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Synthesis, characterization and electrochemical studies of ruthenium(III) heterocyclic Schiff bases

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Abstract

A series of hexacoordinated Ru^{III}–PPh_3 complexes of general formula $[RuCl(PPh_3)L]$ (L = tetradentate Schiff bases derived from the condensation of 2-furaldehyde or thiophene-2-carboxyaldehyde with alkyl and aryl diamines have been synthesized. The complexes were characterized by elemental analyses, spectroscopic and cyclic voltammetric studies. All of the complexes were paramagnetic. Coordination of the Schiff base appears to occur through the two nitrogen and two heterocyclic oxygen/sulphur atoms.

Introduction

The wealth of information available on transition metal complexes of Schiff bases is mostly confined to the first row transition metals. Studies involving ruthenium complexes with heterocyclic Schiff bases are not common [1–5]. There has been considerable interest in ruthenium complexes due to their significant applications in catalytic processes [6–8], photoelectric switch devices [9, 10] and properties such as optical sensors and probes [11, 12]. The preparation of ruthenium(III) triphenylphosphine complexes of general formula $[RuCl(PPh_3)L]$ [L = tetradentate Schiff base derived from the condensation of 2-furaldehyde (fur) or thiophene-2-carboxyaldehyde (thio) and ethylenediamine (en), 1,2-propylenediamine (pn), 1,3-propylenediamine (tn), 1,4-butylenediamine (bn) and *o*-phenylenediamine (oph)] obtained from the reaction of $[RuCl_3(PPh_3)_3]$ with the respective Schiff bases are reported here. The general structure of the tetradentate Schiff base ligands used in the present study are shown in Figure 1, along with the abbreviations for the ligands.

Experimental

Material and methods

All reagents used were of analytical grade. Solvents were purified and dried according to standard procedures [13]. Microanalyses were performed at the Central Electrochemical Research Institute, Karaikudi, India. Magnetic studies were conducted using a Gouy balance and $Hg[CoS(CN)_4Cl]$ as standard. I.r. spectra were recorded in KBr pellets using a Perkin-Elmer 1600 FT-IR spectrophotometer for the 4000–400 cm^{-1} region and a Bruker IFS 66v FT-IR spectrophotometer for the 500–50 cm^{-1} region. Electronic spectra were recorded with a Perkin-Elmer Lambda 35 spectrophotometer in the 800–190 nm range using CH_2Cl_2 as solvent. ^{1}H-n.m.r spectra of the complexes were recorded on a JEOL GSX 400 instrument using $CDCl_3$ as solvent in the Regional Sophisticated Instrumentation Center, IIT Madras. Cyclic voltammetric studies were carried out with a BAS CV-27 instrument using a three electrode cell unit, glassy carbon as working electrode, Ag/AgCl as reference and a Pt wire as auxillary electrode. The glassy carbon electrode was polished using alumina polishing material before use. n-Bu_4NClO_4 (TBAP) was used as the supporting electrolyte. All cyclic voltammetric experiments were performed under a dinitrogen environment. Melting points were determined with a Best instrument and are uncorrected. $[RuCl_3(PPh_3)_3]$ was prepared by the reported method [14].

Bis(2-furaldehyde)ethylenediimine

To a solution of 2-furaldehyde (4.8 g, 50 mmol) in CH_2Cl_2 (10 cm^3), ethylenediamine (1.5 g, 25 mmol) was added and the mixture was stirred for 5 min at room temperature. The solvent was completely evaporated to leave the Schiff base (red liquid), which was used for complex preparation without further purification. The same procedure was adopted for the other bis(2-furaldehyde)diimine Schiff bases.

Bis(thiophene-2-carboxyaldehyde)ethylenediimine

To a solution of thiophene-2-carboxyaldehyde (0.449 g, 4 mmol) in benzene (5 cm^3), ethylenediamine (0.12 g, 2 mmol) was added. The solution was stirred for 1 min, then concentrated to *ca.* half of its original vol and

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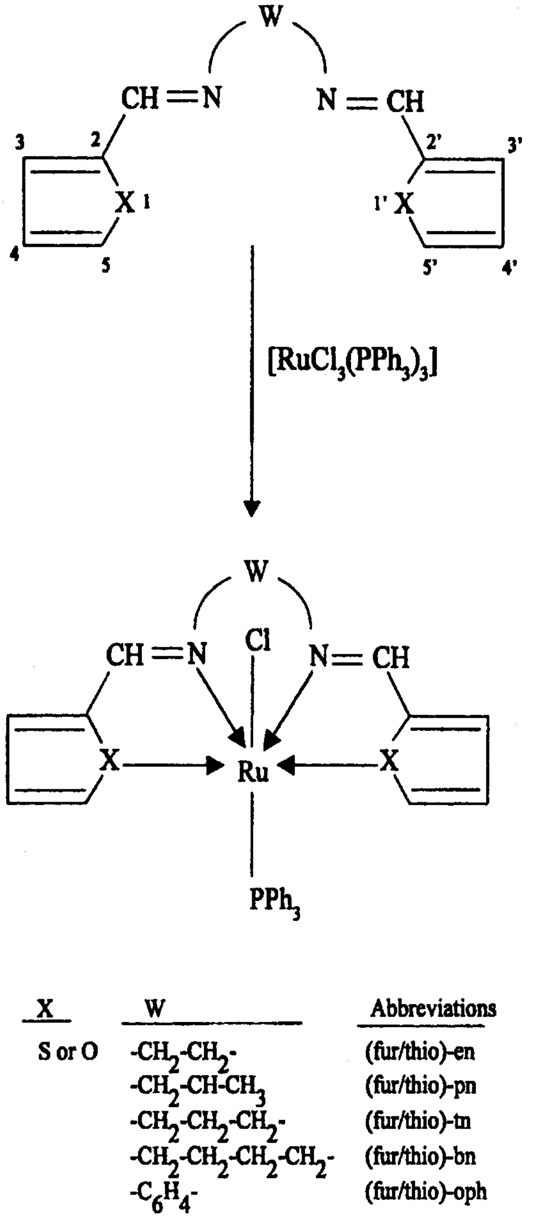

Fig. 1. Proposed scheme of formation of the Ru^{III} Schiff base complexes.

cooled in ice bath. The cream coloured crystals which separated were filtered off, recrystallized thrice with benzene and dried *in vacuo*. The purity was checked by t.l.c. and melting point. The same procedure was adopted for the other bis(thiophene-2-carboxyaldehyde)diimine Schiff bases.

Preparation of the complexes

To a solution of [$RuCl_3(PPh_3)_3$] (0.1 g, 0.1 mmol) in benzene (30 cm^3), the appropriate Schiff base (0.02 g, 0.1 mmol) was added and the solution was boiled under reflux for 5 h. The reaction mixture was then evaporated to a small vol (*ca.* 2 cm^3). The product was allowed to crystallize by the addition of a small quantity of petroleum ether (60–80 °C). The resulting compound was filtered off, washed with petroleum ether and recrystallized thrice from $CHCl_3$/petroleum ether mixture (ratio 20:80), then dried *in vacuo*. The yield was *ca.* 70%. The same procedure was adopted for the remaining complexes.

Results and discussion

The analytical data for the new complexes are consistent with the empirical formula given in Table 1, indicating the 1:1 ligand-to-metal ratio. All of the complexes are 1:2 electrolytes in acetonitrile solution, suggesting the presence of one chloride coordinated to the metal and two chloride ions outside the coordination sphere. The Schiff bases appear to behave as tetradentate donors, coordinating through two nitrogen and two oxygen or two sulphur atoms. Hence two chloride ions and two molecules of triphenylphosphine are displaced from the starting complex.

The μ_{eff} values of all the complexes ranged between 1.37 and 1.96 B.M., corresponding to one unpaired electron. It is therefore concluded that the complexes contain ruthenium (III).

Electronic spectra

Most ruthenium(III) complexes show only charge-transfer bands in their u.v.–vis. spectra [15]. The electronic spectra of the present complexes in dichloromethane

Table 1. Analytical data of the complexes

Compound		Colour	M.p. (°C)	Ω^{-1} cm^2 mol^{-1}	μ_{eff} (B.M.)	Found(calcd.) % C	H	N
(1)	[$RuCl(PPh_3)$(fur–en)]	yellow	153	212	1.72	58.6(58.6)	4.6(4.4)	4.6(4.6)
(2)	[$RuCl(PPh_3)$(fur–pn)]	orange	154	225	1.89	59.2(59.2)	4.6(4.6)	4.3(4.5)
(3)	[$RuCl(PPh_3)$(fur–tn)]	green	135	220	1.90	59.3(59.2)	4.5(4.6)	4.5(4.5)
(4)	[$RuCl(PPh_3)$(fur–bn)]	green	131	242	1.75	59.8(59.8)	4.8(4.8)	4.3(4.4)
(5)	[$RuCl(PPh_3)$(fur–oph)]	brown	193	228	1.83	61.6(61.6)	4.1(4.1)	4.2(4.2)
(6)	[$RuCl(PPh_3)$(thio–en)]	brownish yellow	165	205	1.82	55.6(55.7)	4.2(4.2)	4.2(4.3)
(7)	[$RuCl(PPh_3)$(thio–pn)]	brownish yellow	164	236	1.37	56.3(56.3)	4.4(4.4)	4.3(4.3)
(8)	[$RuCl(PPh_3)$(thio–tn)]	yellowish green	145	218	1.96	56.3(56.3)	4.4(4.4)	4.3(4.3)
(9)	[$RuCl(PPh_3)$(thio–bn)]	green	165	225	1.87	56.9(56.8)	4.6(4.6)	4.2(4.2)
(10)	[$RuCl(PPh_3)$(thio–oph)]	grey	182	232	1.91	58.8(56.8)	4.9(4.9)	4.1(4.0)

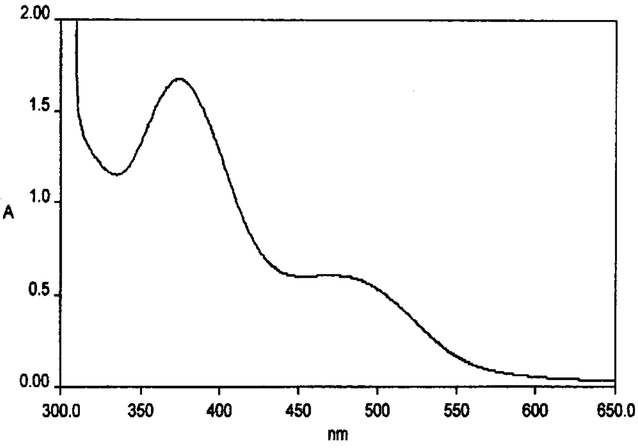

Fig. 2. Electronic absorption spectra of [RuCl(PPh_3)(thio–en)].

exhibited two absorption bands between 478 and 261 nm (Figure 2, Table 2). The extinction coefficients for the bands between 261 and 385 nm of complexes *(1)–(5)*, containing bis(2-furaldehyde)diimine ligands, are much higher than expected for d–d transitions. Hence, we assign these bands to charge-transfer transitions [16–18]. The bands at *ca.* 300 nm for complexes *(6)–(10)* with bis(thiophene-2-carboxyaldehyde) diimine ligands were also assigned as charge-transfer transitions. However, the extinction coefficients for the bands in the 400 nm region were found to be very low compared to those of charge-transfer transitions. The ground state of ruthenium(III) ($^5t_{2g}$ configuration) is $^2T_{2g}$ and the first exited doublet levels in the order of increasing energy are $^2A_{2g}$ and $^2T_{1g}$ which arise from the $^4t_{2g}\,^1e_g$ configuration [19]. Hence, the bands at *ca.* 400 nm have been assigned to the spin-allowed Laporte $^2T_{2g} \rightarrow {}^2A_{2g}$ transition in confirmity with assignments made for similar octahedral ruthenium(III) complexes [20, 21].

FT-IR spectra

The free Schiff bases show a strong i.r. band in the 1644–1667 cm^{-1} region for bis(2-furaldehyde)diimine [22], characteristic of azomethine absorption (CH=N). The i.r. spectra of the complexes show a shift of this band to lower frequency (1613–1627 cm^{-1}) consistent with coordination of the Schiff base azomethine nitrogen atom [23]. The same absorption was observed at 1629–1636 cm^{-1} for the bis(thiophene-2-carboxyaldehyde)diimine free Schiff bases, and was again shifted to lower frequency (1600–1604 cm^{-1}) in the corresponding complexes. The ν(Ru—O) band [24] appeared at 529 cm^{-1} for all the oxygen donor systems and the ν(Ru—S) [25] band appeared at 523–530 cm^{-1}, confirming the binding of the heterocyclic ring through oxygen/sulphur to ruthenium. The ν(Ru—Cl) bands lie in the 271–331 cm^{-1} range [26–29]. In addition to this, metal triphenylphosphine bands are also present in the spectra of the complexes. The bands in 400–500 cm^{-1} region may be assigned to the coordinated phosphorus [30]. The i.r. spectral data for the complexes are given in the Table 3.

^{1}H-n.m.r. spectra

The ^{1}H-n.m.r. spectra for free bis(thiophene-2-carboxyaldehyde)ethylenediimine and complexes *(6)*, *(7)*, *(8)* and *(10)* are given in Table 4. In the n.m.r. spectrum of the free Schiff base the signal due to the azomethine proton appeared at δ 8.35 p.p.m. For complex *(6)* it appeared as two singlets, for complex *(7)* as one singlet, for complex *(8)* it appeared as doublet and again for complex *(10)* as one singlet. In complex *(10)*, the singlet appeared the far upfield which may be due to the extended conjugate system. The shift in the positions of the azomethine proton signal and its split in complexes *(6)* and *(8)* are suggestive of the deshielding of azomethine proton due to coordination to ruthenium through azomethine nitrogen [31]. The broad multiplet observed in the δ 6.87–7.81 p.p.m. range for all the complexes were assigned to the phenyl groups of triphenylphosphine together with the thiophene ring protons and also of the aromatic ring protons of the [RuCl(PPh_3)(thio–oph)] complex, *(10)*. The methylene protons appeared as two singlets for complex *(6)*. For complex *(7)* methylene, methine and methyl protons appeared as singlets. While for complex *(8)*, methylene protons appeared as doublet. Here a resonance from the central —CH_2— moiety appeared as multiplet.

Table 2. Electronic absorption data for the complexes

Compound	λ_{max} (nm)	ε (cm^{-1})	λ_{max} (nm)	ε (cm^{-1})
(1)	279	1400	382	1200
(2)	274	1100	385	950
(3)	273	1200	362	1000
(4)	274	1730	374	1350
(5)	261	1320	340	1040
(6)	374	1700	475	550b
(7)	378	1340	478	150b
(8)	377	1420	460	220b
(9)	361	980	468	340b
(10)	314	1220	420	310b

b denotes broad signal.

Table 3. I.r. spectral data for the complexes

Compound	ν(CH=N) cm^{-1} Free ligand	Complex	ν(Ru—O)/ ν(Ru—S) cm^{-1}	ν(Ru—Cl) cm^{-1}
(1)	1644	1622	529	322
(2)	1644	1619	529	322
(3)	1644	1621	529	327
(4)	1644	1613	529	328
(5)	1667	1627	529	327
(6)	1629	1602	527	281
(7)	1630	1604	527	283
(8)	1633	1601	527	285
(9)	1630	1602	523	271
(10)	1636	1600	530	331

Table 4. ^{1}H-n.m.r. spectral data of bis(thiophene-2-carboxyaldehyde) ethylenediimine and its Ru^{III} complexes

Ligand/Compound	δ (p.p.m.)
(thio–en)	3.91 (s, N—CH$_2$) 7.26 (d, 3,3′) 7.02 (t, 4,4′) 7.36 (d, 5,5′) 8.35 (s, N=CH)
(6)	3.65 (s, N—CH$_2$) 4.23 (s, N—CH$_2$) 6.87–7.79 (m, ap) 8.47 (s, N=CH) 9.08 (s, N=CH)
(7)	1.25 (s, —CH$_3$) 0.84 (s, —CH) 4.18 (s, —CH$_2$) 7.14–7.70 (m, ap) 8.49 (s, N=CH)
(8)	3.80–3.87 (m, —CH$_2$) 4.27 (d, N—CH$_2$) 6.95–7.36 (m, ap) 8.29 (d, N=CH)
(10)	5.7–7.81 (m, ap) (s, N=CHs)

s – Singlet, t – triplet, m – multiplet, ap – aromatic protons.

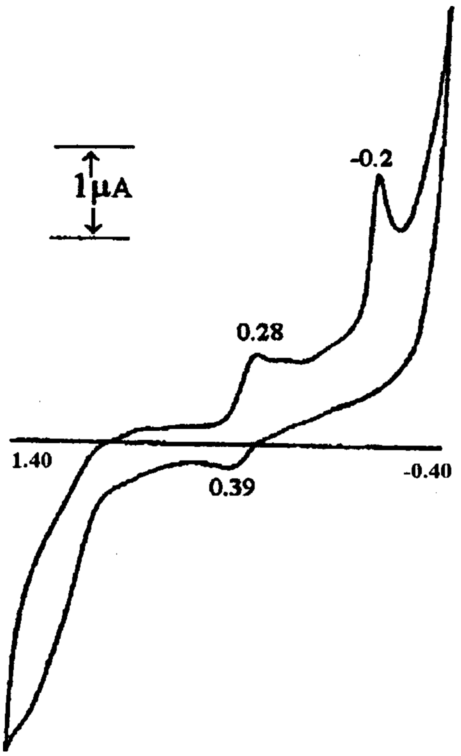

Fig. 3. Cyclic voltammogram of [RuCl(PPh$_3$)(thio–en)]. Glassy carbon – working, Ag/AgCl – reference, Pt wire – counter electrode, TBAP – Supporting electrolyte, Scan rate 100 mv s^{-1}.

Cyclic voltammetry

Cyclic voltammetric studies were performed in acetonitrile solution using a glassy carbon working electrode in order to investigate the suitability of the present ligand system in achieving metal higher oxidation states. The redox potentials of the complexes characterized by well-defined waves are in the 0.36–0.88 V range (oxidation) *versus* Ag/AgCl. The c.v. data are given in Table 5 and a representative case is displayed in Figure 3.

The ligands used in this work are not reversibly reduced or oxidized within the potential limit (+1.4 to −0.40 V), and the observed redox process is metal centered. Most of the complexes showed reversible oxidation (Ru^{IV}–Ru^{III}) with peak to peak separations (ΔE_p) ranging from 70 to 110 mV, suggestive of a single step one electron transfer process [32–35].

Fast electron transfer processes are expected for low spin, six coordinate ruthenium(III) complexes, since electrons can be added or removed from t_{2g} orbitals. These orbitals are sterically more accessible than e_g orbitals and electron changes within the t_{2g} set require less reorganization energy than changes within e_g orbitals [23].

The Ru^{III}–Ru^{II} reduction process for all the complexes is irreversible, indicating either that the charge-transfer process for Ru^{III}–Ru^{II} is not, as rapid as for the Ru^{IV}–Ru^{III} couple, or reduction to a short lived oxidation state of the metal ion [36]. Hence, the electrochemical data indicate that the present ligand system stabilizes the higher oxidation state of the ruthenium ion.

Table 5. Cyclic voltammetric data for the complexes

Compound	Ru^{IV}–Ru^{III}				Ru^{III}–Ru$^{II\,a}$
	E_{pa} (V)	E_{pc} (V)	E_f (V)	ΔE_p (mv)	E_{pc} (V)
(1)	0.80	0.70	0.75	100	−0.20
(2)	0.80	0.71	0.76	90	−0.25
(3)	0.80	0.70	0.75	100	−0.25
(4)	0.86	0.75	0.81	110	−0.20
(5)	0.88	0.77	0.83	110	−0.27
(6)	0.39	0.28	0.34	110	−0.20
(7)	0.69	0.77	0.73	80	−0.20
(8)	0.73	0.64	0.69	90	−0.18
(9)	0.69	0.76	0.73	70	−0.12
(10)	0.36	0.26	0.29	100	−0.25

[a] (Ru^{III}–Ru^{II}) couple is not chemically reversible in all complexes, therefore, only E_{pc} (V) values are quoted.

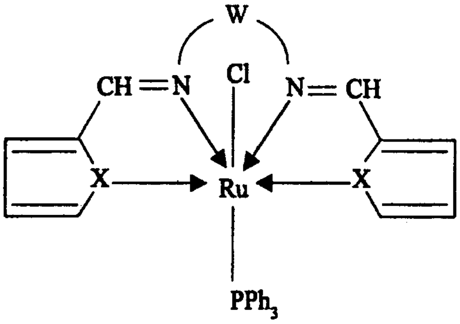

Fig. 4. Proposed structure of the Ru^{III} Schiff base complexes.

On the basis of the data discussed above, the octahedral structure shown in Figure 4 is proposed for these ruthenium(III) complexes.

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