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Minu G. Bhowon [a], H. Li Kam Wah [a], A. Dosieah [a], M. Ridana [a], O. Ramalingum [a] & D. Lacour [a]

[a] Department of Chemistry, Faculty of Science, University of Mauritius, Réduit, Mauritius

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Synthesis, Characterization, and Catalytic Activity of Metal Schiff Base Complexes Derived from Pyrrole-2-carboxaldehyde

Minu G. Bhowon,* **H. Li Kam Wah, A. Dosieah,**
M. Ridana, O. Ramalingum, and D. Lacour

Department of Chemistry, Faculty of Science,
University of Mauritius, Réduit, Mauritius

ABSTRACT

Several ruthenium(II) Schiff base complexes derived from bis(pyrrole-2-carboxaldehyde)-3,4-toluenediimine, bis(pyrrole-2-carboxaldehyde)-1,2-cyclohexanediimine, bis(pyrrole-2-carboxaldehyde)-1,8-naphthalindiimine, bis(pyrrole-2-carboxaldehyde)-1,3-propylenediimine, bis(pyrrole-2-carboxaldehyde)-1,2-phenylenediimine and bis(pyrrole-2-carboxaldehyde)-ethylenediimine, and lanthanide(III) Schiff base complexes derived from N-(2-pyrrolylmethylene)-2-aminophenol were synthesized. All the complexes were characterized by analytical and spectroscopic methods. The ruthenium Schiff base complexes were found to be effective

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*Correspondence: Minu G. Bhowon, Department of Chemistry, Faculty of Science, University of Mauritius, Réduit, Mauritius; E-mail: mbhowon@uom.ac.mu.

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catalysts for the oxidation of primary alcohols in the presence of N-methylmorpholine-N-oxide as oxidant.

Key Words: Pyrrole-2-carboxaldehyde; Schiff base complexes; Synthesis; Characterization.

INTRODUCTION

A wide range of transition and lanthanide metal complexes derived from Schiff base ligands have been isolated.[1−6] These compounds have played a major role in the development of modern inorganic coordination chemistry providing examples of macrocyclic ligand systems[7] and the effects of steric interactions on coordination geometries. Ruthenium Schiff base complexes have also been found to be effective catalysts in the oxidation of alcohols and alkenes using N-methylmorpholine-N-oxide (NMO) as oxidant.[8,9]

We report herein the preparation, characterization and catalytic behaviour of some ruthenium and lanthanide Schiff base complexes derived from pyrrole-2-carboxaldehyde and 3,4-diaminotoluene, 1,2-diaminocyclohexane, 1,8-diaminonaphthalin, 1,3-diaminopropane, 1,2-phenylenediamine, 1,2-diaminoethane and aminophenol. The structures of the Schiff bases are shown in Fig. 1.

RESULTS AND DISCUSSION

The Schiff bases L^1, H_2L^2, H_2L^3, L^4–L^7 were synthesised by the condensation of pyrrole-2-carboxaldehyde with 2-aminophenol, 3,4-diaminotoluene, 1,2-diaminocyclohexane, 1,8-diaminonaphthalin, 1,3-diaminopropane, 1,2-phenylenediamine and 1,2-diaminoethane in ethanol, respectively. The compounds H_2L^2, H_2L^3 and L^4–L^7 are bis-condensed Schiff bases. Table 1 shows the analytical and spectroscopic data of all the Schiff bases prepared.

The lanthanide(III) complexes, $[Ln(L^1)_2(NO_3)_2]NO_3{\cdot}3H_2O$ (**1**)–(**6**) (Ln = Nd, Sm, Gd, Dy, Er and La) were prepared by reacting their respective nitrate salts with the Schiff base L^1 in the molar ratio of 1:2 in ethanol at room temperature according to the general equation:

$$Ln(NO_3)_3{\cdot}nH_2O + 2L^1 \longrightarrow [Ln(L^1)_2(NO_3)_2]NO_3{\cdot}3H_2O + (n\text{-}3)H_2O$$

(n = 5 or 6; Ln = Nd, Sm, Gd, Dy, Er and La)

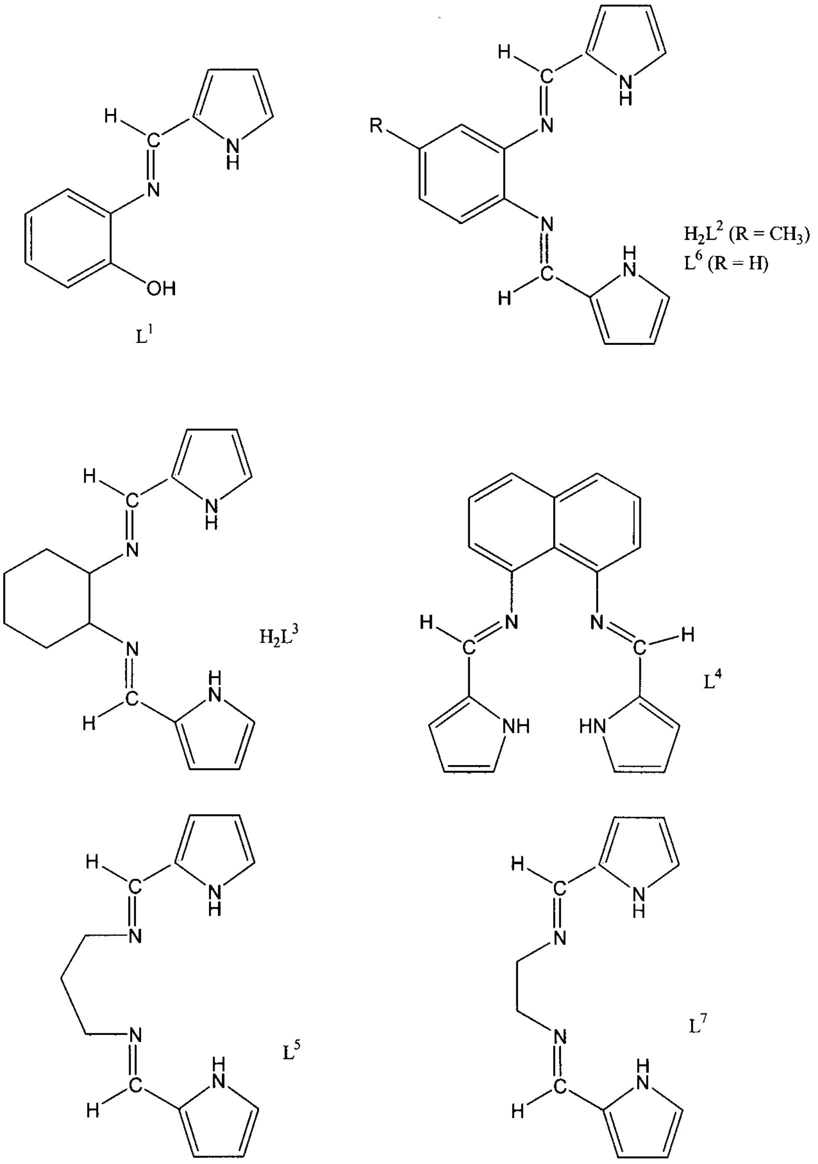

Figure 1. Structures of the Schiff base ligands L^1, H_2L^2, H_2L^3, L^4–L^7.

Table 1. Analytical and spectroscopic data of the Schiff bases.

Schiff base, empirical formula, formula weight	Colour M.p. (°C)	Yield, (%)	Found (calc.), %			IR (cm^{-1}) ν(C=N)	^1H NMR[a] (ppm)	UV-Vis.[b] λ_{max} (nm)
			C	H	N			
L^1 $C_{11}H_{10}N_2O$ 186	Brown 128	75	70.7 (70.9)	5.3 (5.4)	15.2 (15.0)	1626 s	11.8 (s, 1H), 8.8 (s, 1H), 8.6 (s, 1H), 6.2–7.4 (m, 7H)	301, 351
H_2L^2 $C_{17}H_{16}N_4$ 276	Brown 160	37	73.6 (73.9)	5.6 (5.8)	20.2 (20.3)	1619 s	11.6 (b, 2H), 8.2 (s, 2H), 6.1–7.0 (m, 9H), 2.2 (s, 3H)	255–272, 301
H_2L^3 $C_{16}H_{22}N_4O$ 286	Grey 204	54	67.3 (67.1)	7.4 (7.7)	19.4 (19.6)	1631 s	11.2 (b, 2H), 7.9 (s, 2H), 6.0–6.7 (m, 6H), 3.1–3.2 (t, J = 5 Hz, 2H), 1.0–1.7 (m, 8H)	252, 272, 302
L^4 $C_{20}H_{16}N_4$ 312	Purple 192	51	77.1 (76.9)	5.4 (5.2)	17.9 (17.9)	1596 s	11.0 (b, 2H), 8.0 (s, 2H), 6.2–7.1 (m, 12H)	256–288, 300
L^5 $C_{13}H_{16}N_4$ 228	Yellow 118	44	68.6 (68.4)	7.0 (7.1)	24.4 (24.5)	1635 s	11.6 (b, 2H), 8.0 (s, 2H), 6.1–6.8 (m, 6H), 3.5 (t, J = 7 Hz, 4H), 1.8–1.9 (m, 2H)	255–284, 301
L^6 $C_{16}H_{14}N_4$ 262	Brown 172	64	73.4 (73.3)	5.2 (5.4)	21.3 (21.4)	1619 s	11.6 (b, 2H), 8.2 (s, 2H), 6.1–7.1 (m, 10H)	248–255, 302
L^7 $C_{12}H_{14}N_4$ 214	Orange 188	72	67.8 (67.3)	6.7 (6.6)	26.1 (26.1)	1643 s	11.3 (b, 2H), 8.0 (s, 2H), 6.1–6.8 (m, 6H), 3.4–3.7 (m, 4H)	230–255, 339

[a] Solvent: DMSO-d_6.
[b] Solvent: DMSO s: Sharp.

The ruthenium complexes (**7**)–(**12**) were isolated when $RuCl_2(PPh_3)_3$ and the Schiff bases H_2L^2, H_2L^3 and L^4–L^7 were refluxed in THF in the molar ratio of 1:1.

$$RuCl_2(PPh_3)_3 + H_2X + H_2O \longrightarrow [Ru(H_2X)Cl_2(PPh_3)(H_2O)] + 2PPh_3$$

$(X = L^2$ and $L^3)$

$$RuCl_2(PPh_3)_3 + Y + (n+1)H_2O \longrightarrow [Ru(Y)Cl_2(PPh_3)(H_2O)] \times nH_2O + 2PPh_3$$

$(Y = L^4–L^7)$ $(n = 0, 2$ or $3)$

On the other hand, the ruthenium complexes $[Ru(L^2)(PPh_3)_2]$ (**13**) and $[Ru(L^3)(PPh_3)_2]$ (**14**) were obtained after $RuCl_2(PPh_3)_3$ and the Schiff bases H_2L^2 and H_2L^3 were reacted, respectively, in the presence of triethylamine.

$$RuCl_2(PPh_3)_3 + H_2X + 2NEt_3 \longrightarrow [Ru(X)(PPh_3)_2] + PPh_3 + 2Et_3NH^+Cl^-(X = L^2 \text{ and } L^3)$$

Table 2 shows the analytical and spectroscopic data of all the metal complexes.

Infrared Spectra

The infrared spectrum of the Schiff base L^1 showed a strong band at 1626 cm^{-1} attributable to the $\nu(C{=}N)$ stretching frequency vibration. On complexation with the lanthanide nitrates, this band shifted to the 1649–1657 cm^{-1} region indicating that the nitrogen of the azomethine group has coordinated to the lanthanide ion.[10] The presence of a band in the 3265–3321 cm^{-1} region suggested that the nitrogen of the pyrrole group is not involved in bonding or the presence of water molecules. The complexes showed six absorption bands near 1502, 1307, 1047, 809, 754 and 700 cm^{-1} which are assigned, respectively, to ν_4, ν_1, ν_2, ν_6, ν_3 and ν_5 due to the coordinated nitrate groups. The magnitude of $\nu_4-\nu_1$ is about 195 cm^{-1}, indicating that the nitrate groups are coordinated in a bidentate fashion.[11] Furthermore, a band appearing at 1384 cm^{-1} suggested the presence of ionic nitrate in the complexes.[12]

The infrared spectra of the ruthenium complexes $[Ru(H_2L^3)Cl_2(PPh_3)(H_2O)]$ (**8**), $[Ru(L^5)Cl_2(PPh_3)(H_2O)]\cdot 3H_2O$ (**10**), $[Ru(L^6)Cl_2(PPh_3)(H_2O)]$ (**11**), $[Ru(L^7)Cl_2(PPh_3)(H_2O)]$ (**12**), $[Ru(L^2)(PPh_3)_2]$ (**13**) and $[Ru(L^3)(PPh_3)_2]$ (**14**) showed the $\nu(C{=}N)$ stretching frequency in the 1581–1639 cm^{-1} region which is at lower frequency compared to the precursor Schiff bases (1596–1643 cm^{-1}) indicating the coordination of the metal ion to

Table 2. Analytical and spectroscopic data of the metal complexes.

No.	Complex, empirical formula, formula weight	Colour M.p. (°C)	Yield, (%)	Found (calc.), %			IR (cm^{-1}) ν(C=N)	^{1}H NMR[a] (ppm)	UV-Vis. λ_{max} (nm)
				C	H	N			
(**1**)	[Nd(L^1)$_2$(NO_3)$_2$]$NO_3 \cdot 3H_2O$ $C_{22}H_{26}N_7NdO_{14}$, 756	Brown 287	45	35.2 (34.9)	3.1 (3.5)	13.2 (13.0)	1649 s		216–275, 290, 4414[b]
(**2**)	[Sm(L^1)$_2$(NO_3)$_2$]$NO_3 \cdot 3H_2O$ $C_{22}H_{26}N_7O_{14}Sm$, 762	Brown 285	46	35.2 (34.9)	3.4 (3.4)	13.3 (12.9)	1651 s		211–268, 291, 441[b]
(**3**)	[Gd(L^1)$_2$(NO_3)$_2$]$NO_3 \cdot 3H_2O$ $C_{22}H_{26}GdN_7O_{14}$, 769	Brown 291	22	34.1 (34.3)	3.5 (3.4)	13.0 (12.7)	1653 s		209–268, 292, 422[b]
(**4**)	[Dy(L^1)$_2$(NO_3)$_2$]$NO_3 \cdot 3H_2O$ $C_{22}H_{26}DyN_7O_{14}$, 774	Brown 286	48	33.9 (34.1)	3.1 (3.4)	12.7 (12.7)	1653 s		218–264, 294, 431[b]
(**5**)	[Er(L^1)$_2$(NO_3)$_2$]$NO_3 \cdot 3H_2O$ $C_{22}H_{26}ErN_7O_{14}$, 779	Brown 282	23	33.8 (33.9)	3.0 (3.4)	12.8 (12.6)	1657 s		210–266, 294, 431[b]
(**6**)	[La(L^1)$_2$(NO_3)$_2$]$NO_3 \cdot 3H_2O$ $C_{22}H_{26}LaN_7O_{14}$, 750	Brown >300	39	37.5 (37.1)	2.7 (3.1)	13.3 (13.8)	1650 s	11.8 (s, 2H), 8.8 (s, 2H), 8.6 (s, 2H), 6.2–7.5 (m, 14H)	217, 289, 413[b]
(**7**)	[Ru(H_2L^2)Cl_2(PPh_3)(H_2O)] $C_{35}H_{33}Cl_2N_4OPRu$, 728	Black >300	63	57.2 (57.6)	4.6 (4.5)	7.0 (7.6)	1619 s	12.1 (s, 2H), 8.5 (s, 2H), 6.9–7.8 (m, 24H), 2.5 (s, 3H)	256, 310, 588, 870[c]

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(**8**)	$[Ru(H_2L^3)Cl_2(PPh_3)(H_2O)]$ $C_{34}H_{37}Cl_2N_4OPRu$, 720	Black >300	68	58.6 (58.1)	5.0 (4.5)	7.3 (7.7)	1619 m	12.1 (s, 2H), 8.3 (s, 2H), 6.2–7.8 (m, 21H), 3.1 (t, J = 5 Hz, 2H), 1.7–2.1 (m, 8H)	271, 302, 424, 870[c]
(**9**)	$[Ru(L^4)Cl_2(PPh_3)(H_2O)] \cdot 2H_2O$ $C_{38}H_{37}Cl_2N_4O_3PRu$, 800	Black >300	58	56.7 (57.0)	4.3 (4.6)	6.5 (7.0)	1639 s	12.7 (s, 2H), 8.2 (s, 2H), 6.4–7.8 (m, 27H),	256, 324, 448, 870[c]
(**10**)	$[Ru(L^5)Cl_2(PPh_3)(H_2O)] \cdot 3H_2O$ $C_{31}H_{39}Cl_2N_4O_4PRu$, 734	Black >300	65	50.2 (50.6)	4.9 (5.3)	7.4 (7.6)	1631 s	12.1 (s, 2H), 8.1 (s, 2H), 6.2–7.8 (m, 21H), 2.9–3.0 (m, 2H)	256, 312, 417, 870[c]
(**11**)	$[Ru(L^6)Cl_2(PPh_3)(H_2O)]$ $C_{34}H_{31}Cl_2N_4OPRu$, 714	Black >300	66	57.4 (57.1)	4.2 (4.3)	7.6 (7.8)	1604 m	12.4 (s, 2H), 8.2 (s, 2H), 6.2–7.6 (m, 25H)	232, 301, 463, 870[c]
(**12**)	$[Ru(L^7)Cl_2(PPh_3)(H_2O)]$ $C_{30}H_{31}Cl_2N_4OPRu$, 666	Black >300	64	53.8 (54.0)	4.8 (4.7)	8.1 (8.4)	1612 s	12.1 (s, 2H), 8.1 (s, 2H), 6.2–7.8 (m, 21H)	256, 312, 570, 870[c]
(**13**)	$[Ru(L^2)(PPh_3)_2]$ $C_{53}H_{44}N_4P_2Ru$, 899	Black >300	56	70.7 (70.7)	5.1 (4.9)	6.1 (6.2)	1581 s	8.3 (s, 2H), 6.1–7.6 (m, 39H), 1.9 (s, 3H)	
(**14**)	$[Ru(L^3)(PPh_3)_2]$ $C_{52}H_{48}N_4P_2Ru$, 891	Black 213	11	70.5 (70.0)	5.5 (5.4)	6.1 (6.3)	1619 s	8.0 (s, 2H), 6.5–7.7 (m, 36H), 1.2–1.4 (m, 10H)	

[a] Solvent: DMSO-d_6.
[b] Solvent: methanol.
[c] Solvent: DMSO s: sharp m: medium.

the azomethine nitrogen. On the other hand, $[Ru(H_2L^2)Cl_2(PPh_3)(H_2O)]$ (**7**) and $[Ru(L^4)Cl_2(PPh_3)(H_2O)]\cdot 2H_2O$ (**9**) exhibited the ν(C=N) stretching frequency at 1635 and 1639 cm^{-1}, which is higher when compared to the Schiff bases H_2L^2 and L^4 (1619 and 1596 cm^{-1}), respectively. It is noteworthy that this is a common feature as reported in the literature.[13] The presence of the triphenylphosphine ligand in the ruthenium complexes was confirmed by characteristic bands[14] in the 500–1480 cm^{-1} region.

^{1}H NMR Spectra

The ^{1}H NMR spectrum of the lanthanum complex $[La(L^1)_2(NO_3)_2]NO_3\cdot 3H_2O$ (**6**) in DMSO-d_6 indicated a sharp peak corresponding to 2H at δ 8.56 ppm (downfield compared to the Schiff base L^1) corresponding to azomethine protons. The downfield shift is due to the deshielding effect upon donation of electrons from the azomethine nitrogen to the metal. The presence of signals due to O–H protons at δ 8.56 ppm and N–H protons at δ 11.79 ppm indicated that neither the pyrrole nitrogens nor the hydroxyl oxygens were deprotonated. No deprotonation of the hydroxyl group has also been observed in the literature for lanthanide Schiff base complexes derived from 2,3-dihydroxybenzaldehyde and 1,2-diaminoethane[2] and from *o*-vanillin and naphthylamine.[10]

The ^{1}H NMR spectra of $[Ru(H_2L^2)Cl_2(PPh_3)(H_2O)]$ (**7**), $[Ru(H_2L^3)Cl_2(PPh_3)(H_2O)]$ (**8**), $[Ru(L^4)Cl_2(PPh_3)(H_2O)]\cdot 2H_2O$ (**9**), $[Ru(L^5)Cl_2(PPh_3)(H_2O)]\cdot 3H_2O$ (**10**), $[Ru(L^6)Cl_2(PPh_3)(H_2O)]$ (**11**) and $[Ru(L^7)Cl_2(PPh_3)(H_2O)]$ (**12**) in DMSO-d_6 showed signals in the range δ 6.15–7.84 ppm attributed to the protons of triphenylphosphine, benzene rings and pyrrole ligands. The peaks due to azomethine protons occurred at δ 8.00–8.45 ppm, downfield compared to the corresponding Schiff bases H_2L^2, H_2L^3 and L^4–L^7 (δ 7.92–8.18 ppm), indicating the coordination of the azomethine nitrogen to the metal ion in the complexes. The presence of a signal at δ12.06–12.68 ppm confirmed the non-deprotonation and non-coordination of the pyrrole nitrogen. On the other hand, the ^{1}H NMR spectra of $[Ru(L^2)(PPh_3)_2]$ (**13**) and $[Ru(L^3)(PPh_3)_2]$ (**14**) showed the absence of a peak at δ 12 ppm indicating bonding through the pyrrole nitrogen after deprotonation. The four aliphatic protons in $[Ru(L^5)Cl_2(PPh_3)(H_2O)]\cdot 3H_2O$ (**10**) and $[Ru(L^7)Cl_2(PPh_3)(H_2O)]$ (**12**) were not observed due to overlapping with the DMSO signal.

UV-Visible Spectra

The UV-Visible spectra of the lanthanide and ruthenium complexes in methanol or DMSO showed bands in the range 209–275 nm corresponding to

$\pi-\pi^*$ transitions of the aromatic ring. Another band at 290–324 nm was assigned to the $n-\pi^*$ transition of the non-bonding electrons present on the nitrogen of the azomethine group of the Schiff base. A band in the region 417–588 nm is attributed to a charge transfer transition of ligand (π) to metal (d). Another weak peak around 870 nm for the ruthenium complexes could be due to d–d transitions.

Conductivity Measurements

The conductance values of the lanthanide complexes (10^{-3} M in methanol) (**1**)–(**6**) are found to be 108, 123, 102, 124 and 123 and 80 $\text{ohm}^{-1}\,\text{cm}^2\,\text{mole}^{-1}$, respectively. These results indicated that all the lanthanide complexes exhibited 1:1 electrolytic behaviour[11] in methanol at 27°C and they have most probably the structure $[\text{Ln}(\text{L}^1)_2(\text{NO}_3)_2]\text{NO}_3 \cdot 3\text{H}_2\text{O}$.

On the other hand, all the ruthenium complexes were found to be non-electrolytic in DMSO.

Magnetic Measurements

All the lanthanide complexes except that of lanthanum were found to be paramagnetic. The values of the magnetic moment (μ_{eff}) are 3.68, 1.63, 8.41, 10.92, 10.06 B.M. for (**1**)–(**5**), respectively. The magnetic moment values obtained for the complexes compare favourably with those observed in the literature indicating that the 4f electrons did not take part in bonding.[15] On the other hand, all the ruthenium(II) complexes were found to be diamagnetic in accord with a $t_{2g}{}^6$ low-spin configuration.

Based on analytical, spectroscopic, magnetic and conductivity data, the proposed structures of the complexes (**1**)–(**14**) are shown in Fig. 2.

Catalytic Activity

All the synthesized ruthenium complexes (**7**)–(**14**) have been used to catalyse the oxidation of alcohols in the presence of N-methylmorpholine-N-oxide (NMO) as oxidant and the results are summarised in Table 3. The oxidations were carried out at room temperature in CHCl_3 solutions, from which water was removed using molecular sieves. There was no detectable oxidation of alcohols when a blank consisting of NMO and the substrate in chloroform in the absence of the ruthenium complex was carried out.

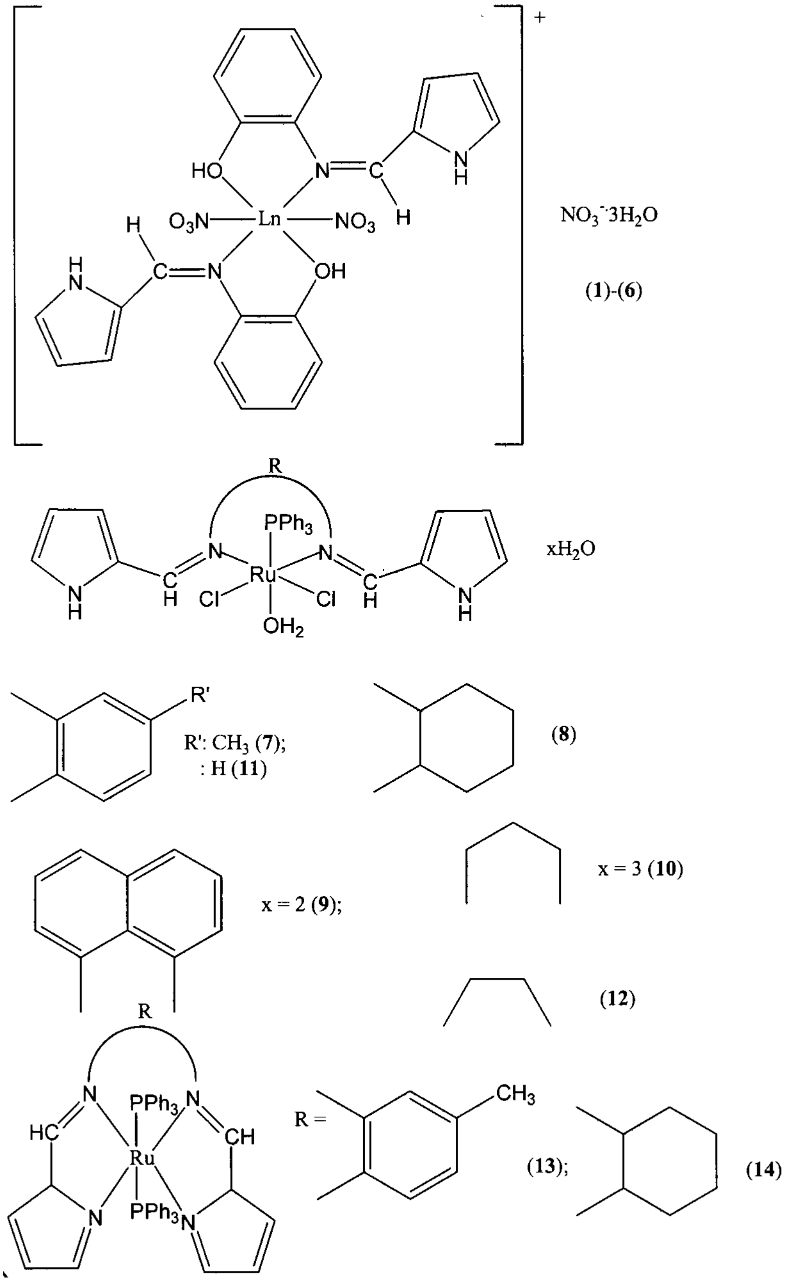

Figure 2. Proposed structures of the metal complexes (**1**)–(**14**).

Table 3. Oxidations catalysed by synthezised ruthenium complexes.

Complex	Amount of complex used (mmol)	Yield, % (turnover[a])		
		Cinnamaldehyde	*p*-Methoxybenzaldehyde	Piperonal
$RuCl_2(PPh_3)_3$	2.00×10^{-2}	65.1 (32.5)	72.5 (36.3)	64.5 (32.3)
$[Ru(H_2L^2)Cl_2(PPh_3)(H_2O)]$ **(7)**	1.04×10^{-2}	78.2 (75.2)	74.7 (73.0)	85.2 (81.9)
$[Ru(H_2L^3)Cl_2(PPh_3)(H_2O)]$ **(8)**	1.02×10^{-2}	72.4 (71.0)	76.6 (75.1)	66.4 (65.1)
$[Ru(L^4)Cl_2(PPh_3)(H_2O)]\cdot 2H_2O$ **(9)**	1.03×10^{-2}	87.2 (85.0)	77.5 (75.6)	76.9 (75.0)
$[Ru(L^5)Cl_2(PPh_3)(H_2O)]\cdot 3H_2O$ **(10)**	1.07×10^{-2}	66.0 (61.7)	73.4 (68.6)	66.9 (62.6)
$[Ru(L^6)Cl_2(PPh_3)(H_2O)]$ **(11)**	1.01×10^{-2}	74.7 (73.9)	82.9 (82.1)	73.6 (72.9)
$[Ru(L^7)Cl_2(PPh_3)(H_2O)]$ **(12)**	1.00×10^{-2}	69.2 (67.8)	73.3 (73.2)	58.2 (56.9)
$[Ru(L^2)(PPh_3)_2]$ **(13)**	1.05×10^{-2}	76.8 (73.1)	81.8 (77.9)	59.4 (56.6)
$[Ru(L^3)(PPh_3)_2$ **(14)**	1.06×10^{-2}	68.9 (65.0)	71.3 (67.3)	61.9 (58.4)

[a] Turnover = moles of product/moles of catalyst.

All the ruthenium complexes were found to oxidize primary alcohols such as cinnamyl, *p*-methoxybenzyl and piperonyl alcohol to their respective aldehydes. All the ruthenium complexes were found to be selective towards oxidation of alcohols and were efficient catalysts as evidenced by the turnovers. Also, the catalysts in the presence of NMO were effective towards oxidation of unsaturated alcohols e.g., cinnamyl alcohol without competing with double bond attack.[9] The synthesised ruthenium Schiff base complexes were found to be better catalysts than $RuCl_2(PPh_3)_3$ for the oxidation of cinnamyl and *p*-methoxybenzyl alcohol with higher yield and turnover. For the oxidation of cinnamyl alcohol, complex (**9**) proved to be the best catalyst compared to the other complexes with a turnover of 85, while for *p*-methoxybenzyl alcohol, complex (**11**) gave the highest yield (82.9%) and turnover (82). The percentage yield of piperonal and turnover were found to be low except for complex (**7**). The oxidation effected by the catalysts is likely to occur *via* ruthenium high oxidation states (Ru(IV) or Ru(V)), which should be accessible through chemical oxidation with the oxidant.[16,17]

EXPERIMENTAL

General

All chemicals were purchased from either Aldrich or BDH Chemicals and were used without purification. IR spectra (KBr pellets) were recorded on a Mattson 1000 FT IR spectrometer in the 4000–400 cm^{-1} range. UV-Visible spectra were recorded in methanol and DMSO solutions on a PU 8700 series UV-Visible spectrometer. ^1H and ^{13}C NMR spectra were obtained using a Bruker Spectrospin spectrometer at 250 MHz. The melting points of all samples were determined using a Stuart Scientific electric melting point apparatus. Magnetic susceptibility data for the metal complexes were recorded on a Sherwood Scientific magnetic balance. Carbon, hydrogen and nitrogen contents were obtained using a Leco 932 CHNS analyser. $RuCl_2(PPh_3)_3$[18] and the Schiff bases derived from pyrrole-2-carboxaldehyde with 2-aminophenol,[19,20] 1,2-diaminoethane.[21,22] 1,2-phenylenediamine[21,22] and 1,3-diaminopropane[22] were prepared by previously reported methods.

Synthesis of Schiff Bases H_2L^2, H_2L^3, and L^4

Pyrrole-2-carboxaldehyde (0.95 g, 10 mmol) and diamine (5 mmol) were refluxed in ethanol (5–10 mL) for 2–6 hours and the resulting solution was then allowed to stand at room temperature for 1 hour. The obtained solid was filtered, washed with ethanol and dried *in vacuo*. The reaction with 1,8-diaminonaphthalin was carried out at room temperature by stirring overnight. The obtained violet crystals were filtered, washed with ethanol (5 mL) and diethyl ether (5 mL), and recrystallized with ethanol before drying *in vacuo.*

Synthesis of Lanthanide Metal Complexes $[Ln(L^1)(NO_3)_2]NO_3 \cdot 3H_2O$ (1)–(6) (Ln = La, Nd, Sm, Gd, Dy, and Er)

A hot ethanolic (5 mL) solution of the Schiff base L^1 (0.2 g, 1.07 mmol) was added with stirring to a solution of hydrated lanthanide(III) nitrate (0.5 mmol) in ethanol (5 mL). The reaction mixture was stirred at room temperature. The product, formed after 3–15 hours, was collected by filtration, washed thoroughly with ethanol and diethyl ether and dried *in vacuo*.

Synthesis of Ruthenium Complexes $[Ru(H_2L^2)Cl_2(PPh_3)(H_2O)]$ (7), $[Ru(H_2L^3)Cl_2(PPh_3)(H_2O)]$ (8), $[Ru(L^4)Cl_2(PPh_3)(H_2O)] \cdot 2H_2O$ (9), $[Ru(L^5)Cl_2(PPh_3)(H_2O)] \cdot 3H_2O$ (10), $[Ru(L^6)Cl_2(PPh_3)(H_2O)]$ (11), and $[Ru(L^7)Cl_2(PPh_3)(H_2O)]$ (12)

$RuCl_2(PPh_3)_3$ (0.95 g, 1 mmol) was added to the solution of the Schiff base (1 mmol) in THF (30 mL). The resulting mixture was refluxed under an inert atmosphere (nitrogen) for 5 hours. After allowing to stand at room temperature for 1 hour, the obtained solid was filtered, washed with THF, hot ethanol, diethyl ether, petroleum ether and dried *in vacuo*. For the synthesis of (**7**), (**10**) and (**11**), the dark brown solutions obtained were filtered and concentrated to 1/10th of their initial volume on a rotary evaporator. The products were precipitated on addition of petroleum ether (60–80 °C). Black solids were obtained which were thoroughly washed with THF, ethanol, petroleum ether and diethyl ether (60–80 °C) and finally dried *in vacuo*.

Synthesis of $[Ru(L^2)(PPh_3)_2]$ (13) and $[Ru(L^3)(PPh_3)_2]$ (14)

$RuCl_2(PPh_3)_3$ (0.95 g, 1 mmol) was added to the solution of Schiff base H_2L^2 or H_2L^3 (1 mmol) in THF (30 mL), followed by the addition of triethylamine (0.30 g, 3 mmol). The resulting solution was refluxed under an inert atmosphere for 3 hours. The resulting solution was filtered and the red or green solid was precipitated on addition of petroleum ether (60–80 °C). The product was filtered, washed with THF, ethanol, petroleum ether (60–80 °C) and diethyl ether and then dried *in vacuo*.

Catalytic Oxidation of Alcohols

To a solution of cinnamyl, *p*-methoxybenzyl or piperonyl alcohol (1 mmol) in chloroform (10 mL), NMO (0.30 g, 3 mmol) was added followed by the ruthenium Schiff base complex ($1.00–2.00 \times 10^{-2}$ mmol). The solution was stirred for 3 hours in the presence of 4 Å molecular sieves (0.5 g). The mixture was filtered and evaporated to dryness and extracted with diethyl ether (2 × 25 mL). The combined ether extracts were filtered and evaporated to give the corresponding aldehydes. Piperonal, cinnamaldehyde and *p*-methoxybenzaldehyde were then quantified as their respective 2,4-dinitrophenylhydrazones.

REFERENCES

1. Liu, G.; Na, C.; Li, B.; Mao, K. Complexes of lanthanide nitrates with a Schiff base derived from *o*-vanillin and *p*-toluidine. Polyhedron **1990**, *9*, 2019–2022.
2. Casellato, U.; Guerriero, P.; Tamburini, S.; Vigato, P.A.; Benelli, C. Mononuclear, homo- and heteropolynuclear complexes with acyclic compartmental Schiff bases. Inorg. Chim. Acta **1993**, *207*, 39–58.
3. Manseki, K.; Kumagai, M.; Sakamoto, M.; Sakiyama, H.; Nishida, Y.; Matsumoto, A.; Sadaoka, Y.; Ohba, M.; Okawa, H. Copper(II)-lanthanide(III) complexes of symmetric dinucleating macrocycle with two phenolate bridges. Bull. Chem. Soc. Jpn. **1998**, *71* (2), 379–383.
4. Casellato, U.; Tamburini, S.; Tomasin, P.; Vigato, P.A.; Aime, S.; Botta, M. Synthesis, X-ray structure and solution NMR studies of Ln(III) complexes with a macrocyclic asymmetric compartmental Schiff base. Preference of the Ln(III) ions for a crown-like coordination site. Inorg. Chem. **1999**, *38*, 2906–2916.
5. Rajagopal, G.; Prasanna, N.; Athappan, P. Copper(II) and ruthenium(II)/(III) Schiff base complexes. Transition Met. Chem. **1999**, *24*, 251–257.
6. Tofazzal, M.; Tarafder, H.; Ali, M.A.; Wee, D.J.; Azahari, K.; Silong, S.; Crouse, K.A. Complexes of a tridentate ONS Schiff base. Synthesis and biological properties. Transition Met. Chem. **2000**, *25*, 456–460.
7. Atkins, A.J.; Black, D.; Blake, A.J.; Marin-Becerra, A.; Parsons, S.; Ruiz-Raminez, L.; Schroder, M.J. Schiff-base compartmental macro-sr]cyclic complexes. J. Chem. Soc. Chem. Commun. **1996**, 457–464.

8. El-Hendawy, A.M.; Alkubaisi, A.H.; El-Ghany El-Kourashy, A.; Shanab, M.M. Ruthenium(II) complexes of O,N-donor Schiff base ligands and their use as catalytic organic oxidants. Polyhedron **1993**, *12* (19), 2343–2350.
9. Bhowon, M.G.; Li Kam Wah, H.; Narain, R. Schiff base complexes of ruthenium(II) and their use as catalytic oxidants. Polyhedron **1999**, *18*, 341–345.
10. Zhang, L.; Xu, X.; Liu, G.; Shi, T. Studies on coordination compounds of rare earth chlorides with some Schiff bases. Synth. React. Met.-Org. Chem. **1999**, *29* (2), 233–244.
11. Liu, G.; Liu, X.; Cao, X. Coordination compounds of rare earth nitrate with Schiff base derived from vanillin and 2-naphthylamine. Synth. React. Met.-Org. Chem. **1992**, *22*, 123–130.
12. Bastida, R.; de Blas, A.; Castro, P.; Fenton, D.E.; Macias, A.; Rial, R.; Rodriguez, A.; Rodriguez-Blas, T. Complexes of lanthanide(III) ions with macrocyclic ligands containing pyridine head units. J. Chem. Soc. Dalton Trans. **1996**, 1493–1497.
13. El-Hendawy, A.M.; El-Ghany El-Kourashy, A.; Shanab, M.M. Schiff base complexes of ruthenium(III), molybdenum(VI) and uranium(VI), and use of the former as catalytic organic oxidants. Polyhedron **1992**, *11* (5), 523–530.
14. Ashok, R.F.N.; Gupta, M.; Arulsamy, K.S.; Agarwala, U.C. Cyclopentadienyl ruthenium complexes Part I. Reactivity of some η^5-cyclopentadienyl-bis(triphenylphosphine) ruthenium(II) complexes with N-donor heterocyclic ligands. Inorg. Chim. Acta **1985**, *98*, 161–167.
15. Kettle, S.F. Magnetism of lanthanide and actinide ions. In *Physical Inorganic Chemistry*; Oxford University Press: Oxford, 1998; 265–266.
16. El-Hendawy, A.M.; Griffith, W.P.; Taha, F.I.; Moussa, M.N. Studies on transition-metal oxo and nitrido complexes. New oxo-ruthenium and oxo-osmium pyridine complexes, and use of the former as catalysts for oxidation of alcohols. J. Chem. Soc. Dalton Trans. **1989**, *5*, 901–906.
17. El-Hendawy, A.M.; El-Shahawi, M.S. Complexes of ruthenium(III) derived from O,O donor ligands. Polyhedron **1989**, *8* (23), 2813–2816.
18. Stephenson, T.A.; Wilkinson, G.J. New complexes of ruthenium(II) and (III) with triphenylphosphine, triphenylarsine, trichlorostannate, pyridine and other ligands. J. Inorg. Nucl. Chem. **1966**, *28*, 945–956.
19. Capitan, F.; Molina, F.; Espinosa, P.; Capitan-Vallvey, L.F. Studies on metal complexes of 2-(*o*-hydroxyphenyliminomethyl)thiophene and 2-(*o*-hydroxyphenyliminomethyl)pyrrole. Acta. Chim. Hung. **1986**, *121* (4), 373–376.

20. Capitan, F.; Molina, F.; Espinosa, P.; Capitan-Vallvey, L.F. Studies on metal complexes of 2-(*o*-hydroxyphenyliminomethyl)thiophene and 2-(*o*-hydroxyphenyliminomethyl)pyrrole. Chem. Abstr. **1986**, *105*, 18272h.
21. Thornback, J.R.; Wilkinson, G. Schiff-base complexes of ruthenium(II). J. Chem. Soc. Dalton Trans. **1978**, 110–115.
22. Weber, J.H. Complexes of pyrrole-derivative ligands. I. Planar nickel(II) complexes with tetradentate ligands. Inorg. Chem. **1967**, *6*, 258–262.

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