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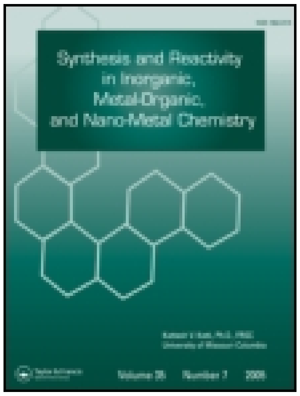

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SYNTHESIS AND CHARACTERIZATION OF NEW RUTHENIUM(III) COMPLEXES CONTAINING TETRADENTATE SCHIFF BASES

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SYNTHESIS AND CHARACTERIZATION OF NEW RUTHENIUM(III) COMPLEXES CONTAINING TETRADENTATE SCHIFF BASES

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ABSTRACT

Several new hexa-coordinated ruthenium(III) complexes of the type $[RuX(EPh_3)(LL')]$ ($X = Cl$, Br; $E = P$, As; $LL' =$ anthacac, anthdibm, 2-amtpacac or 2-amtpdibm) 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(anthranilic acid)acetylacetimine (H_2-anthacac), bis(anthranilic acid)dibenzoylmethimine (H_2-anthdibm), bis(2-aminothiophenol)acetylacetimine (H_2-2-amptacac) or bis(2-aminothiophenol)dibenzoylmethimine (H_2-2-amtpdibm). All of the complexes have been characterised by elemental analyses, IR, electronic spectra, EPR, magnetic moment and cyclic voltammetric data. An octahedral structure has been tentatively proposed for the

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complexes. These complexes were also tested for their antibacterial properties.

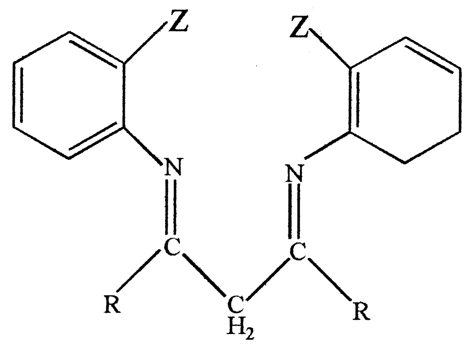
INTRODUCTION

Several low-spin d^5 complexes of second and third row transition metal ions with tertiary phosphines and arsines as ligands have been reported[1–6]. The interest in the synthesis and characterisation of transition metal complexes containing Schiff bases lies in their catalytic and biological activity in many reactions[7–10]. Furthermore, tetradentate Schiff base complexes are important for designing metal complexes related to synthetic and natural oxygen carriers[11]. An extensive amount of information is available on the chemistry of transition metal complexes containing Schiff bases and it is related mostly to first row transition metals[12–14]. Relatively little work has been done on ruthenium complexes containing Schiff bases[15,16]. Though investigations on the reactions of O_2N_2 and O_2S_2 chromophores containing Schiff bases with ruthenium(II) and ruthenium(III) are available[17–22], no work has been done with Schiff bases containing N_2S_2 chromophores. Besides, a study of compounds containing S and N atoms is interesting due to their significant antifungal, antibacterial and anticancer activities[23]. With the view to not only investigate the coordination behaviour of Schiff bases containing N_2S_2 chromophores, but also to assess the biological activity of the new complexes, we report in the present communication the synthesis and characterisation of some stable ruthenium(III) Schiff base complexes of the type $[RuX(EPh_3)(LL')]$ ($X = Cl$ or Br; $E = P$ or As; $LL' =$ anthacac, anthdibm, 2-amtpacac or 2-amtpdibm) and their biological activities. 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, India and was used without further purification. $[RuCl_3(PPh_3)_3]$[2], $[RuCl_3(AsPh_3)_3]$[24], $[RuBr_3(AsPh_3)_3]$[25] and $[RuBr_3(PPh_3)_2(MeOH)]$[4] were prepared by reported literature methods.

The analyses of carbon, hydrogen and nitrogen were performed on Carlo Erba 1106 and model 240 Perkin-Elmer CHN analyzers at the Central Drug Research Institute, Lucknow, India. IR spectra were recorded in KBr pelletes in the 4000–500 cm^{-1} region using a Shimadzu FTIR-8200 spectrophotometer. Electronic spectra were recorded in dichloromethane



Z	R	Acronym
COOH	CH_3	H_2-anthacac
COOH	C_6H_5	H_2-anthdibm
SH	CH_3	H_2-2-amtpacac
SH	C_6H_5	H_2-2-amtpdibm

Figure 1. Structure of the Schiff base ligands.

solution with a Hitachi Perkin-Elmer 20/200 spectrophotometer in the range 800–200 nm. EPR spectra of powdered samples at room tempreature were recorded with a model ER 200-D Bruker spectrometer at X-band frequencies. Magnetic susceptibilities were recorded on an EG and G-PARC vibrating sample magnetometer. Cyclic voltammetric studies were carried out with a BAS CV-27 cyclic voltammeter 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 Schiff Bases

The dibasic tetradentate Schiff base ligands have been prepared by the condensation reaction of β-diketones [acetylacetone (2.6 mL, 0.025 mol) or

Table I. Analytical Data of the Ligands and their Ru(III) Complexes

					Analysis % Found (Calc.)		
S. No.	Complex (Empirical Formula) (Formula Weight)	Colour	M.p. (°C)	Yield (%)	Carbon	Hydrogen	Nitrogen
(1)	[H_2-anthacac]($C_{19}H_{18}N_2O_4$) (338.163)	Yellowish Brown	102	80	67.45 (67.42)	5.40 (5.36)	8.19 (8.28)
(2)	[H_2-anthdibm]($C_{29}H_{22}N_2O_4$) (462.205)	Yellowish Brown	97	78	75.35 (75.29)	4.78 (4.80)	6.10 (6.05)
(3)	[H_2-2-amtpacac]($C_{17}H_{18}N_2S_2$) (314.161)	Yellow	100	81	64.90 (64.94)	5.80 (5.77)	8.85 (8.91)
(4)	[H_2-2-amtpdibm] ($C_{27}H_{22}N_2S_2$) (438.203)	Yellow	89	74	73.87 (73.94)	5.10 (5.06)	6.45 (6.39)
(5)	[RuCl(anthacac)(PPh_3)] ($C_{37}H_{31}N_2O_4RuPCl$) (734.805)	Green	120	66	60.70 (60.42)	4.30 (4.25)	3.90 (3.81)
(6)	[RuCl(anthacac)($AsPh_3$)] ($C_{37}H_{31}N_2O_4RuAsCl$) (778.715)	Brown	150	63	57.10 (57.02)	4.10 (4.01)	3.57 (3.59)
(7)	[RuBr(anthacac)($AsPh_3$)] ($C_{37}H_{31}N_2O_4RuAsBr$) (822.275)	Green	112	60	54.12 (54.00)	3.78 (3.80)	3.43 (3.40)
(8)	[RuBr(anthacac)(PPh_3)] ($C_{37}H_{31}N_2O_4RuPBr$) (778.355)	Green	110	68	57.10 (57.04)	4.12 (4.01)	3.62 (3.59)
(9)	[RuCl(anthdibm)(PPh_3)] ($C_{47}H_{35}N_2O_4RuPCl$) (859.176)	Green	118	67	66.01 (65.68)	4.20 (4.16)	3.30 (3.25)
(10)	[RuCl(anthdibm)($AsPh_3$)] ($C_{47}H_{35}N_2O_4RuAsCl$) (903.096)	Brown	122	65	63.10 (62.49)	4.00 (3.90)	3.15 (3.10)

(**11**)	[RuBr(anthdibm)(AsPh$_3$)] ($C_{47}H_{35}N_2O_4RuAsBr$) (946.646)	Brown	147	70	60.01 (59.61)	3.75 (3.73)	3.01 (2.96)
(**12**)	[RuBr(anthdibm)(PPh$_3$)] ($C_{47}H_{35}N_2O_4RuPBr$) (902.726)	Brown	110	61	62.73 (62.52)	4.01 (3.90)	3.13 (3.10)
(**13**)	[RuCl(2-amtpacac)(PPh$_3$)] ($C_{35}H_{31}N_2S_2RuPCl$) (710.923)	Brown	124	64	60.01 (60.08)	4.43 (4.40)	4.02 (3.90)
(**14**)	[RuCl(2-amtpacac)(AsPh$_3$)] ($C_{35}H_{31}N_2S_2RuAsCl$) (754.843)	Green	129	65	55.80 (55.65)	4.19 (4.14)	3.80 (3.71)
(**15**)	[RuBr(2-amtpacac)(AsPh$_3$)] ($C_{35}H_{31}N_2S_2RuAsBr$) (798.383)	Brown	137	68	52.90 (52.61)	3.98 (3.91)	3.62 (3.51)
(**16**)	[RuBr(2-amtpacac)(PPh$_3$)] ($C_{35}H_{31}N_2S_2RuPBr$) (754.463)	Brown	120	62	55.77 (55.67)	4.20 (4.14)	3.77 (3.71)
(**17**)	[RuCl(2-amtpdibm)(PPh$_3$)] ($C_{45}H_{35}N_2S_2RuPCl$) (834.905)	Brown	118	64	65.01 (64.68)	4.31 (4.22)	3.50 (3.35)
(**18**)	[RuCl(2-amtpdibm)(AsPh$_3$)] ($C_{45}H_{35}N_2S_2RuAsCl$) (878.955)	Brown	130	62	61.79 (61.44)	4.17 (4.01)	3.30 (3.18)
(**19**)	[RuBr(2-amtpdibm)(AsPh$_3$)] ($C_{45}H_{35}N_2S_2RuAsBr$) (922.435)	Brown	126	60	59.01 (58.55)	3.90 (3.82)	3.10 (3.03)
(**20**)	[RuBr(2-amtpdibm)(PPh$_3$)] ($C_{45}H_{35}N_2S_2RuPBr$) (878.515)	Brown	118	62	61.50 (61.47)	4.10 (4.01)	3.20 (3.12)

dibenzoylmethane (5.55 g, 0.025 mol)] with anthranilic acid (6.85 g, 0.050 mol) or 2-aminothiophenol (5.34 mL, 0.050 mol) in 1:2 molar ratio in ethyl alcohol (25 mL). The solution was heated under reflux for 7 h and then concentrated to 5 mL. On cooling the solutions, the products separated out. The crude products were purified by column chromatography on silica gel using petroleum ether/ethyl acetate (95/5%) as eluant. The purity of the compounds was checked by TLC. They were dried under vacuum.

Characterisation of the Schiff Bases

The Schiff bases namely, H_2-anthacac, H_2-anthdibm, H_2-2-amtpacac and H_2-2-amtpdipm, have been characterised on the basis of elemental analyses and IR spectra. The elemental analyses (Table I) agree very well with the molecular formulas.

The IR spectra of all the Schiff bases showed a strong band in the region 1620–1590 cm^{-1} characteristic of the azomethine $\nu(C{=}N)$[27]. The Schiff bases H_2-anthacac and H_2-anthdibm showed the $\nu(OH)$ stretching frequency in the region 3500–3300 cm^{-1} and a strong band around 1670 cm^{-1} due to $\nu(C{=}O)$[26]. The Schiff bases H_2-2-amtpacac and H_2-2-amtpdibm showed a weak absorption band in the region 2600–2500 cm^{-1} due to $\nu(SH)$.

Preparation of the Complexes

All the preparations were carried out under strictly anhydrous conditions. The Schiff bases (0.012–0.026 g, 0.01 mmol) were added to a solution of $[RuX_3(EPh_3)_3]$ (0.10–0.13 g, 0.01 mmol) (where $E = P$, $X = Cl$; $E = As$, $X = Cl$, Br) or $[RuBr_3(PPh_3)_2(MeOH)]$ (0.09 g, 0.01 mmol) in 1:1 molar ratio in benzene (20 mL) and the mixtures were refluxed for 5 h. The dark coloured solutions obtained were concentrated to about 3 mL. The complexes were precipitated by the addition of a small quantity of petroleum ether (60–80 °C). The complexes were then filtered, washed with petroleum ether and recrystallised from CH_2Cl_2/petroleum ether (1:4 v/v) and dried under vacuum. All of the complexes were prepared using the above procedure.

Experimental Procedure for Antibacterial Activity Studies

The nutrient agar (NA) medium was prepared by adding 3 g of beef extract to 5 g of peptone. Then 5 g of sodium hydroxide was added to the solution and stirred well to get a clear solution. The resulting solution was made up to 1000 mL by adding distilled water and 15 g of agar was added to it. The required pH was adjusted to 7.0 by adding sufficient acid or base. A quantity of 10 mL of the medium was poured into the sterilised Petri plates and allowed to solidify. The plates were inoculated with spore suspensions of *Eenterobacteria feacalis* and *Aeromonas hydrophilla*. By using a sterilised cork borer (9 cm diameter), wells were dug in the centre of the culture plates. The test complex solutions in DMF were added (0.5 mL) to these wells, and the plates were incubated at 35 °C for 24 h. Then, the inhibition zone appearing around the wells in each plate was measured and recorded as the cytotoxic effect of the appropriate complexes. A solvent only treated plate was maintained separately in order to avoid the activity due to solvent if any.

RESULTS AND DISCUSSION

The tetradentate Schiff bases react with the ruthenium(III) complexes of the type of $[RuX_3(EPh_3)_3]$ (X = Cl, E = P; X = Cl or Br, E = As) or $[RuBr_3(PPh_3)_2(MeOH)]$ to yield complexes of the type $[RuX(EPh_3)(LL')]$ (X = Cl or Br; E = P or As, LL′ = dianion of the tetradentate Schiff bases). The analytical data (Table I) confirm the molecular formula arrived at for the new complexes. It has been found that the Schiff bases replace two of the phosphines/arsines and two halides from the starting complexes indicating binegative tetradentate behaviour of the Schiff bases.

IR Spectra

The IR spectra of the free Schiff base ligands have been compared with those of the complexes formed with the corresponding Schiff bases in order to confirm the coordination of the ligands to the metal atom.

The $\nu(OH)$ absorption observed around 3500–3300 cm^{-1} in the free Schiff bases H_2-anthacac and H_2-anthdibm disappeared in the corresponding complexes indicating deprotonation prior to the coordination through the oxygen atom. The $\nu(C{=}O)$ frequency of the carboxyl group was seen as a band around 1670 cm^{-1} in the free Schiff bases. In the complexes, the absorptions due to the carbonyl group were observed at around 1630–1610 cm^{-1} and around 1430–1390 cm^{-1} arising from asymmetric and symmetric stretchings, respectively. The difference between ν_{as} and ν_{sym} vibrations of the carbonyl group has been found to be around 220 cm^{-1}. This is a clear indication of the monodentate coordination of the carboxyl group with the free carbonyl group[26].

In the IR spectra of the other two Schiff bases, H_2-2-amtpacac and H_2-2-amtpdibm, the ν(SH) stretching frequency has been observed at around $2600-2500\,cm^{-1}$ which disappeared in the complexes due to the coordination through the sulphur atom. In the IR spectra of the complexes, the ν(C=N) stretching frequency was observed in the region $1595-1575\,cm^{-1}$ indicating coordination through the azomethine nitrogen[27]. In addition, the other characteristic bands due to triphenylphosphine and triphenylarsine were also present in the expected region.

Electronic Spectra

The electronic spectra of all the complexes in CH_2Cl_2 showed one to four bands in the region 660−300 nm (Table II). The ground state of Ru(III) (t_{2g}^5 configuration) is ${}^2T_{2g}$ and the first excited doublet levels in the order of increasing energy are ${}^2A_{2g}$ and ${}^2T_{1g}$ 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[25]. It has been observed that charge transfer bands of the type $L_{\pi y} \rightarrow t_{2g}$ are prominent in the low-energy region which obscure the weaker d-d transitions. Hence, it is difficult to assign conclusively the bands of ruthenium(III) complexes in the visible region. However, the bands around 660−610 nm have been assigned to the ${}^2T_{2g} \rightarrow {}^2A_{2g}$ transition based on the low extinction coefficient value (ε) as compared to charge transfer bands. This is in conformity with assignments made for other similar octahedral Ru(III) complexes[28,29]. The bands in the region 480−315 nm have been assigned to charge transfer bands (Fig. 2).

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 the metal. The redox potentials of the complexes are characterised by well-defined waves in the range 0.60 to 0.80 V (oxidation) and −0.31 to −0.74 V (reduction) versus a saturated calomel electrode. The cyclic voltammogram data are given in Table III 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 limits of +1.20 to −1.20 V, we believe that

Table II. IR Electronic Spectral Data of Ru(III) Complexes[a]

S. No.	Complex	ν(C=O) cm^{-1}		ν(C=N) cm^{-1}	λ_{max} (ε) (nm)	Assignment
		ν_{asy}	ν_{sym}			
(5)	[RuCl(anthacac)(PPh$_3$)]	1620 s	1400 s	1590 vs	400 (2010)	Charge transfer
(6)	[RuCl(anthacac)(AsPh$_3$)]	1630 s	1410 s	1580 vs	350 (2925), 400 (2540), 475 (2110), 600 (930)	Charge transfer $^2T_{2g} \rightarrow {}^2A_{2g}$
(7)	[RuBr(anthacac)(AsPh$_3$)]	1630 s	1390 s	1580 vs	300 (3175), 450 (1780)	Charge transfer
(8)	[RuBr(anthacac)(PPh$_3$)]	1630 s	1410 s	1585 vs	450 (2730) 600 (1020)	Charge transfer $^2T_{2g} \rightarrow^2 A_{2g}$
(9)	[RuCl(anthdibm)(PPh$_3$)]	1620 s	1400 s	1580 vs	340 (4172), 470 (2371) 655 (1132)	Charge transfer $^2T_{2g} \rightarrow {}^2A_{2g}$
(10)	[RuCl(anthdibm)(AsPh$_3$)]	1615 s	1390 s	1590 vs	435 (3174)	Charge transfer
(11)	[RuBr(anthdibm)(AsPh$_3$)]	1610 s	1400 s	1590 vs	393 (5124) 650 (1117)	Charge transfer $^2T_{2g} \rightarrow {}^2A_{2g}$
(12)	[RuBr(anthdibm)(PPh$_3$)]	1630 s	1410 s	1580 vs	420 (2317)	Charge transfer
(13)	[RuCl(2-amtpacac)(PPh$_3$)]	–	–	1590 vs	375 (4119)	Charge transfer
(14)	[RuCl(2-amtpacac)(AsPh$_3$)]	–	–	1590 vs	315 (6173), 480 (3201)	Charge transfer
(15)	[RuBr(2-amtpacac)(AsPh$_3$)]	–	–	1590 vs	320 (5441), 475 (3124)	Charge transfer
(16)	[RuBr(2-amtpdibm)(PPh$_3$)]	–	–	1590 vs	400 (4234)	Charge transfer
(17)	[RuCl(2-amtpdibm)(PPh$_3$)]	–	–	1590 vs	330 (4987)	Charge transfer
(18)	[RuCl(2-amtpdibm)(AsPh$_3$)]	–	–	1585 vs	350 (5417), 432 (3318)	Charge transfer
(19)	[RuBr(2-amtpdibm)(AsPh$_3$)]	–	–	1585 vs	375 (5519)	Charge transfer
(20)	[RuBr(2-amtpdibm)(PPh$_3$)]	–	–	1585 vs	360 (6114), 465(4918) 610 (1020)	Charge transfer $^2T_{2g} \rightarrow {}^2A_{2g}$

[a] ε in dm^3 mol^{-1} cm^{-1}; s-strong; vs-very strong.

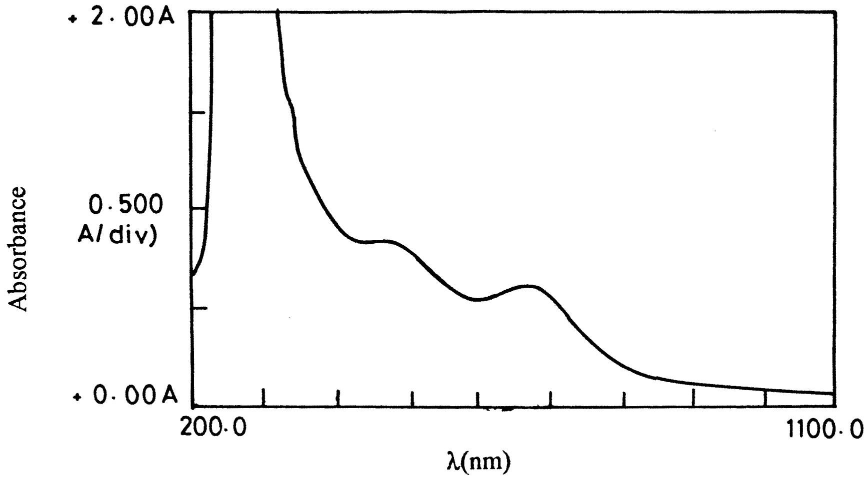


Figure 2. Electronic spectrum of [RuCl(anthdibm)(PPh$_3$)] in dichloromethane.

the redox processes observed for these complexes are metal-centered only. Although the ruthenium(III) complexes (**12**) and (**16**) showed only oxidation potentials, the ruthenium(III) complexes (**8**) and (**10**) showed only reduction potentials. The reason for the irreversibility observed for these complexes may be due to short-lived oxidation states of the metal ion[30] or due to oxidative degradation[31] of the ligands. The complex (**7**) showed lesser positive (0.69 V) and lesser negative potentials (–0.74 V) when compared to complex (**18**) (0.80 V and –0.31 V). For the complex (**18**) the reduction potential value indicates that the reduction takes place more easily than for the corresponding reduction in the complex (**7**). This is due to the increased donor ability of the sulphur atom in complex (**18**) compared to the oxygen donor atom in complex (**7**). A similar behaviour is shown in the oxidation potentials found for these two complexes. Nearly the same pattern is observed in the oxidation reduction potentials of complex (**7**) when it is compared to complex (**19**). The higher donor ability of the arsine ligand compared to the phosphine ligand has been demonstrated by a reduction potential of –0.74 V for the arsine complex (**7**) compared to a reduction potential of –0.32 V for the phosphine complex (**8**). However, other complexes showed both oxidation and reduction with peak-to-peak separation (ΔEp) values ranging from 60 mV to 100 mV suggesting a single step, one-electron transfer process[24,32]. The oxidation response for the complexes (**14**), (**19**) and (**20**) are irreversible at 50 mV s^{-1}.

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

		Ru(IV)-Ru(III)				Ru(III)-Ru(II)			
S. No.	Complex	Ep_a(V)	Ep_c(V)	E_f(V)	ΔE_p(mV)	Ep_a(V)	Ep_c(V)	E_f(V)	ΔE_p(mV)
(**7**)	[RuBr(anthacac)($AsPh_3$)]	0.69	0.60	0.65	90	−0.74	−0.66	−0.70	80
(**8**)	[RuBr(anthacac)(PPh_3)]	–	–	–	–	−0.32	−0.40	−0.36	80
(**10**)	[RuCl(anthdibm)($AsPh_3$)]	–	–	–	–	−0.37	−0.44	−0.41	70
(**12**)	[RuBr(anthdibm)(PPh_3)]	0.72	0.64	0.68	80	–	–	–	–
(**14**)	[RuCl(2-amtpacac)($AsPh_3$)]	–	0.68	–	–	−0.54	−0.46	−0.50	80
(**15**)	[RuBrCl(2-amtpacac)($AsPh_3$)]	0.71	0.64	0.68	70	−0.49	−0.57	−0.53	80
(**16**)	[RuBr(2-amtpacac)(PPh_3)]	0.68	0.60	0.64	80	–	–	–	–
(**18**)	[RuCl(2-amtpdibm)($AsPh_3$)]	0.80	0.70	0.75	100	−0.31	−0.38	−0.35	70
(**19**)	[RuBr(2-amtpdibm)($AsPh_3$)]	0.78	–	–	–	−0.34	−0.42	−0.38	80
(**20**)	[RuBr(2-amtpdibm)(PPh_3)]	0.75	–	–	–	−0.36	−0.42	−0.39	60

[a] Solvent: acetonitrile; supporting electrolyte [0.05 M] TEAP; concentration of the metal complex: 0.001 M; scan rate 50 mV s^{-1}; all potentials are referenced to saturated calomel electrode (SCE).

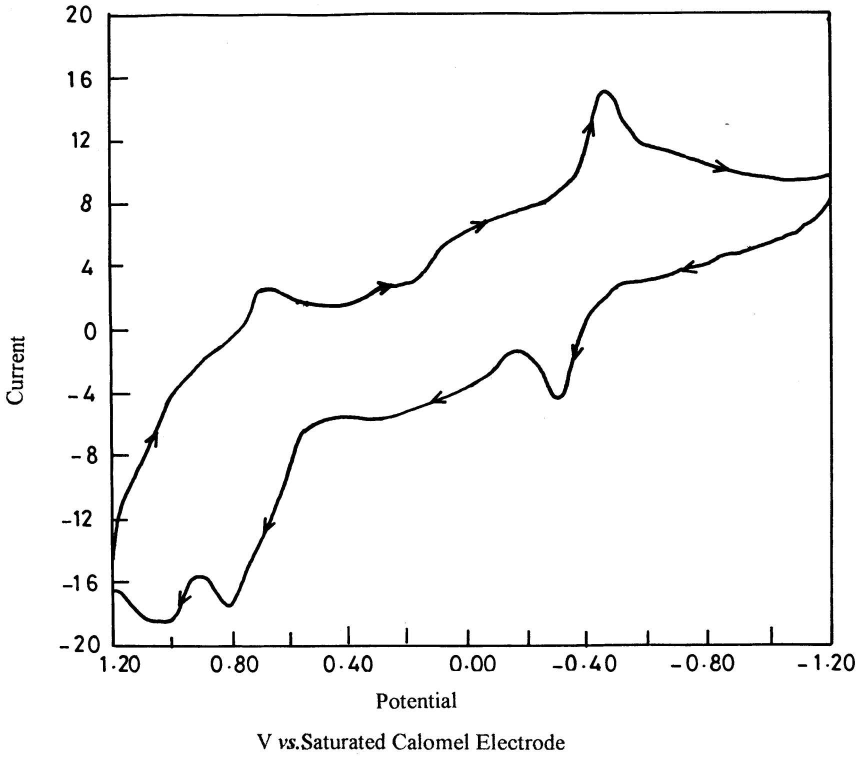


Figure 3. Cyclic voltammogram of [RuCl(2-amtpdibm)($AsPh_3$)] in acetonitrile at a glassy carbon electrode.

EPR Spectra

EPR spectra of powdered samples were recorded at room temperature. The complexes showed no indication for any hyperfine interaction of nuclei with magnetic moments *viz.*, Ru, As, P, Cl and Br. All of the complexes exhibit a single isotropic resonances with 'g' values in the range 2.10–2.40 (Fig. 4). Such isotropic lines are usually observed either due to the intermolecular spin exchange which can broaden the lines or due to occupancy of the unpaired electron in a degenerate orbital. However, similar chloro complexes[28] showed a single line due to the presence of one unpaired electron in a low-spin state with a degenerate d_{xz}, d_{yz} ground state indicating Jahn-Teller instability[28] resulting in an averaged single 'g' values. The position of the lines and the nature of the EPR spectra of all the complexes

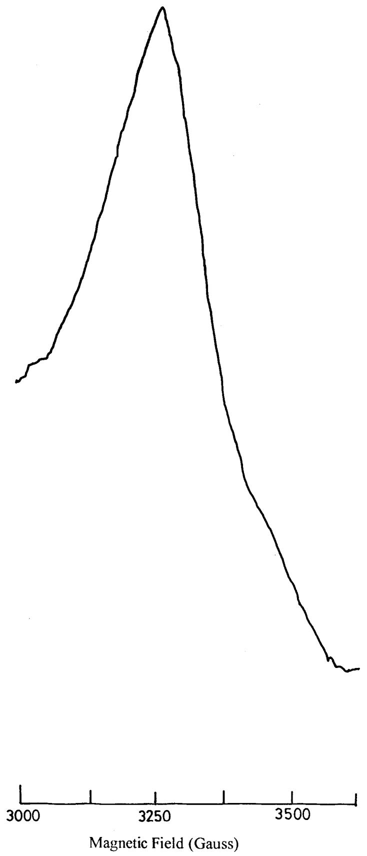


Figure 4. EPR spectrum of [RuCl(anthdibm)(PPh_3)].

suggest an almost perfect octahedral environment around the ruthenium ion in the complexes[28,33].

Magnetic Moment Studies

The magnetic moments for some of the complexes have been measured at room temperature using a vibrating sample magnetometer and diamagnetic corrections have been applied. The values obtained range from 1.74 to 1.81 BM indicating the presence of one unpaired electron, suggesting a low-spin t_{2g}^5 configuration for the ruthenium(III) ion in an octahedral environment in all these complexes.

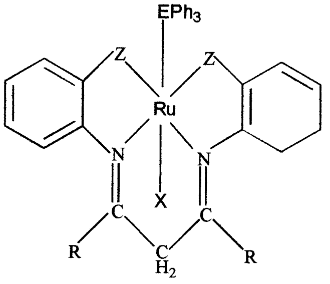
Antibacterial Activity Studies

The *in vitro* antibacterial screening of the ligands H_2-anthacac, H_2-anthdibm and H_2-2-amtpdibm and their ruthenium complexes have been carried out against *Eenterobacteria feacalis* and *Aeromonas hydrophilla* using a nutrient agar (NA) medium by the agar-well diffusion method[34] (incubation period 18–24 h at 35 °C). The test solutions were prepared in DMF. Among the complexes and ligands tested, the ligand H_2-2-amtpdibm and the complexes [RuCl(2-amtpdibm)($AsPh_3$)] and [RuBr(2-amtpdibm)($AsPh_3$)] have been found to be more toxic against both species of bacteria than the other ligands and complexes under similar conditions. The increased activity of these compounds may possibly be due to the presence of a sulphur atom. It has also been observed from the antibacterial screening studies that the ruthenium chelates have higher activity than the corresponding free ligands against the same microorganism under identical experimental conditions (Table IV), which is consistent with earlier reports[35]. 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[36–38], according to which chelation reduces the polarity of the central metal atom because of partial sharing of its positive charge with the ligand which

Table IV. Antibacterial Activity Data of Ligand and Ru(III) Schiff Base Complexes

		Diameter of Minimum Inhibition Zone (mm)[a]			
		Eenterobacteria feacalis		*Aeromonas hydrophilla*	
S. No.	Compound	1%	2%	1%	2%
	(H_2-anthacac)	9	12	14	16
(**5**)	[RuCl(anthacac)(PPh_3)]	16	20	20	24
(**6**)	[RuCl(anthacac)($AsPh_3$)]	17	22	21	26
	(H_2-anthdibm)	12	14	15	18
(**11**)	[RuBr(anthdibm)($AsPh_3$)]	17	18	19	23
(**12**)	[RuBr(anthdibm)(PPh_3)]	20	22	21	26
	(H_2-2-amtpdibm)	19	21	20	22
(**18**)	[RuCl(2-amtpdibm)($AsPh_3$)]	26	29	27	29
(**19**)	[RuBr(2-amtpdibm)($AsPh_3$)]	30	32	31	34

[a] 1% and 2% indicate 1 g and 2 g of the compound in 100 mL of test solution.



Complex No.	X	E	R	Z
(5)	Cl	P	CH_3	COO^-
(6)	Cl	As	CH_3	COO^-
(7)	Br	As	CH_3	COO^-
(8)	Br	P	CH_3	COO^-
(9)	Cl	P	C_6H_5	COO^-
(10)	Cl	As	C_6H_5	COO^-
(11)	Br	As	C_6H_5	COO^-
(12)	Br	P	C_6H_5	COO^-
(13)	Cl	P	CH_3	S^-
(14)	Cl	As	CH_3	S^-
(15)	Br	As	CH_3	S^-
(16)	Br	P	CH_3	S^-
(17)	Cl	P	C_6H_5	S^-
(18)	Cl	As	C_6H_5	S^-
(19)	Br	As	C_6H_5	S^-
(20)	Br	P	C_6H_5	S^-

Figure 5. Structure of the ruthenium(III) complexes.

favours the permeation of the complexes through the lipid layer of cell membranes. Furthermore, the mode of action of the compounds may involve the formation of hydrogen bonds through the azomethine ($>C{=}N$) group of the complexes with the active centres of cell constituents resulting in the interference with normal cell processes[39].

Suggested Structure

Based on the elemental analyses, IR, electronic and EPR spectral and electrochemical data, the octahedral structure shown in Figure 5 has been tentatively proposed for all of the ruthenium(III) Schiff base complexes of the present study.

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