

Synthesis, characterization, redox property and biological activity of Ru(II) carbonyl complexes containing O,N-donor ligands and heterocyclic bases

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Abstract

Stable ruthenium(II) carbonyl complexes having the general composition $[\text{RuCl}(\text{CO})(\text{PPh}_3)(\text{B})(\text{L})]$ (where B = PPh_3 , pyridine, piperidine or morpholine; L = anion of bidentate Schiff bases (Vanmet, Vanampy, Vanchx)) were synthesized from the reaction of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2(\text{B})]$ with bidentate Schiff base ligands derived from condensation of *o*-vanillin with primary amines such as methylamine, 2-aminopyridine and cyclohexylamine. The new complexes were characterized by elemental analysis, IR, UV-Vis and ^1H NMR spectral data. The redox property of the complexes were studied by cyclic voltammetric technique and the stability of the complexes towards oxidation were related to the electron releasing or electron withdrawing ability of the substituent in the phenyl ring of *o*-vanillin. An octahedral geometry has been assigned for all the complexes. In all the above reactions, the Schiff bases replace one molecule of PPh_3 and hydride ion from the starting complexes, which indicate that the Ru–N bonds present in the complexes containing heterocyclic nitrogen bases are stronger than the Ru–P. The Schiff bases and their ruthenium(II) complexes have been tested in vitro to evaluate their activity against bacteria, viz., *Staphylococcus aureus* (209p) and *E. coli* (ESS 2231).

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1. Introduction

The interest in the synthesis and characterization of transition metal complexes containing a Schiff base lies in their biological and catalytic activity in many reactions [1,2]. Schiff bases derived from the condensation of aldehyde with primary amines represent an important class of chelating ligands, the metal complexes of which have been studied widely [3]. The transition metal complexes having oxygen and nitrogen donor Schiff bases possess unusual configuration, structural lability and are sensitive to molecular environment. The environment around the metal center 'as co-ordination geometry, number of coordinated ligands and their donor group' is the key factor for metalloprotein to carry out specific physiological function [4,5]. Further,

Schiff bases offer opportunities for inducing substrate chirality, tuning metal centered electronic factor, enhancing solubility and stability of either homogeneous or heterogeneous catalyst [6–8]. In the use of transition metal carbonyls as reactive species in homogeneous catalytic reactions such as hydrogenation, hydroformylation and carbonylation, carbon monoxide serves simply as ligand providing the complex with the necessary reactivity and stability to allow reaction [9]. In contrast to the considerable growth of literature on the chemistry of Schiff base complexes of first row transition metal, the chemistry of ruthenium complexes is less well developed [10–13].

As a part of our continuous work reported on syntheses and characterization of several ruthenium(II) and ruthenium(III) complexes containing tertiaryphosphine/arsine [14–17], we report here the synthesis, spectral characterization and antibacterial activity of a series of ruthenium(II) bidentate Schiff base complexes with triphenylphosphine and nitrogen heterocycles. The Schiff base ligands used in this study are shown in (Fig. 1).

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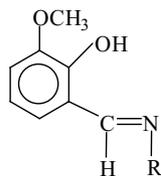


Fig. 1. Structure of the Schiff bases. R = $-\text{CH}_3$, $-\text{C}_5\text{H}_4\text{N}$, $-\text{C}_6\text{H}_{12}$.

2. Experimental

2.1. Material and physical measurements

All the reagents used were chemically pure or analytical reagent grade. Solvents were purified and dried according to standard procedures. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Loba chemie Pvt. Ltd., Bombay, India and was used without further purification. $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ [18], $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2(\text{B})]$ [19] (where B = py, pip or morp) and the ligands [20] were prepared by reported literature methods. The analysis of carbon, hydrogen and nitrogen were performed on Carlo Erba 1160 and model 240 Perkin-Elmer CHN analyzer at the Central Drug Research Institute, Lucknow, India. IR spectra were recorded in KBR pellets in the $4000\text{--}200\text{ cm}^{-1}$ region in Jasco 400 plus spectrophotometer. Electronic spectra were recorded in CH_2Cl_2 solution with a Cary 300 Bio UV-Vis Varian spectrophotometer in the range of $800\text{--}200\text{ nm}$. ^1H NMR spectra were recorded on a Bruker 400 MHz instrument using TMS as an internal reference. Cyclic voltammetric measurements were carried out on a Bio Analytical System (BAS) model CV-50W electrochemical analyzer using acetonitrile as solvent. Antibacterial activity studies were carried out at the Nicholas Piramal India Ltd., Quest Institute of Life Science, Mumbai. Melting points were recorded with a Boetius micro-heating table and are uncorrected.

2.2. Preparation of Schiff base ligands

The monobasic bidentate Schiff base ligands were prepared by the condensation of *o*-vanillin (0.38 g; 0.0025 mmol) with primary amine such as methylamine, 2-aminopyridine and cyclohexylamine (0.23 g; 0.0025 mmol) in 1:1 molar ratio in EtOH (25 cm^3). The solution was heated under reflux for 2 h and then concentrated to 5 cm^3 . On cooling the product was separated out. The crude products were purified by column chromatography on silica gel using petroleum ether/EtOAc (95/5%) as eluent.

2.3. Synthesis of Ru(II) carbonyl Schiff base complexes

All the new complexes were prepared by the following general procedure. To a solution of $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2(\text{B})]$ (where B = PPh_3 , py, pip or morp) (100 mg; 0.10–0.13 mmol) in benzene the appropriate Schiff base (15–23 mg; 0.10–0.13 mmol) was added and under reflux for 6 h. The

resulting solution was concentrated to ca. 3 cm^3 and cooled. Light petroleum ether ($60\text{--}80^\circ\text{C}$) (5 cm^3) was then added where upon the complex was separated. The solid was filtered off, washed and recrystallised from CH_2Cl_2 /light petroleum ether mixture and dried in vacuo. The purity of the compounds were checked by TLC (yield: 62–73%).

2.4. Antibacterial study

The in vitro antimicrobial activity of the investigated complexes were tested against the bacteria such as *Staphylococcus aureus* (209P) and *E. coli* (2231) by well diffusion method using agar nutrient as the medium. The bacterial cultures were incubated at 37°C for 18 h. The ligands and the complexes were stored dry at room temperature and dissolved in 10% DMSO in methanol. In a typical procedure [21], a well was made on the agar medium inoculated with micro-organisms. The well was filled with test solution using a micropipette and the plate was incubated at 35°C for 24 h for bacteria. During this period, the test solution was diffused and the growth of the inoculated microorganisms was affected. The inhibition zone developed on the plate was measured.

3. Results and discussion

Diamagnetic low spin ruthenium(II) complexes of general formula $[\text{RuCl}(\text{CO})(\text{PPh}_3)(\text{B})(\text{L})]$ (where B = PPh_3 , py, pip or morp; L = bidentate Schiff bases) were prepared by reacting $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_2(\text{B})]$ with Schiff bases in a 1:1 molar ratio in benzene as shown in (Fig. 2). All of the new Schiff base ruthenium(II) complexes are highly colored, stable to air and light and soluble in chloroform, methylene chloride, benzene, DMF and DMSO. The analytical data (Table 1) are in good agreement with the general molecular formula proposed for all the complexes.

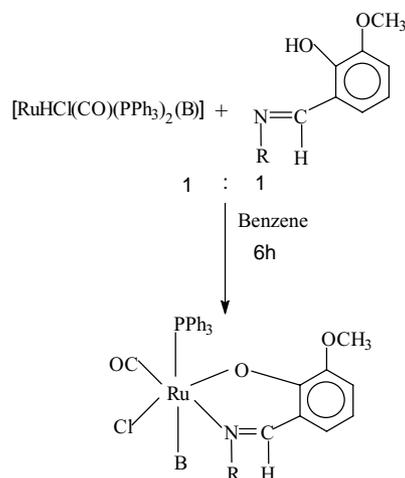


Fig. 2. Formation of new ruthenium(II) carbonyl complexes. (Where B = PPh_3 or py or pip or morp; R = $-\text{CH}_3$, $-\text{C}_5\text{H}_4\text{N}$, $-\text{C}_6\text{H}_{12}$).

Table 1
Analytical data of Ru(II) carbonyl Schiff base complexes

| Complex | Empirical formula | Colour | Melting point (°C) | Found (calculated) (%) | | |
|--|---|--------|--------------------|------------------------|-----------|-----------|
| | | | | C | H | N |
| [RuCl(CO)(PPh ₃) ₂ (Vanmet)] | C ₄₆ H ₄₀ NO ₃ ClP ₂ Ru | Green | 124 | 59.9 (60.4) | 4.2 (4.4) | 1.4 (1.5) |
| [RuCl(CO)(PPh ₃) ₂ (Vanampy)] | C ₄₀ H ₄₂ N ₂ O ₃ ClP ₂ Ru | Brown | 120 | 55.6 (55.9) | 4.7 (4.9) | 2.9 (3.3) |
| [RuCl(CO)(PPh ₃) ₂ (Vanchx)] | C ₄₀ H ₄₂ NO ₃ ClP ₂ Ru | Green | 129 | 57.5 (57.1) | 5.5 (5.6) | 1.5 (1.6) |
| [RuCl(CO)(PPh ₃)(py)(Vanmet)] | C ₄₁ H ₄₈ N ₂ O ₃ ClP ₂ Ru | Green | 126 | 56.1 (56.5) | 4.6 (4.3) | 2.2 (2.0) |
| [RuCl(CO)(PPh ₃)(py)(Vanampy)] | C ₃₁ H ₃₇ N ₃ O ₃ ClPRu | Brown | 132 | 57.9 (58.2) | 4.0 (4.2) | 5.3 (5.5) |
| [RuCl(CO)(PPh ₃)(py)(Vanchx)] | C ₃₈ H ₃₈ N ₃ O ₃ ClPRu | Green | 105 | 59.4 (59.3) | 4.8 (4.9) | 3.8 (3.6) |
| [RuCl(CO)(PPh ₃)(pip)(Vanmet)] | C ₃₃ H ₃₆ N ₂ O ₃ ClPRu | Green | 125 | 55.9 (56.1) | 5.1 (4.9) | 3.5 (3.9) |
| [RuCl(CO)(PPh ₃)(pip)(Vanampy)] | C ₃₇ H ₃₇ N ₃ O ₃ ClPRu | Brown | 130 | 57.6 (57.8) | 4.9 (4.7) | 5.1 (5.5) |
| [RuCl(CO)(PPh ₃)(pip)(Vanchx)] | C ₃₉ H ₄₄ N ₂ O ₃ ClPRu | Green | 112 | 59.7 (59.6) | 5.4 (5.5) | 3.8 (3.6) |
| [RuCl(CO)(PPh ₃)(morp)(Vanmet)] | C ₃₂ H ₃₄ N ₂ O ₃ ClPRu | Green | 131 | 56.5 (56.8) | 4.8 (4.9) | 4.3 (4.1) |
| [RuCl(CO)(PPh ₃)(morp)(Vanampy)] | C ₃₆ H ₃₅ N ₃ O ₄ ClPRu | Brown | 129 | 58.5 (58.4) | 4.7 (4.6) | 5.5 (5.7) |
| [RuCl(CO)(PPh ₃)(morp)(Vanchx)] | C ₃₇ H ₄₂ N ₂ O ₄ ClPRu | Green | 110 | 59.2 (59.6) | 5.7 (5.5) | 3.6 (3.8) |

3.1. FT-IR spectra

The infrared spectra of the free Schiff base ligands showed a strong band in the region 1610–1617 cm⁻¹ which is characteristic of the azomethine (>C=N) group [22]. Co-ordination of the Schiff bases to the metal through nitrogen atom is expected to reduce the electron density in the azomethine link and lower the $\nu_{C=N}$ absorption frequency. The band due to $\nu_{C=N}$ showed a negative shift and appeared at 1588–1608 cm⁻¹ indicating co-ordination of azomethine nitrogen [23] to ruthenium metal (Table 2). A strong band observed at 1265–1276 cm⁻¹ in free Schiff bases has been assigned to phenolic C–O stretching. On complexation, this band is shifted to higher frequency range 1270–1286 cm⁻¹ indicating co-ordination through the phenolic oxygen [23,24]. This has been further supported by the disappearance of the broad ν_{OH} band around 3410 cm⁻¹ in the complexes indicating deprotonation of the phenolic proton prior to co-ordination [22]. A sharp band appeared around 1935–1952 cm⁻¹ due to $\nu_{C\equiv O}$ of the carbonyl group in all the complexes. In addition other characteristic

bands due to triphenylphosphine are also present around 1435 cm⁻¹ in the spectra of all the Schiff base complexes. A medium intensity band is observed in the 1020 cm⁻¹ region characteristic of the coordinated pyridine or piperidine [25]. The co-ordination of the azomethine nitrogen and phenolic oxygen are further supported by the appearance of two bands at 510–540 and 400–460 cm⁻¹ due to ν_{M-O} [24] and ν_{M-N} [25], respectively. For all the complexes, the ν_{Ru-Cl} absorption has been observed around 320 cm⁻¹ region [26].

3.2. Electronic absorption spectra

The electronic spectra of all the complexes in dichloromethane showed two to three bands in the region 709–290 nm. All the Schiff base ruthenium complexes are diamagnetic, indicating the presence of ruthenium in the +2 oxidation state. The ground state of ruthenium(II) in octahedral environment is ¹A_{1g} arising from the t_{2g}⁶ configuration and the excited states corresponding to the t_{2g}⁵e_g¹ configuration are ³T_{1g}, ²T_{2g}, ¹T_{1g} and ¹T_{2g}. Hence, four bands corresponding to the transition ¹A_{1g} → ³T_{1g}, ¹A_{1g} → ³T_{2g},

Table 2
Important IR (cm⁻¹) and Electronic spectral data (nm) of the Ru(II) carbonyl Schiff base complexes

| Complexes | $\nu_{C=N}$ (cm ⁻¹) | ν_{C-O} (cm ⁻¹) | $\nu_{C\equiv O}$ (cm ⁻¹) | λ_{max} (ϵ) ^a (dm ³ mol ⁻¹ cm ⁻¹) |
|-----------|---------------------------------|---------------------------------|---------------------------------------|---|
| 1 | 1609 | 1282 | 1952 | 391 ^b (6690), 294 ^c (34200) |
| 2 | 1604 | 1270 | 1949 | 469 ^b (2769), 290 ^c (31849) |
| 3 | 1605 | 1274 | 1942 | 709 ^a (980), 399 ^b (5871), 295 ^c (35770) |
| 4 | 1606 | 1282 | 1941 | 657 ^a (1780), 390 ^b (5460), 293 ^c (25510) |
| 5 | 1605 | 1270 | 1945 | 446 ^b (664), 294 ^b (7678) |
| 6 | 1610 | 1280 | 1937 | 656 ^a (2480), 393 ^b (14530), 294 ^c (29920) |
| 7 | 1588 | 1286 | 1943 | 401 ^b (3228), 298 ^c (24932) |
| 8 | 1604 | 1270 | 1943 | 453 ^b (6196), 359 (9267), 298 ^c (38569) |
| 9 | 1606 | 1270 | 1935 | 675 ^a (1230), 473 ^b (2970), 290 ^c (8721) |
| 10 | 1588 | 1283 | 1940 | 385 ^b (2310), 293 ^c (21770) |
| 11 | 1588 | 1283 | 1940 | 457 ^b (13400), 298 ^c (41090) |
| 12 | 1606 | 1273 | 1935 | 395 ^b (3420), 329 ^c (6450) |

^a ¹A_{1g} → ¹T_{1g}.

^b Charge transfer.

^c Ligand-centered transitions.

Table 3
 ^1H NMR data for Ru(II) carbonyl Schiff base complexes

| Complexes | ^1H NMR data (ppm) |
|-----------|---|
| 1 | 6.8–7.8 (Ar. m), 8.72 (CH, s), 3.9 (OCH ₃ ,s), 2.5 (CH ₃ ,s) |
| 2 | 6.8–8.1 (Ar. m), 8.72 (CH, s), 3.9 (OCH ₃ ,s) |
| 3 | 6.8–8.2 (Ar. m), 8.9 (CH ₃ , s), 3.9 (OCH ₃ , s), 1.4 (CH ₂ , s) |
| 4 | 6.9–7.8 (Ar. m), 8.72 (CH, s), 3.9 (OCH ₃ , s), 2.4 (CH ₃ , s) |
| 5 | 6.7–8.0 (Ar. m), 8.9 (CH, s), 3.9 (OCH ₃ , s) |
| 6 | 6.8–8.1 (Ar. m), 8.8 (CH, s), 4.1 (OCH ₃ , s), 1.45 (CH ₂ , s) |
| 7 | 6.7–8.0 (Ar. m), 8.7 (CH, s), 4.0 (OCH ₃ , s), 2.5 (CH ₃ , s), 1.5 (CH ₂ , s), 9.8 (NH, s) |
| 8 | 6.8–7.9 (Ar. m), 8.7 (CH, s), 3.9 (OCH ₃ , s), 1.63 (CH ₂ , s), 9.6 (NH, s) |
| 9 | 6.8–7.9 (Ar. m), 8.9 (CH, s), 3.8 (OCH ₃ , s), 1.35 (CH ₂ , s), 10.1 (NH, s) |
| 10 | 6.8–8.1 (Ar. m), 8.72 (CH, s), 3.9 (OCH ₃ , s), 2.5 (CH ₃ , s), 3.8 (CH ₂ , s), 2.8 (CH ₂ , s), 9.9 (NH, s) |
| 11 | 6.9–8.0 (Ar. m), 8.7 (CH, s), 4.0 (OCH ₃ , s), 3.6 (CH ₂ , s), 2.9 (CH ₂ , s), 9.8 (NH, s) |
| 12 | 6.9–8.1 (Ar. m), 8.9 (CH, s), 4.2 (OCH ₃ , s), 3.7 (CH ₂ , s), 2.73 (CH ₂ , s), 1.35 (CH ₂ , s), 10.1 (NH, s) |

$^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ are possible in order of increasing energy. The bands around 709–656 nm are assigned to $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$. The bands around 476–359 nm have been assigned to charge transfer transitions arising from the excitation of electron from the metal t_{2g} level to the empty molecular orbitals derived from π^* level of the ligands [15,27–29]. The other high intensity bands in the 329–290 nm region were characterized by ligand-centered (LC) bands and has been designated as $\pi-\pi^*$ and $n-\pi^*$ transitions for the electrons localized on the azomethine group of the Schiff base. The pattern of the electronic spectra of all the complexes indicated the presence of an octahedral environment around ruthenium(II) ion, similar to that of other ruthenium(II) octahedral complexes [15,27,28].

3.3. ^1H NMR spectra

The ^1H NMR spectra of all the complexes were recorded to confirm the binding of Schiff bases to the ruthenium ion (Table 3). Spectra of all the complexes showed a singlet in the region δ 8.6–8.9 ppm, which has been assigned to azome-

thine proton ($>\text{CH}=\text{N}$). The position of azomethine signal in the complexes are downfield in comparison with that of the free ligands, suggesting deshielding of the azomethine proton due to its co-ordination to ruthenium through the azomethine nitrogen. Multiplet are observed around δ 6.8–8.1 ppm in all the complexes have been assigned to aromatic protons of triphenylphosphine, pyridine and Schiff base ligands [30,31]. One sharp singlet appeared at δ 3.8–4.2 ppm indicates the presence of methoxy proton in all the complexes [32]. Methyl protons appear as singlet in the region δ 2.4–2.5 ppm in 1, 4, 7 and 10 and a representative spectra of 1 is shown in Fig. 3. The signal for methylene protons appear as a broad singlet in the region δ 1.35–1.63 ppm in 3, 7–9 and 12. The spectra of 11, 11 and 12 showed two signals for methylene protons which are nearer to oxygen and nitrogen. The signal in the region δ 3.6–3.7 ppm is due to methylene protons nearer to oxygen and the region δ 2.7–2.9 ppm is due to methylene protons nearer to the nitrogen. The spectra of 7–11 and 12 showed a singlet in the δ 9.6–10.1 ppm which have been assigned to NH proton of piperidine and morpholine. This signal was not found in 1–6 which con-

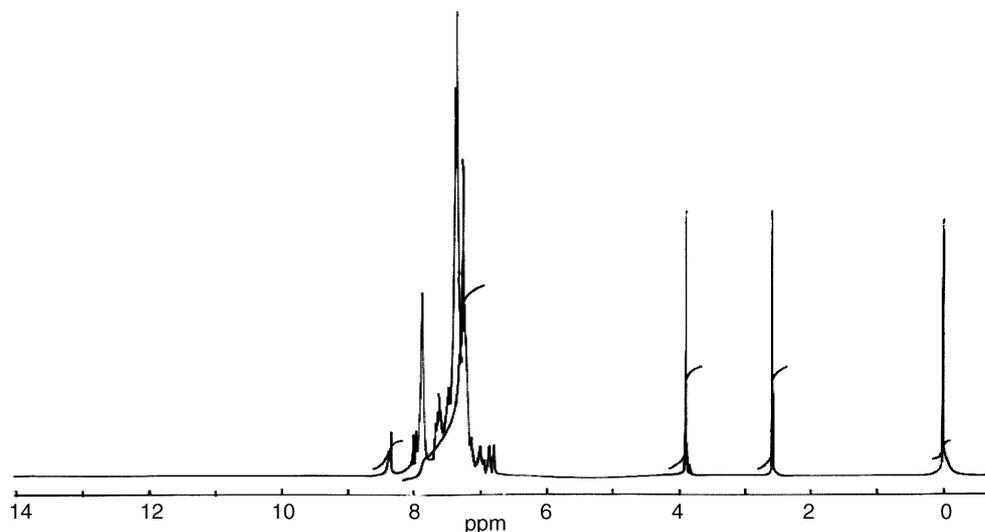


Fig. 3. ^1H NMR spectrum of $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2(\text{Vanmet})]$.

Table 4
Cyclic voltammetric data of Ru(II) carbonyl Schiff base complexes

| Complexes | Metal based oxidation | | | Metal based reduction | | | Ligand based reduction | | |
|-----------|-----------------------|--------------|---------------|-----------------------|--------------|--------------|------------------------|---------------|-------------------|
| | Ru(III)/Ru(II) | | | Ru(II)/Ru(I) | | | | | |
| | E_{pa} (V) | E_{pc} (V) | $E_{1/2}$ (V) | ΔE_p (mV) | E_{pc} (V) | E_{pc} (V) | E_{pa} (V) | $E_{1/2}$ (V) | ΔE_p (mV) |
| 1 | 0.93 | 0.86 | 0.80 | 70 | -0.80 | -1.07 | -0.76 | -0.92 | -310 |
| 2 | 0.94 | 0.87 | 0.91 | 70 | -0.79 | -0.96 | -0.76 | -0.86 | -200 |
| 3 | 0.80 | 0.86 | 0.83 | 60 | -0.76 | -1.07 | -0.75 | -0.91 | -320 |
| 4 | 0.96 | 0.90 | 0.93 | 70 | -0.69 | -1.07 | -0.72 | -0.90 | -350 |
| 5 | 0.98 | 0.91 | 0.95 | 70 | -0.73 | -1.02 | -0.69 | -0.86 | -330 |
| 6 | 0.93 | 0.86 | 0.90 | 70 | -0.73 | -1.05 | -0.73 | -0.89 | -320 |
| 7 | 0.80 | 0.87 | 0.84 | 70 | -0.77 | -1.09 | -0.73 | -0.91 | -360 |
| 8 | 0.91 | 0.83 | 0.87 | 80 | -0.76 | -1.08 | -0.74 | -0.91 | -340 |
| 9 | 0.80 | 0.87 | 0.84 | 70 | -0.78 | -1.08 | -0.75 | -0.92 | -330 |
| 10 | 0.82 | 0.89 | 0.86 | 70 | -0.75 | -1.05 | -0.75 | -0.90 | -300 |
| 11 | 0.92 | 0.86 | 0.89 | 60 | -0.78 | -1.05 | -0.72 | -0.89 | -330 |
| 12 | 0.93 | 0.86 | 0.90 | 70 | -0.76 | -1.07 | -0.74 | -0.91 | -330 |

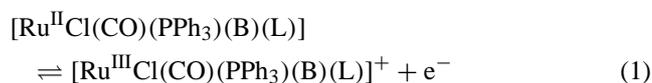
Note: Supporting electrolyte, $[\text{NBu}_4]\text{ClO}_4$ (0.05 mol); all potentials are referenced to Ag/AgCl; $E_f = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; scan rate, 100 mV s^{-1} .

firmly the absence of nitrogen bases in these complexes. A sharp singlet observed for OH protons for all the ligands in the region 13.0 ppm was disappeared in all the complexes.

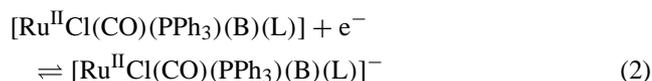
3.4. Electrochemical study

The electrochemical properties of all the complexes were studied in acetonitrile solution by cyclic voltammetry and voltammetric data are presented in (Table 4). Cyclic voltammogram of all the complexes ($1 \times 10^{-3} \text{ M}$) exhibit a reversible oxidation and an irreversible reduction peaks at the scan rate of 100 mV s^{-1} . Representative cyclic voltammogram of 5 is shown in Fig. 4. All the complexes showed well defined waves in the range 0.80–0.95 V ($\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$) and -0.69 to -0.80 V ($\text{Ru}^{\text{II}}/\text{Ru}^{\text{I}}$) versus Ag/AgCl. The oxidation processes are reversible with peak-to-peak separation (ΔE_p) values ranging from 60 to 80 mV, close to that anticipated for a Nernstian One-electron process [33,34]. For scan rate (SR) 100 mV s^{-1} , the ratio i_p/SR (i_p = peak current) was approximately one, the peak separation being independent of the scan rate. This indicates that the electron transfer is

reversible or approaches reversibility and the mass transfer is limited. The electron donating group (OCH_3) ability of the substituent in the phenyl ring of the Schiff bases favored oxidation of Ru^{2+} to Ru^{3+} [31]:



The reason for irreversibility observed for reduction of all the complexes may be due to short lived reduced state of the metal ion [35] or due to oxidative degradation [36] of the ligands. Further, a quasi-reversible ligand based reduction peak is observed in the range -0.86 to -0.92 V in all the complexes, which corresponds to reduction of azomethine ($\text{C}=\text{N}$) moiety of the Schiff base ligands and the reductions occurred at more negative values:



It has also been observed from the electrochemical data that there is little variation in the redox potentials due to replacement of triphenylphosphine by pyridine or piperidine or morpholine [14]. Hence, it is inferred from the electrochemical data that the present ligand system is ideally suitable for stabilizing the higher oxidation state of ruthenium ion.

3.5. Antibacterial activity

The in vitro antibacterial screening of the ligands Vanmet, Vanampy and Vanchx and their ruthenium(II) complexes has been carried out against gram-positive bacteria, viz., *S. aureus* (209p) and gram-negative *E. coli* (ESS 2231) using agar medium and the test solutions were prepared in DMSO. It has been observed from the antibacterial screening studies that the ruthenium chelates have higher activity than the corresponding free ligands against the same microorganisms

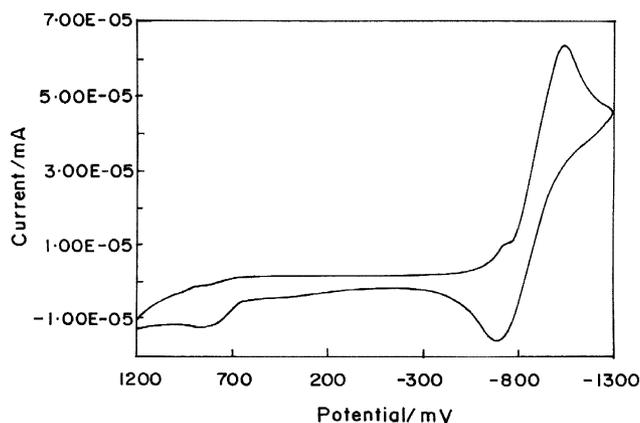


Fig. 4. Cyclic voltammogram of $[\text{RuCl}(\text{CO})(\text{PPh}_3)(\text{py})(\text{Vanampy})]$.

Table 5
Antibacterial activities of Ru(II) carbonyl Schiff base complexes

| Complexes | Diameter of inhibition zone (mm) | |
|-----------|----------------------------------|---------------------------|
| | <i>S. aureus</i> (209p) | <i>E. coli</i> (ESS 2231) |
| Vanmet | – | – |
| Vanampy | – | – |
| Vanchx | – | – |
| 1 | 10 | 9 |
| 2 | 12 | 9 |
| 3 | 11 | 10 |
| 4 | 10 | 9 |
| 5 | 11 | 9 |
| 6 | 10 | 10 |
| 7 | 10 | 9 |
| 8 | 9 | 10 |
| 9 | 11 | 10 |
| 10 | 11 | 10 |
| 11 | 10 | 11 |
| 12 | 10 | 12 |

Symbol “–” denotes no activity.

under identical experimental conditions (Table 5) which is consistent with earlier reports [37–39]. The possible mode of increased toxicity of the ruthenium complexes compared to that of the free ligands may be explained in terms of Tweedy's chelation theory [40]. Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with donor groups and possible π -electron delocalization over the whole chelate ring. Such a chelation could enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layers of cell membrane [41] and blocking the metal binding sites on enzymes of microorganism. The variation in the effectiveness of different compound against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells. Though there is a marked increase in the bacterial activity of ruthenium complexes as compared to the free ligands, it could not reach the effectiveness of Streptomycin [16].

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