) complexes were found to exhibit catalytic yield and turnovers comparable to those reported for similar ruthenium complexes[21]. All of the synthesized complexes were found to catalyze the oxidation of alcohols to carbonyl compounds. The relative higher prod-

Streptococcus aureus, Salmonella typhimurium, Escherichia coli by using a nutrient agar medium by disc diffusion method (Table 4). The toxicity increases with increasing concentration[29]. 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 Tweed's chelation theory[30]. Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and

Table 1. Analytcial data of new Ru^{II} complexes

Complex	M.p. (°C)	Yield (%)	Analysis (%) : Calcd. (Found)		
			C	H	N
$[RuCl(CO)(PPh_3)_2(L_1)]$	261	80	65.55 (65.48)	4.50 (4.40)	4.41 (4.40)
$[RuCl(CO)(PPh_3)_2(L_2)]$	242	80	63.16 (63.15)	3.95 (4.04)	4.25 (4.37)
$[RuCl(CO)(PPh_3)_2(L_3)]$	178	75	64.52 (64.46)	4.24 (4.44)	5.80 (5.78)
$[RuCl(CO)(AsPh_3)_2(L_1)]$	274	70	59.89 (59.95)	3.75 (3.83)	4.03 (3.98)
$[RuCl(CO)(AsPh_3)_2(L_2)]$	266	73	58.12 (58.04)	3.63 (3.72)	3.91 (3.97)
$[RuCl(CO)(AsPh_3)_2(L_3)]$	212	70	59.14 (59.15)	3.90 (3.90)	5.31 (5.33)
$[RuCl(CO)(py)(PPh_3)(L_1)]$	180	75	60.85 (60.66)	3.90 (3.85)	7.28 (7.36)
$[RuCl(CO)(py)(PPh_3)(L_2)]$	167	80	58.28 (58.40)	3.62 (3.78)	6.99 (6.79)
$[RuCl(CO)(py)(PPh_3)(L_3)]$	153	75	59.69 (59.74)	3.95 (4.02)	8.92 (8.76)
$[RuH(CO)(PPh_3)_2(L_1)]$	268	75	67.97 (67.89)	4.46 (4.54)	4.57 (4.51)
$[RuH(CO)(PPh_3)_2(L_2)]$	250	85	65.40 (65.34)	4.19 (4.30)	4.40 (4.46)
$[RuH(CO)(PPh_3)_2(L_3)]$	261	70	66.88 (66.80)	4.50 (4.55)	6.00 (5.89)

Table 2. IR and UV, ^1H NMR, ^{31}P NMR spectral data for the ligands and new Ru^{II} complexes

Complex	ν(C=N)	ν(C-O)	λ_{max}	Aromatic protons	^{31}P NMR
HL_1	1624	1273			
$[RuCl(CO)(PPh_3)_2(L_1)]$	1580	1345	250, 365, 412	6.9–7.9 (m)	29.28
$[RuCl(CO)(AsPh_3)_2(L_1)]$	1580	1345	370, 406, 437, 473	6.9–8.1 (m)	a
$[RuCl(CO)(py)(PPh_3)(L_1)]$	1579	1340	248, 315, 368, 396	7.0–7.9 (m)	a
$[RuH(CO)(PPh_3)_2(L_1)]$	1580	1345	250, 325, 580, 640	6.9–8.2 (m)	29.21
HL_2	1623	1270			
$[RuCl(CO)(PPh_3)_2(L_2)]$	1580	1342	250, 425, 483, 583	6.9–7.7 (m)	28.63
$[RuCl(CO)(AsPh_3)_2(L_2)]$	1591	1342	246, 456, 587, 620	6.9–7.6 (m)	a
$[RuCl(CO)(py)(PPh_3)(L_2)]$	1591	1342	273, 527, 610	7.0–8.2 (m)	a
$[RuH(CO)(PPh_3)_2(L_2)]$	1591	1342	250, 365, 412	6.9–8.1 (m), 5.2 (s) for $-NH_2$	29.42
HL_3	1604	1248			
$[RuCl(CO)(PPh_3)_2(L_3)]$	1587	1334	243, 312, 368	6.6–7.7 (m), 5.2 (s) for $-NH_2$	a
$[RuCl(CO)(AsPh_3)_2(L_3)]$	1580	1346	250, 376, 462, 590	7.1–8.2 (m), 5.3 (s) for $-NH_2$	a
$[RuCl(CO)(py)(PPh_3)(L_3)]$	1585	1339	246, 353, 376, 392	7.0–8.1 (m), 5.1 (s) for $-NH_2$	a
$[RuH(CO)(PPh_3)_2(L_3)]$	1581	1347	250, 350, 485, 580	6.9–8.0 (m), 5.6 (s) for $-NH_2$	a

a – not recorded.

Table 3. Catalytic oxidation of alcohols by Ru^{II} complexes

Complex	Substrate	Product	Yield[a]	Turnover[b]
$[RuCl(CO)(PPh_3)_2(L_1)]$	Benzylalcohol	Benzaldehyde	74	76
	Cyclohexanol	Cyclohexanone	76	79
$[RuCl(CO)(AsPh_3)_2(L_1)]$	Benzylalcohol	Benzaldehyde	80	81
	Cyclohexanol	Cyclohexanone	72	75
$[RuCl(CO)(py)(PPh_3)(L_1)]$	Benzylalcohol	Benzaldehyde	74	78
	Cyclohexanol	Cyclohexanone	76	80

Table-3 (contd.)

$[RuH(CO)(PPh_3)_2(L_1)]$	Benzylalcohol	Benzaldehyde	75	79
	Cyclohexanol	Cyclohexanone	77	82
$[RuCl(CO)(PPh_3)_2(L_2)]$	Benzylalcohol	Benzaldehyde	81	85
	Cyclohexanol	Cyclohexanone	80	83
$[RuCl(CO)(AsPh_3)_2(L_2)]$	Benzylalcohol	Benzaldehyde	82	81
	Cyclohexanol	Cyclohexanone	81	85
$[RuCl(CO)(py)(PPh_3)(L_2)]$	Benzylalcohol	Benzaldehyde	79	84
	Cyclohexanol	Cyclohexanone	80	84
$[RuH(CO)(PPh_3)_2(L_2)]$	Benzylalcohol	Benzaldehyde	76	79
	Cyclohexanol	Cyclohexanone	74	78
$[RuCl(CO)(PPh_3)_2(L_3)]$	Benzylalcohol	Benzaldehyde	75	78
	Cyclohexanol	Cyclohexanone	68	72
$[RuCl(CO)(AsPh_3)_2(L_3)]$	Benzylalcohol	Benzaldehyde	73	77
	Cyclohexanol	Cyclohexanone	65	69
$[RuCl(CO)(py)(PPh_3)(L_3)]$	Benzylalcohol	Benzaldehyde	75	78
	Cyclohexanol	Cyclohexanone	65	69
$[RuH(CO)(PPh_3)_2(L_3)]$	Benzylalcohol	Benzaldehyde	67	70
	Cyclohexanol	Cyclohexanone	65	70

[a]Yields based on substrate. [b]Moles of product per mole of catalysts.

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 permeation 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[31]. 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 depends either on the impermeability of the cells of the microbes or differences in ribosome of microbial cells[32,33].

Experimental

Material and methods :

$RuCl_3.3H_2O$, purchased from Loba-Chemie, was used as supplied. All chemicals were of grade. Solvents were purified according to standard procedures[34]. Elemental analysis were performed at Sophisticated Test and Instrumentation Centre, Cochin. IR spectra were recorded in KBr pellets with Perkin-Elmer spectrophotometer in the 4000–450 cm^{-1} range. Electronic spectra were recorded in CH_2Cl_2 solution with Systronic spectrophotometer in the 800–200 nm range. ^1H NMR spectra were recorded on a Bruker WM 400 instrument using DMSO-d_6 solvent. Melting points were recorded on Boetius micro heating table and are uncorrected.

The starting complexes $[RuHCl(CO)(PPh_3)_3]$[35], $[RuHCl(CO)(AsPh_3)_3]$[36], $[RuHCl(CO)(py)(PPh_3)_2]$[37], $[RuH_2(CO)(PPh_3)_3]$[38] were prepared according to published procedures. The procedure for catalytic oxidation is similar to that reported in the earlier reports[39]. The Schiff base ligands were prepared according to published procedures[40].

Preparation of new ruthenium(II) complexes, [Ru(X)(CO)(EPh$_3$)(B)(L)] :

To a solution of $[RuH(X)(CO)(EPh_3)_2(B)]$ [X = H or Cl; B = EPh_3 or py or $AsPh_3$; E = P or As] (0.1 g, 0.1–0.13 mmol) in benzene (25 cm^3), was added the appropriate Schiff base (0.021–0.051 g, 0.1–0.13 mmol) (molar ratio of ruthenium complex : Schiff base was 1 : 1). The solution was heated under reflex for 6 h. Then, it was concentrated to *ca.* 3 cm^3, cooled and new complexes were separated upon addition of small quantity (6 cm^3) of light petroleum (60–80 °C). The products were filtered, washed with light petroleum, recrystallised from CH_2Cl_2/light petroleum mixture and dried *in vacuo* (yield : 75–80%).

Table 4. Antimicrobial activity of ligands and Ru^{II} complexes

Ligand/Complex	*Bacillus subtilis*		*Pseudomonas aeruginosa*		*Staphylococcus aureus*		*Streptococcus aureus*		*Salmonella typhimurium*		*Escherichia coli*	
	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%	0.5%	1.0%
HL_1	7	8	7	8	8	10	7	8	-	-	8	9
$[RuCl(CO)(PPh_3)_2(L_1)]$	8	10	8	9	8	10	8	9	-	-	9	10
$[RuCl(CO)(AsPh_3)_2(L_1)]$	8	9	8	11	9	10	9	10	-	-	9	10
$[RuCl(CO)(py)(PPh_3)(L_1)]$	9	10	15	17	9	10	7	8	-	-	10	11
$[RuH(CO)(PPh_3)_2(L_1)]$	10	12	11	12	8	9	8	9	-	-	9	9
HL_2	8	10	6	7	7	8	7	8	6	8	7	8
$[RuCl(CO)(PPh_3)_2(L_2)]$	8	10	8	9	8	10	8	9	8	10	9	10
$[RuCl(CO)(AsPh_3)_2(L_2)]$	9	11	9	11	9	11	9	11	7	7	7	9
$[RuCl(CO)(py)(PPh_3)(L_2)]$	9	12	9	12	8	9	7	9	7	8	7	9
$[RuH(CO)(PPh_3)_2(L_2)]$	8	10	6	8	8	8	10	12	7	9	9	12
HL_3	8	10	6	7	7	8	7	9	6	8	7	9
$[RuCl(CO)(PPh_3)_2(L_3)]$	12	15	12	17	8	10	7	10	6	9	8	9
$[RuCl(CO)(AsPh_3)_2(L_3)]$	9	11	9	12	8	9	6	9	6	9	7	10
$[RuCl(CO)(py)(PPh_3)(L_3)]$	-	10	7	8	8	11	8	10	6	10	8	10
$[RuH(CO)(PPh_3)_2(L_3)]$	8	12	10	12	8	9	7	9	7	10	7	10
Streptomycin	18	23	18	22	15	19	17	20	12	15	12	16

Acknowledgement

One of the authors (VVR) thanks the University Grants Commission, SERO, Hyderabad, India for the award of the minor research project.

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