Synthesis, spectroscopic characterization and catalytic oxidation properties of ONO/ONS donor Schiff base ruthenium(III) complexes containing PPh₃/AsPh₃

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Abstract. Six different ruthenium(III) complexes of Schiff bases derived from 2-hydroxy-1-naphthaldehyde and *o*-aminophenol/*o*-aminothiophenol have been synthesized. The compounds with the general formula [RuX(EPh₃)₂(L)] (X = Cl or Br; E = P or As; L = bifunctional tridentate ONO/ONS donor Schiff base ligand) were characterized by infrared, electronic, electron paramagnetic resonance spectroscopy and elemental analyses. Spectroscopic investigation reveals coordination of Schiff base ligand through ONO/ONS donor atoms and octahedral geometry around ruthenium metal. Redox property of complexes has been examined by using cyclic voltammetry. The catalytic oxidation property of ruthenium(III) complexes were also investigated.

Keywords. Ruthenium(III); Schiff base ligand; triphenylphosphine; triphenylarsine; catalytic oxidation.

1. Introduction

Complexes of transition and non-transition metals with Schiff bases have been investigated extensively for many years because of their importance in many applications.[1–5] These complexes have important contribution in the development of catalysis, magnetism, molecular architectures and materials chemistry.

Oxidation of alcohols to carbonyl compounds is one of the most pivotal functional group transformations in organic synthesis. Three important natural enzymes used for oxidation reactions are cytochrome P-450, peroxidases and catalases. All these enzymes have iron(III) porphyrin as the central unit. Hence, several investigations have been made on the reactions of synthetic metalloporphyrins to understand the mechanism of action of porphyrin containing enzymes.[6] Though metalloporphyrins catalyse oxidation reactions, the catalytic yield is not satisfactory to have any commercial viability. Moreover, it is not easy to synthesize metalloporphyrins and this led scientists to look for other ligands to make novel complexes to be employed as catalysts in oxidation reactions.[7] Hence, studies on synthesis and catalytic activity of metal complexes derived from Schiff base ligands have gained greater momentum.[8] In addition, triphenylphosphine/triphenylarsine transition metal complexes are well known for its catalytic applications in various organic transformations.[9,10] The synthesis, characterization and catalytic applications of several hexa coordinated ruthenium(III) complexes containing Schiff base and triphenylphosphine have been reported by us earlier.[11] This paper deals with the synthesis, spectroscopic characterization and catalytic oxidation properties of ruthenium(III) Schiff base complexes obtained from the reactions of [RuCl₃(PPh₃)₃], [RuCl₃(AsPh₃)₃] or [RuBr₃(AsPh₃)₃] with Schiff bases derived from 2-hydroxy-1-naphthaldehyde and *o*-aminophenol/*o*-aminothiophenol.

2. Experimental

All the solvents used were dried and purified by standard methods. IR spectra were recorded as KBr pellets with a Nicolet FT-IR spectrophotometer in the 4000–400 cm⁻¹ range. Electronic spectra of the complexes were recorded in acetonitrile solution using a Shimadzu spectrophotometer in the 800–200 nm range. Magnetic susceptibility measurements were made with auto magnetic susceptibility balance. Microanalyses were

carried out with a VarioEL AMX-400 elemental analyzer. EPR spectra of powdered samples were recorded with a Jeol TEL-100 instrument at X-band frequencies at room temperature. Cyclic voltammetric studies were carried out with a BAS CV-27 model electrochemical analyzer in acetonitrile using a glassy-carbon working electrode and the potentials were referenced to an Ag/AgCl electrode. Melting points were recorded with a Boetius micro heating table and were uncorrected. The starting complexes [RuCl₃(PPh₃)₃],[12] [RuCl₃(AsPh₃)₃],[13] [RuBr₃(AsPh₃)₃][14] and the ligands[15,16] were prepared by reported literature methods.

2.1 *Preparation of ruthenium(III) complexes*

To a solution of [RuX₃(EPh₃)₃] (X = Cl or Br; E = P or As) (0.1 mmol) in toluene (15 mL), appropriate Schiff base ligand (0.1 mmol) in CH₂Cl₂ (10 mL) was added (molar ratio of ruthenium complex : Schiff base was 1:1). The solution was heated under reflux for 6 h. Then it was concentrated to a small volume (3 mL) and the new complex was separated from it by the addition of a small quantity (6 mL) of *n*-hexane. The product was filtered, washed with *n*-hexane and crystallized from CH₂Cl₂/*n*-hexane mixture and dried *in vacuo*. Yield: 61–69%.

2.2 *Procedure for catalytic oxidation*

To a solution of alcohol (1 mmol) in dichloromethane (20 mL), *N*-methylmorpholine-*N*-oxide (0.35 g;3 mmol) and the ruthenium complex (0.01 mmol) were added. The solution was refluxed for 5 h. The mixture was evaporated to dryness and extracted with petroleum ether (60–80°C). The extract was filtered and evaporated to give the corresponding carbonyl compound which were then quantified as their 2,4-dinitrophenylhydrazones.

3. Results and discussion

3.1 *Synthesis*

The tridentate Schiff bases (H₂L) react with the ruthenium(III) complexes of the general formula [RuX₃(EPh₃)₃] (X = Cl or Br; E = P or As) in 1:1 molar ratio in CH₂Cl₂-toluene mixture to yield complexes of the type [RuX(EPh₃)₂(L)] (scheme 1). The analytical data obtained for the new complexes are in good agreement with the proposed molecular formulae (table 1). It is found that the Schiff bases behave as binegative tridentate ligands.

[X = Cl or Br; E = P or As; Y = O(L1) or S(L2)].
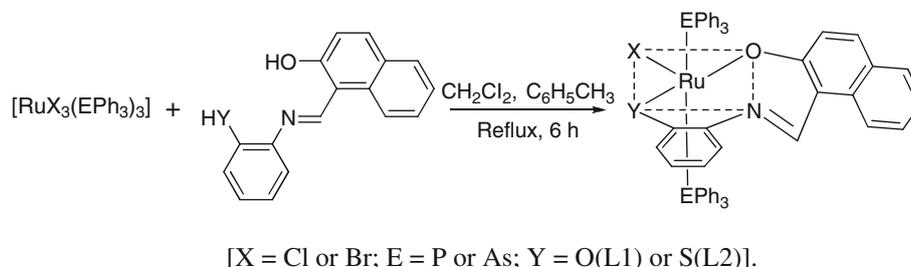
Scheme 1. Formation of ruthenium(III) complexes.

Table 1. Analytical data for the ruthenium(III) complexes.

Complex	Colour	m.p. (°C)	Elemental analysis, Found (Calc.) (%)			
			C	H	N	S
[RuCl(PPh₃)₂(L1)] (**1**)	green	178	68.64 (69.01)	4.13 (4.48)	1.30 (1.52)	–
[RuCl(PPh₃)₂(L2)] (**2**)	brown	224	67.29 (67.83)	4.17 (4.40)	1.44 (1.50)	3.03 (3.42)
[RuCl(AsPh₃)₂(L1)] (**3**)	brick red	138	62.83 (63.00)	3.93 (4.06)	1.18 (1.39)	–
[RuCl(AsPh₃)₂(L2)] (**4**)	brown	130	61.67 (62.01)	3.74 (4.03)	1.22 (1.36)	2.70 (3.12)
[RuBr(AsPh₃)₂(L1)] (**5**)	dark green	144	60.02 (60.34)	3.67 (3.92)	1.12 (1.33)	–
[RuBr(AsPh₃)₂(L2)] (**6**)	dark brown	128	59.08 (59.44)	3.51 (3.86)	1.16 (1.31)	2.70 (2.99)

3.2 *Electronic spectra*

The ground state of ruthenium(III) is $^2T_{2g}$ and the first excited doublet levels in the order of increasing energy are $^2A_{2g}$ and $^2A_{1g}$ which arises from the $t_{2g}^4 e_g^1$ configuration.[17] In most of the ruthenium(III) complexes, the UV-Vis spectra show only charge transfer bands.[18] Since in a d^5 system, and especially in ruthenium(III) which has relatively high oxidizing properties, the charge transfer bands of the type $L_{\pi y} \rightarrow t_{2g}$ are prominent in the low energy region which obscure the weaker bands due to d–d transition. It is therefore becomes difficult to assign conclusively the bands of ruthenium(III) complexes which appear in the visible region. The electronic spectra of all the complexes in acetonitrile showed four to five bands in the region 500–210 nm (table 2, figure 1). A band around 440–500 nm (ε = 3840–11877 mol^{-1} cm^{-1} dm^3) has been assigned as due to d–d transition. The extinction coefficients of the bands in the region 210–390 nm (ε = 7983–52371 mol^{-1} cm^{-1} dm^3) have been found to be higher than those generally expected for d–d transitions. Hence, these bands have been assigned to charge transfer transitions. Similar observations have been made for other ruthenium(III) octahedral complexes.[19]

Table 2. IR and electronic spectral data[a] for the ruthenium(III) Schiff base complexes.

Compound	ν (C=N)	ν (C–O)	ν (C–S)	Bands due to PPh₃/AsPh₃	$\lambda_{max}(\varepsilon)$
H₂L1	1631	1320	–	–	–
H₂L2	1622	1323	1244	–	–
1	1582	1385	–	1432, 1075, 685	213(48931), 221(48540), 265(20426), 320(9703), 442(9720)
2	1604	1390	1262	1432, 1092, 695	227(51051), 269(32880), 390(11371), 477(8948)
3	1626	1350	–	1434, 1079, 689	223(52371), 317(11714), 386(9825), 442(11443), 461(10937)
4	1582	1396	1262	1433, 1077, 690	217(47462), 262(18629), 290(14700), 497(10937)
5	1599	1391	–	1434, 1093, 694	218(50222), 228(52280), 320(11537), 441(12368), 462(11877)
6	1581	1391	1261	1433, 1076, 687	225(51114), 265(20877), 322(7983), 465(3840)

[a] ν in cm^{-1}; λ in nm, ε in mol^{-1} cm^{-1} dm^3
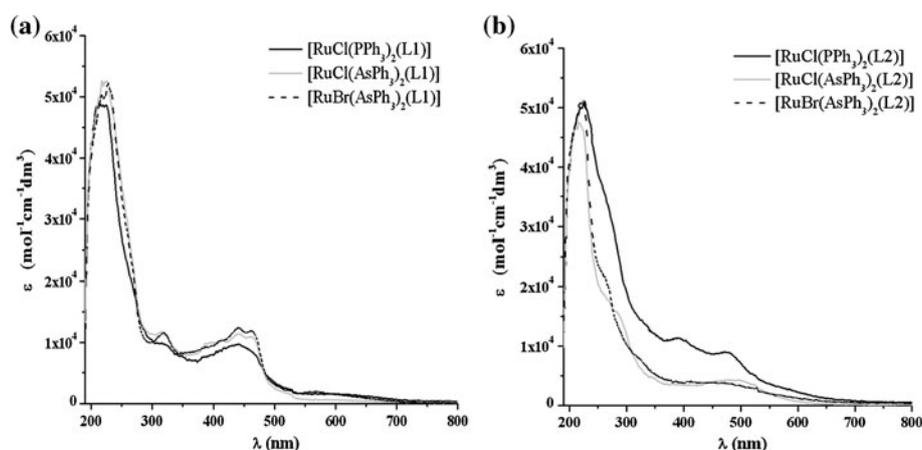

Figure 1. Electronic spectra of ruthenium(III) complexes (**a, b**).

3.3 *IR spectra*

The results of IR measurements are given in table 2. The IR spectra of all the free Schiff bases show the characteristic $-CH=N$, $-OH$ and $-SH$ frequencies around 1630, 3500 and 2600 cm^{-1} respectively. A strong band observed at 1320–1323 cm^{-1} in the ligands has been assigned to phenolic C–O stretching. On complexation, the band due to $-C=N$ stretching underwent a negative shift (1581–1626 cm^{-1}), suggesting the involvement of azomethine group in coordination.[20] The phenolic C–O stretching band has been shifted to 1325–1396 cm^{-1} region in the complexes, which shows that the other coordination site is phenolic oxygen atom.[21] The binding mode of the Schiff base ligands to the ruthenium ion in these complexes is further confirmed by the disappearance of broad band at 3500 cm^{-1} attributed to –OH in the complexes. The band corresponding to S–H also disappears in the complexes containing H$_2$L2 ligand. The band due to C–S of H$_2$L2 (1244 cm^{-1}) is shifted into the range 1261–1262 cm^{-1} in these complexes, providing an additional evidence for the participation of the –SH group in complex formation. The bands due to PPh$_3$/AsPh$_3$ are also observed in the expected region.[22]

Table 3. EPR spectral data for ruthenium(III) complexes.

Complex	g_x	g_y	g_z	$<g>$*
1	1.68	1.68	1.85	1.74
2	–	1.87	–	–
3	1.62	1.62	1.88	1.71
4	–	1.86	–	–

$<g>$* $= [1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2]^{1/2}$

3.4 *Magnetic moments*

The magnetic moments of all the complexes have been measured at room temperature using an auto magnetic susceptibility balance. The μ_{eff} value for these complexes is in the range of 1.7 to 1.8 B.M. This shows that these complexes are paramagnetic corresponding to one unpaired electron, which supports the trivalent state of ruthenium.

3.5 *EPR spectra*

The new ruthenium(III) complexes are paramagnetic and hence EPR spectra were recorded for powdered samples in solid state at X-band frequencies. The g values listed in table 3 show that [RuCl(PPh$_3$)$_2$(L1)] and [RuCl(AsPh$_3$)$_2$(L1)] exhibit spectra with a g$_\perp$ at 1.62−1.68 and g$_{||}$ at 1.85–1.88 (figure 2a). The presence of two g values is an indication of an octahedral field with tetragonal distortion ($g_x = g_y \neq g_z$) and also points out an axial symmetry for the complexes and hence *trans* positions are assigned to PPh$_3$/AsPh$_3$ groups.[23] The [RuCl(PPh$_3$)$_2$(L2)] and [RuCl(AsPh$_3$)$_2$(L2)] complexes show a well-defined single isotropic line with g values in the range of 1.86–1.87 (figure 2b). Such isotropic lines are usually the results of either intramolecular spin exchange, which may broaden the lines, or occupancy of the unpaired electron in a degenerate orbital. Similar EPR behaviour was observed for Schiff base ruthenium(III) complexes.[11,24]

3.6 *Cyclic voltammetry*

The electrochemical behaviour of all the synthesized complexes was studied by cyclic voltammetry in the range +2.0 to −2.0 V in acetonitrile using glassy
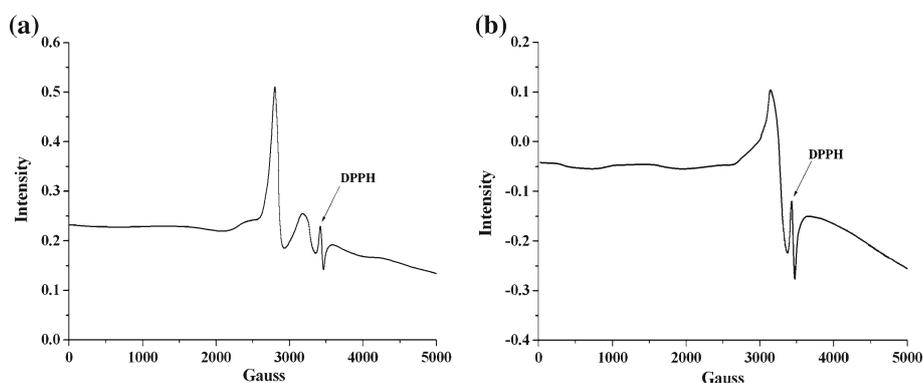

Figure 2. EPR spectra of **3** and **2** (**a**, **b**).

carbon as working electrode, Ag/AgCl as reference electrode and [NBu₄]ClO₄ (0.1 M) as supporting electrolyte. The solution was degassed with a continuous flow of nitrogen gas before scanning. All the complexes are electroactive only with respect to metal centre. The complexes (10^{-3} M) gave only quasi reversible cyclic voltammetric response due to Ru^{III}–Ru^{II} couple in the range of $E_{1/2} = -0.87$ to -0.82 V, with peak to peak separation (ΔE_p) of 210–240 mV (table 4). This is attributed to slow electron transfer and adsorption of the complexes onto the electrode surface.[25] The $E_{1/2}$ and ΔE_p values are in good agreement with those recently reported for other similar ruthenium(III) Schiff base complexes.[19,23] A representative voltammogram has been depicted in figure 3. The $E_{1/2}$ (reduction) values of

the complexes containing one phenyl ring in the aldehyde part of the Schiff base ligands range from -0.52 to -0.63 V.[11] When these values are compared with that of new complexes, it has been observed that the addition of one phenyl ring in the ligand causes positive shift in the $E_{1/2}$ (reduction) values. This can be explained by the fact that the additional phenyl ring, by its electron withdrawing nature decreases the electron density around the metal centre.[26] There is no variation in the redox potential of the complexes due to the replacement of triphenylphosphine by triphenylarsine.[19]

Our attempts to grow crystals suitable for X-ray structural determination were unsuccessful. Hence, *trans* positions of PPh₃/AsPh₃ and the equatorial position of remaining ligands have been assigned on the basis of single crystal X-ray structure of other similar octahedral ruthenium(III) complexes.[27,28] The alternate structure in which 'X' is *trans* to 'O' is not ruled out.

Table 4. Cyclic voltammetric data^a for ruthenium(III) Schiff base complexes.

Complex	$E_{1/2}^b$ (ΔE_p)^c
1	−0.835 (210)
2	−0.820 (220)
3	−0.860 (240)
4	−0.870 (220)
5	−0.865 (210)
6	−0.860 (220)

^{a} Supporting electrolyte:[NBu₄]ClO₄ (0.1 M); scan rate, 100 mV s^{-1}; reference electrode, Ag–AgCl.
^{b} $E_{1/2}$ in Volts; $E_{1/2} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials in Volts, respectively.
^{c} ΔE_p in mV; $\Delta E_p = E_{pa} - E_{pc}$

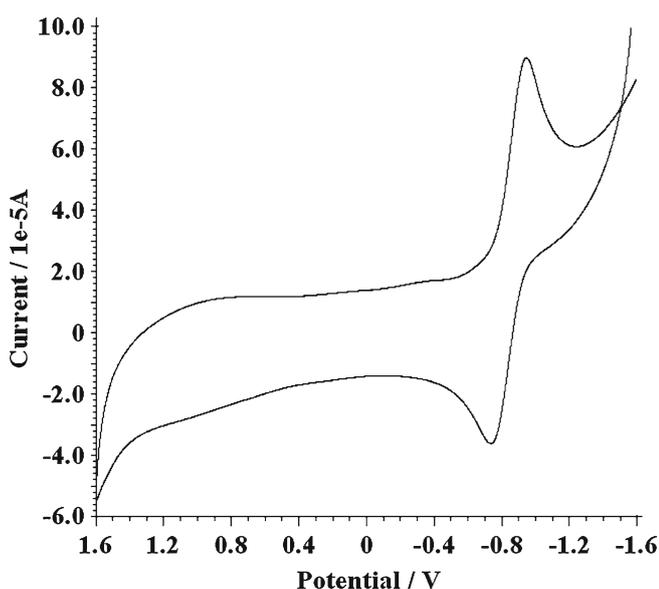## 4. Catalytic activities

The oxidation of benzyl alcohol, 1-phenylethanol and cyclohexanol, using ruthenium complexes as catalysts in the presence of *N*-methylmorpholine-*N*-oxide (NMO) as co oxidant, was carried out in CH₂Cl₂. The reaction is also carried out with H₂O₂, O₂, air or

Figure 3. Cyclic voltammogram of **1**.

Table 5. Catalytic activity data^a of ruthenium(III) complexes.

Complex	Substrate	Product	Yield (%)^b
1	Benzyl alcohol	Benzaldehyde	64
	1-Phenylethanol	Acetophenone	72
	Cyclohexanol	Cyclohexanone	61
2	Benzyl alcohol	Benzaldehyde	68
	1-Phenylethanol	Acetophenone	70
	Cyclohexanol	Cyclohexanone	57
3	Benzyl alcohol	Benzaldehyde	60
	1-Phenylethanol	Acetophenone	68
	Cyclohexanol	Cyclohexanone	54
4	Benzyl alcohol	Benzaldehyde	61
	1-Phenylethanol	Acetophenone	70
	Cyclohexanol	Cyclohexanone	57
5	Benzyl alcohol	Benzaldehyde	57
	1-Phenylethanol	Acetophenone	69
	Cyclohexanol	Cyclohexanone	51
6	Benzyl alcohol	Benzaldehyde	57
	1-Phenylethanol	Acetophenone	65
	Cyclohexanol	Cyclohexanone	49

^{a} Reaction time, 5 h.
^{b} Yields based on substrate.

t-BuOOH as oxidant; but conversion is not satisfactory. Use of H_5IO_6 as oxidant alters the nature of catalyst. Hence, NMO is used as oxidant in catalytic reactions. Benzaldehyde and acetophenone were formed from benzyl alcohol and 1-phenylethanol respectively. Cyclohexanol was converted into cyclohexanone after refluxing for about 5 h. The carbonyl compounds were then quantified as its 2,4-dinitrophenylhydrazone derivatives (table 5). There was no detectable oxidation of alcohol in the presence of NMO alone. The starting complexes, $[RuX_3(EPh_3)_3]$ (X = Cl or Br; E = P or As) do not show significant catalytic activity (yield = 10–15%) compared to new Schiff base Ru(III) complexes. All the synthesized complexes were found to catalyse the oxidation of alcohols to carbonyl compounds. But the yield and the turnover vary with the different catalysts used. The low product yield obtained for oxidation of cyclohexanol compared to benzyl alcohol and 1-phenylethanol is due to the fact that α–CH unit of cyclohexanol is less acidic than benzyl alcohol and 1-phenylethanol.[29] The yields obtained from the reactions catalysed by Ru–PPh$_3$ complexes are slightly higher compared to that of Ru–AsPh$_3$ complexes because Ru–P bond is more labile than Ru–As bond.[30] To study the effect of additional phenyl ring in the aldehyde part of Schiff base ligands, catalytic activity of new Ru(III) complexes was compared with already reported Ru(III) complexes containing Schiff base ligand that posses only one phenyl ring in the aldehyde part.[11] It has been observed that no significant change in catalytic oxidation of benzyl alcohol but catalytic activity is significantly enhanced for the oxidation of cyclohexanol. This may be attributed to the increase in electron withdrawing nature of the ligand due to the increased resonance by the additional phenyl ring.[31] In general, the new ruthenium(III) complexes exhibit lower catalytic activity compared to other similar ruthenium(III) complexes of the type $[RuX_2(EPh_3)_2(L)]$ (X = Cl or Br; E = P or As; L = *N*-[di(alkyl/aryl)carbamothioyl]benzamide derivatives).[32] This may be due to the fact that the present ligand system is not suitable for stabilizing higher oxidation states. This is inferred from electrochemical studies as cyclic voltammogram did not show Ru^{IV}–Ru^{III} couple. Hence the relationship between catalytic activity and $E_{1/2}$ values could not be made.

5. Conclusion

Mononuclear Ru(III) complexes of the type $[RuX(EPh_3)_2(L)]$ (X = Cl or Br; E = P or As; L = bifunctional tridentate Schiff base ligand) were prepared and characterized by UV-Vis, IR and EPR spectroscopy. Electrochemical behaviour of the complexes has been examined. The complexes act as catalysts for the oxidation of alcohols to carbonyl compounds in presence of NMO.

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