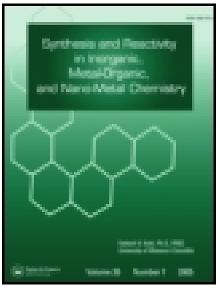

Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

Synthesis, Spectra and Electrochemistry of Ru(III) Complexes with Tetradentate Schiff Bases

R. Ramesh [a] , P. K. Suganthy [a] & K. Natarajan [a]

[a] Department of Chemistry, Bharathiar University, Coimbatore, 641046, India

To cite this article: R. Ramesh , P. K. Suganthy & K. Natarajan (1996): Synthesis, Spectra and Electrochemistry of Ru(III) Complexes with Tetradentate Schiff Bases, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 26:1, 47-60

To link to this article: http://dx.doi.org/10.1080/00945719608004245

SYNTH. REACT. INORG. MET.-ORG. CHEM., 26(1), 47-60 (1996)

SYNTHESIS, SPECTRA AND ELECTROCHEMISTRY OF Ru(III) COMPLEXES WITH TETRADENTATE SCHIFF BASES

R. Ramesh, P. K. Suganthy and K. Natarajan*
Department of Chemistry, Bharathiar University,
Coimbatore-641 046, India

ABSTRACT

A series of low-spin ruthenium(III) complexes of the type $[RuX(EPh_3)(LL')]$ (X = Cl, Br; E = P, As; LL' = Salen, Salpn and Saldien) have been synthesised by reacting $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$, $[RuBr_3(AsPh_3)_3]$ or $[RuBr_3(PPh_3)_2(MeOH)]$ with tetradentate Schiff bases such as bis(salicylaldehyde)ethylenediimine (H_2-Salen), bis(salicylaldehyde)propylenediimine (H_2-Salpn) and bis(salicylaldehyde)diethylenetriimine (H_2-Saldien). All complexes have been characterized by elemental analyses, IR and electronic spectra, EPR, magnetic moment and cyclic voltammetric data.

INTRODUCTION

Schiff bases derived from the reactions of salicylaldehyde with primary amines represent a series of ligands, the metal complexes of which have been widely studied.[1-3] Although there is a wealth of information available on transition metal complexes of Schiff bases[4], it is largely confined to the first-row metals, notably iron, cobalt and nickel.[5,6] Very little has been reported for the Schiff base complexes of ruthenium.[7-10] In recent years, the continued interest in the ruthenium complexes is due to their importance in catalytic oxidative processes[11-13]. In view of growing interest in oxygenations and carboxylations and of Ru(III) complexes as new catalysts, we report in the present communication the synthesis and characterisation of some stable Ru(III) Schiff base complexes of the type $[RuX(EPh_3)(LL')]$ (X = Cl, Br; E = P, As; LL' = Salen, Salpn and Saldien).

The ligands used in this study are of the type as shown in Fig 1.

EXPERIMENTAL

All reagents used were chemically pure or analytical reagent grade. Solvents were purified and dried according to standard procedures. $RuCl_3.3H_2O$ was purchased from Loba Chemie Pvt. Ltd., Bombay and was used without further purification. $[RuCl_3(PPh_3)_3]$[14], $[RuCl_3(AsPh_3)_3]$[15], $[RuBr_3(AsPh_3)_3]$[16], $[RuBr_3(PPh_3)_2(MeOH)]$[17] and the Schiff bases[18] were prepared by reported literature methods.

The analyses of carbon, hydrogen and nitrogen were performed at the Microanalytical Section of Hindustan Photo Film, R & D Centre, Ooty. IR spectra were recorded in KBr pellets in the 4000-200 cm^{-1} region using a Perkin-Elmer 597 spectrophotometer. Electronic spectra were recorded in dichloromethane solution with a Hitachi Perkin-Elmer 20/200 spectrophotometer in the range 900-

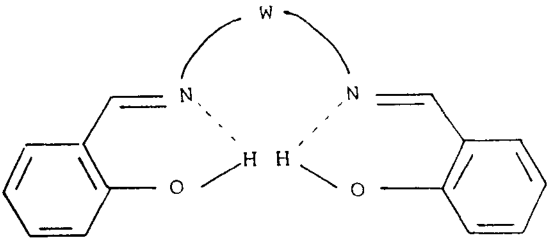

Fig. 1. Schiff Base Ligand

where

W = $-(CH_2)_2-$ (H_2-Salen)

= $-(\underset{\displaystyle CH_3}{CH}-CH_2)-$ (H_2-Salpn)

= $-(C_2H_4)NH(C_2H_4)-$ (H_2-Saldien)

200 nm. EPR spectra of the powdered samples were recorded with a Bruker Model ER 200-D spectrometer at X-band frequencies. Magnetic susceptibilities were recorded on an EG and G-PARC vibrating sample magnetometer. Cyclic voltammetric studies were carried out in acetonitrile using a glassy-carbon electrode as working electrode and the potentials were referenced to a saturated calomel electrode. Melting points were recorded with a Boetius micro heating table and are uncorrected.

Preparation of the Complexes

All operations were carried out under strictly anhydrous conditions. The Schiff bases (0.034-0.039 g; 0.125 mmol) were added to a solution of $[RuX_3(EPh_3)_3]$ (0.12-0.16 g; 0.125 mmol) (where E = P, X = Cl; E = As, X = Cl, Br) or $[RuBr_3(PPh_3)_2(MeOH)]$

Table I. Analytical and Spectroscopic Data for Ru(III) Complexes

Complex (Empirical formula)	Yield %	M.pt. °C	Elemental analyses % Found (Calc.)			IR[a,b] (cm^{-1})		Electronic spectral data λ (nm) (ε $M^{-1}cm^{-1}$)
			C	H	N	ν(C=N)	ν(C-O)	
[RuCl(PPh_3)(Salen)]	63	155	61.42	4.36	4.21	1590	1280	630(750), 500(767), 355(2958)
[$C_{34}H_{29}O_2N_2ClPRu$]			(61.35)	(4.36)	(4.11)			
[RuCl($AsPh_3$)(Salen)]	65	158	57.61	4.09	3.95	1590	1280	650(945), 540(1682)[c], 400(3046),
($C_{34}H_{29}O_2N_2ClAsRu$)			(57.80)	(4.21)	(3.88)			345(2636)
[RuBr($AsPh_3$)(Salen)]	61	170	54.21	3.85	3.72	1590	1285	690(1321), 510(943)[c], 400(4811),
[$C_{34}H_{29}O_2N_2BrAsRu$]			(53.92)	(3.77)	(3.56)			325(3679)
[RuBr(PPh_3)(Salen)]	64	95	57.57	4.09	3.95	1595	1275	680(1050), 500(1331)[c], 395(7631),
[$C_{34}H_{29}O_2N_2BrPRu$]		(dec.)	(57.22)	(3.98)	(4.03)			340(5945)
[RuCl(PPh_3)(Salpn)]	60	152	61.92	4.57	4.13	1590	1280	630(990), 510(1273), 350(5942)
($C_{35}H_{31}O_2N_2ClPRu$)			(61.66)	(4.59)	(4.12)			
[RuCl($AsPh_3$)(Salpn)]	58	136	58.16	4.29	3.87	1600	1280	650(785), 495(1536)[c], 400(3975),
($C_{35}H_{31}O_2N_2ClAsRu$)			(58.47)	(4.00)	(3.55)			330(3523)
[RuBr($AsPh_3$)(Salpn)]	65	140	54.79	4.04	3.65	1590	1275	685(1160), 510(1490)[c], 395(7308),
($C_{35}H_{31}O_2N_2BrAsRu$)			(54.39)	(4.32)	(3.60)			345(7019)

[RuBr(PPh$_3$)(Salpn)]	68	130	58.11	4.29	3.87	1590	1285	680(1125), 500(1351), 395(8018)[c], 350(8919)
($C_{35}H_{31}O_2N_2BrPRu$)			(58.42)	(4.44)	(3.66)			
[RuCl(PPh$_3$)(Saldien)]	69	135	61.08	4.80	5.93	1605	1280	640(1239), 315(4690), 320(3009)
($C_{36}H_{34}O_2N_3ClPRu$)			(60.87)	(5.12)	(5.80)			
[RuCl(AsPh$_3$)(Saldien)]	71	165	57.51	4.52	5.59	1600	1280	650(1369), 490(3195), 370(1739)
($C_{36}H_{34}O_2N_3ClAsRu$)			(57.77)	(4.29)	(5.38)			
[RuBr(AsPh$_3$)(Saldien)]	63	90	54.30	4.27	5.27	1610	1285	650(896), 490(4084), 315(6855)
($C_{36}H_{34}O_2N_3BrAsRu$)		(dec.)	(54.24)	(4.02)	(5.16)			
[RuBr(PPh$_3$)(Saldien)]	60	90	57.47	4.52	5.58	1615	1280	660(1038), 475(3988), 375(4760), 325(6935)
($C_{36}H_{34}O_2N_3BrAsRu$)			(56.99)	(4.81)	(5.33)			

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[a] All the bands are sharp and strong; [b] In KBr disc; [c] Shoulder to the main peak

(0.11 g; 0.125 mmol) in a 1:1 molar ratio in benzene (20 mL) and the mixture was refluxed for 3 hr. A dark green colored solution was obtained which was concentrated to about 3 mL. The complex was precipitated by addition of a small quantity of petroleum ether (60-80°C), recrystallized from CH_2Cl_2/petroleum ether (60-80°C) and dried under vaccum. All the other complexes were prepared using a similar procedure.

RESULTS AND DISCUSSION

The Schiff bases used in this work were synthesised by the condensation of salicylaldehyde with the appropriate amines in a 2:1 molar proportion, respectively. These Schiff bases react with $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$, $[RuBr_3(AsPh_3)_3]$ and $[RuBr_3(PPh_3)_2(MeOH)]$ in a 1:1 molar ratio to give hexa-coordinated ruthenium(III) Schiff base complexes of the type $[RuX(EPh_3)(LL')]$ (X = Cl, Br; E = P, As; LL' = Salen, Salpn and Saldien). All Schiff base complexes crystallise as dark green crystals and are quite stable in air. The analytical data given in Table 1 for the complexes are in good agreement with the formulae proposed.

IR Spectra

The characteristic IR frequencies for all complexes are listed in Table 1. A strong band is observed at 1630-1650 cm^{-1} in the spectra of the free Schiff bases which is characteristic of the azomethine (-HC=N-) group. It is expected that coordination of the nitrogen to the metal atom would reduce the electron density in the azomethine link and thus lower the -C=N frequency. In the IR spectra of the Schiff base complexes, this band is shifted to the region 1590-1615 cm^{-1}, indicating the coordination of the Schiff bases through the azomethine nitrogen.[19] A strong band observed at 1260-1270 cm^{-1} in the free Schiff bases has been assigned to phenolic C-O stretching. On complexation this band is shifted to a higher frequency range, 1280-1285 cm^{-1}, indicating that the other coordination is through the phenolic oxygen.[20] This has been further supported by the disappearance of the broad ν (O-H) band at 2700-2800 cm^{-1} in the complexes. In addition to the above, other characteristic bands due to triphenylphosphine and triphenylarsine were also present in the spectra of the complexes.

Electronic Spectra

Electronic spectra of all the complexes in dichloromethane showed three to four bands in the region 690-315 nm (Fig. 2; Table 1). The ground state of Ru(III) (t_{2g}^{5} configuration) is $^{2}T_{2g}$ and the first excited doublet levels in the order of increasing energy are $^{2}A_{2g}$ and $^{2}T_{1g}$ which arise from the $t_{2g}^{4}\,e_{g}^{1}$ configuration. In most of the Ru(III) complexes the electronic spectra show only charge transfer bands.[21] However, the extinction coefficients for the bands around 690-630 nm are found to be very low as compared to that of charge transfer bands. Hence, the bands around 690-630 nm have been assigned to the $^{2}T_{2g} \longrightarrow {}^{2}A_{2g}$ transition which is in conformity with assignments made for similar octahedral Ru(III) complexes.[9,22] The other bands in the region 510-315 nm have been assigned to charge transfer transitions.

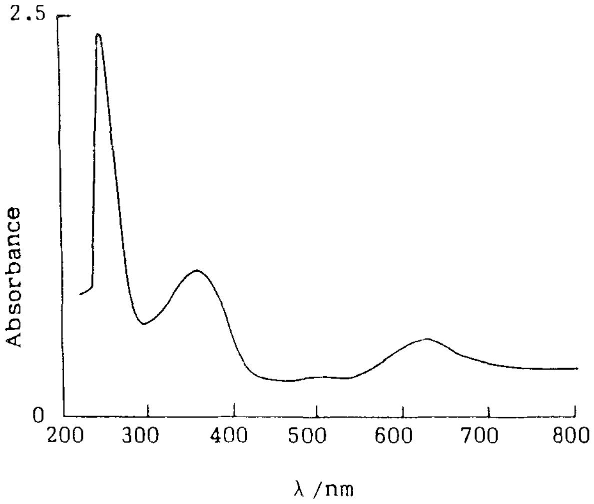


Fig. 2. Electronic Spectra of [RuCl(PPh$_3$)(Salen)] in Dichloromethane

Magnetic Moments and EPR

The magnetic moments of the complexes [RuCl(PPh$_3$)(Salen)], [RuCl(PPh$_3$)(Salpn)] and [RuCl(AsPh$_3$)(Saldien)] have been measured at room temperature by a vibration sample magnetometer. The values obtained are in the range 1.71 to 1.91 BM corresponding to one unpaired electron and suggesting a low spin t_{2g}^5 configuration for the ruthenium(III) ion in an octahedral environment.

EPR spectra of some of the complexes as powdered samples were recorded at room temperature. All the spectra show no indication for any hyperfine interaction of nuclei, viz. Ru, As, P, Cl and Br, with magnetic moments. All the complexes exhibit single isotropic resonances with 'g' values in the range 2.16 to

2.18. Such isotropic lines are usually observed either due to the intermolecular spin exchange which can broaden the lines or due to the occupancy of the unpaired electron in a degenerate orbital. The position of lines and nature of the EPR spectra for all the complexes suggest an almost perfect octahedral structure.[9,23]

Cyclic Voltammetry

Cyclic voltammetric studies were performed for some of the complexes in acetonitrile solution at a glassy carbon working electrode. The purpose of the electrochemical experiments was to investigate the suitability of the present ligand system in achieving higher oxidation states of metal. The redox potentials of the complexes characterised by well defined waves are in the range 0.65 to 0.91 V (oxidation) and -0.20 to -0.45 V (reduction) versus a saturated calomel electrode. The cyclic voltammogram data are given in Table 2 and a representative case is displayed in Fig. 3.

As the ligands used in this work are not reversibly reduced or oxidised within the potential limit (+1.0 V to -1.0 V), we believe that the redox processes observed for these complexes are metal centered. Most of the complexes show reversible oxidation (Ru^{IV}-Ru^{III} couple) with peak-to-peak separation (Δ Ep) values ranging from 60 mV to 80 mV suggestive of a single step one-electron-transfer process.[10-12,24] Fast electron transfer processes are expected for low-spin, six-coordinate ruthenium(III) complexes, since electrons can be added to or removed from t_{2g} orbitals. These orbitals are sterically more accessible than the e_g orbitals and electron changes within the t_{2g} set require less reorganisation energy than changes within e_g orbitals. The oxidation response

Table 2. *Cyclic Voltammetric Data*[a] *for some Ru(III) Complexes*

Complex	$Ru^{IV}-Ru^{III}$				$Ru^{III}-Ru^{II}$
	Epa(V)	Epc(V)	Ef(V)	Δ Ep(mV)	Epc(V)
$[RuCl(PPh_3)(Salen)]$	0.95	0.87	0.91	80	-0.24
$[RuCl(AsPh_3)(Salen)]$	0.72	0.65	0.68	70	-0.25
$[RuBr(PPh_3)(Salen)]$	0.75	-	-	-	-0.36
$[RuCl(PPh_3)(Salpn)]$	0.64	0.70	0.67	60	-0.45
$[RuCl(AsPh_3)(Salpn)]$	0.70	0.62	0.66	80	-0.22
$[RuBr(AsPh_3)(Salpn)]$	0.78	0.84	0.81	60	-0.27
$[RuCl(PPh_3)(Saldien)]$	0.72	0.66	0.69	60	-0.27
$[RuCl(AsPh_3)(Saldien)]$	0.70	-	-	-	-0.20
$[RuBr(AsPh_3)(Saldien)]$	0.86	-	-	-	-0.25

[a] Supporting electrolyte: $[NBu_4]ClO_4$ (0.05 mol); all potentials are referenced to S.C.E.; $E_f = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are the anodic and cathodic peak potentials respectively; Scan rate : 50 mVS^{-1}.

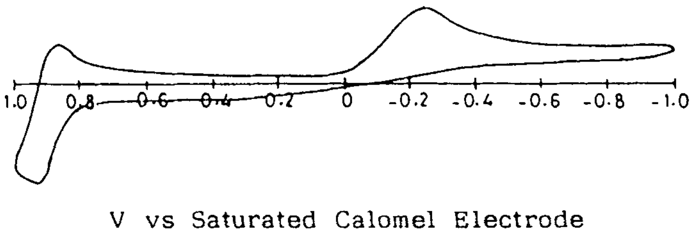


Fig.3. Cyclic Voltammogram of [RuCl(PPh$_3$)(Salen)] in Acetonitrile at a Glassy-carbon Electrode
Scan Rate : 50 mVs^{-1}

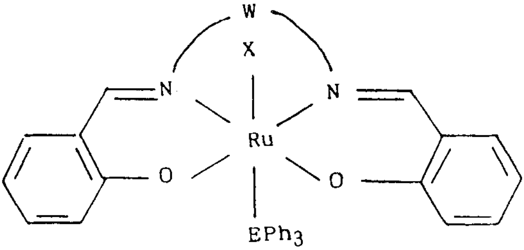
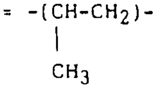


Fig. 4. Ru(III) Complexes of Schiff Base

X = Cl , Br

E = P , As

W = -(CH$_2$)$_2$-



$= -(\underset{\substack{|\\ CH_3}}{CH}-CH_2)-$

= -(C$_2$H$_4$)NH(C$_2$H$_4$)-

for [RuBr(PPh$_3$)(Salen)], [RuCl(AsPh$_3$)(Saldien)] and [RuBr(AsPh$_3$)(Saldien)] are irreversible at 50 mVs^{-1}. At a faster scan rate (200 mVs^{-1}) the oxidation processes in the above complexes become reversible with Δ Ep values in the range 80-100 mV and have E$_f$ values of 0.79 V, 0.74 V and 0.80 V, respectively. A similar observation[25] has been made for dithiocarbamate complexes of Co, Rh and Ir.

The reduction processes Ru^{III}-Ru^{II} for all the complexes show irreversible cyclic voltammograms. These observations indicate that the charge transfer process for the Ru^{III}-Ru^{II} state is not, in general, as rapid as is the case for the Ru^{IV}-Ru^{III} couple. Hence, it has been observed from the electrochemical data that the present ligand system is ideally suited for stabilizing the higher oxidation states of the ruthenium ion.

Based on the analytical, spectroscopic data (IR, electronic and EPR spectra) and electrochemical data an octahedral structure as shown in Fig. 4 has been proposed for all Ru(III) complexes.

ACKNOWLEDGEMENT

We are grateful to the Council of Scientific and Industrial Research (India) for financial support in the form of a research grant.

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Received: 21 February 1995
Accepted: 19 July 1995

Referee I: R. H. Schmehl
Referee II: J. H. Nelson