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RUTHENIUM(III) COMPLEXES CONTAINING MONOFUNCTIONAL BIDENTATE SCHIFF BASES

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ABSTRACT

Several new hexa-coordinated ruthenium(III) complexes of the type $[RuX_2(EPh_3)_2(L)]$ (X = Cl, Br; E – P, As; LH = *o*-vanillideneaniline, *o*-vanillidene-*o*-toluidine, *o*-vanillidene-*m*-toluidine and *o*-vanillidene-*p*-toluidine) have been prepared by reacting $[RuX_3(EPh_3)_3]$ or $[RuBr_3(EPh_3)_2(MeOH)]$ (X = Cl, Br; E = P, As) with Schiff bases derived from the condensation of *o*-vanillin with aniline, *o*-toluidine, *m*-toluidine or *p*-toluidine in benzene in the presence of triethylamine. In all of the reactions the Schiff bases behave as monobasic bidentate ligands. The new complexes have been characterised on the basis of elemental analyses, spectral (IR, electronic, EPR) and cyclic voltammetric studies. An octahedral structure has been tentatively proposed for all of the new complexes. The Schiff bases and the new complexes have been tested *in vitro* against the pathogenic fungi *Aspergillus niger* and *Fusarium Sp*.

INTRODUCTION

The chemistry of the complexes of ruthenium(II) and ruthenium(III) containing strong donor ligands such as tertiary phosphines and arsines is very important due to the catalytic activity of these compounds.¹⁻⁵ There has also been considerable interest in the chemistry of metal complexes containing ligands with O, N; O, S; N, S and S, S donor

atoms owing to their industrial importance and carcinostatic, antitumour, antiviral and antifungal activities.⁶⁻⁹ Although, there is a wealth of information available on transition metal complexes of Schiff bases, it is largely confined to first-row transition metals, notably iron, cobalt and nickel.^{10,11} Only very little attention has been given to the corresponding Schiff base complexes of ruthenium.¹²⁻¹⁹ In view of the growing interest in the biological and catalytic activities of ruthenium complexes, we reported in earlier communications the synthesis and characterisation of several new hexa-coordinated ruthenium(II) and ruthenium(III) complexes of tetradentate Schiff bases.²⁰⁻²² In continuation of our systematic investigation on the substitutions of ruthenium(III) complexes and on their biological activities, we report in this communication the synthesis, characterisation and antifungal activities of ruthenium(III) complexes containing the bidentate Schiff bases shown in Fig. 1.

EXPERIMENTAL

Commercially available RuCl₃.3H₂O was used without further purifications. All of the reagents used were of Analar or chemically pure grade. Solvents were purified and dried according to standard procedures.²³ Carbon, hydrogen and nitrogen were analysed on a PE 240C model elemental analyser. Infrared spectra were recorded as KBr pellets using a Perkin-Elmer spectrophotometer in the range 4000 - 200 cm⁻¹. Electronic spectra of the complexes were recorded in dichloromethane solutions using a Hitachi Perkin-Elmer 20/200 recording spectrometer in the 800 - 200 nm range. EPR spectra of powdered samples were recorded on a Bruker ER-200D-SRC instrument at X-band frequencies at room temperature. Cyclic voltammetric studies were carried out with a BAS CV-27 cyclic voltammeter in acetonitrile using a glassy-carbon working electrode. A platinum wire and saturated calomel electrode were used as counter and reference electrodes, respectively. All the melting points were recorded with a Boetius microheating table and are uncorrected.

The starting complexes $[RuCl_3(PPh_3)_3]$,²⁴ $[RuCl_3(AsPh_3)_3]$,²⁵ $[RuBr_3(AsPh_3)_3]$ ²⁶ and $[RuBr_3(PPh_3)_2(MeOH)]$ ²⁷ were prepared according to the reported procedure.

Preparation of the Schiff Bases

To an ethanolic solution (15 mL) of an appropriate amine (aniline, o-toluidine, *m*-toluidine or *p*-toluidine; 0.09-0.10 g; 0.1 mmol), a solution of o-



Fig. 1. Structure of the Ligands

vanillin (0.15 g; 0.1 mmol) in 15 mL of freshly distilled ethanol was added dropwise with vigorous stirring. The mixture was then refluxed for half an hour, cooled in ice and the product formed was filtered and recrystallised from ethanol and dried *in vacuo*. The analytical and IR data (Table I and II) confirm the molecular formula for the new Schiff base ligands.

Preparation of New Ruthenium(III) Complexes

All of the new complexes were prepared by the following general procedure. To a solution of $[RuX_3(EPh_3)_3]$ (X = Cl. Br; E = P, As) or $[RuBr_3(PPh_3)_2(MeOH)]$ (0.1 g; 0.08-0.11 mmol) in benzene (25 mL), the appropriate Schiff base (0.018-0.026 g; 0.08-0.11 mmol) was added. To this mixture a few drops of triethylamine were added and the mixture was refluxed for 5 h. The precipitated triethylaminehydrochloride was removed by filtration and the resulting solution was concentrated to 3 mL and cooled at room temperature. Light petroleum (60-80 °C) (5 mL) was then added, whereupon the product separated out. The product was filtered off, washed with light petroleum and recrystallised from CH₂Cl₂/light petroleum (60-80 °C) and dried *in vacuo*. Yields : 60 - 75 %

Complex	Yield %	M.P. °C	Elemental analysis % Found (calc.)		
			С	нÌ	Ń
H-o-val-aniline (C ₁₄ H ₁₃ NO ₂) (227.24)	80	40	73.53 (73.99)	5.57 (5.76)	6.16 (6.02)
H-0-val-0-toldn (C15H15NO2) (241.27)	75	50	74.45 (74.66)	6.08 (6.26)	5.65 5.80
H-o-val-m-toldn (C15H15NO2) (241.27)	72	44	74.52 (74.66)	6.18 (6.26)	5.60 5.80
H-o-val-p-toldn (C15H15NO2) (241.27)	75	98	74.60 (74.66)	6.15 (6.26)	5.70 5.80
[RuCl ₂ (PPh ₃) ₂ (o-val-aniline)] (C ₅₀ H ₄₂ NO ₂ P ₂ Cl ₂ Ru) (922.83)	75	112	64.91 (65.07)	4.32 (4.58)	1.48 (1.51)
$[RuCl_{2}(AsPh_{3})_{2}(o-val-aniline)] \\ (C_{50}H_{42}NO_{2}As_{2}Cl_{2}Ru) (1010.70)$	73	90	59.26 (59.41)	4.07 (4.18)	1.43 (1.38)
[RuBr ₂ (AsPh ₃) ₂ (o-val-aniline)] (C ₅₀ H ₄₂ NO ₂ As ₂ Br ₂ Ru) (1099.60)	70	95	54.79 (54.61)	3.75 (3.84)	1.08 (1.27)
[RuBr ₂ (PPh ₃) ₂ (o-val-aniline)] (C ₅₀ H ₄₂ NO ₂ P ₂ Br ₂ Ru) (1011.71)	64	97	59.17 (59.35)	4.24 (4.18)	1.18 (1.38)
[RuCl ₂ (PPh ₃) ₂ (o-val-o-toldn)] (C ₅₁ H ₄₄ NO ₂ P ₂ Cl ₂ Ru) (936.83)	75	89	65.25 (65.38)	4.65 (4.73)	1.51 (1.49)
$[RuCl_{2}(AsPh_{3})_{2}(o-val-o-toldn)]$ (C ₅₁ H ₄₄ NO ₂ As ₂ Cl ₂ Ru) (1024.73)	70	90	59.40 (59.77)	4.29 (4.32)	1.24 (1.36)
$[RuBr_{2}(AsPh_{3})_{2}(o-val-o-toldn)]$ (C ₅₁ H ₄₄ NO ₂ As ₂ Br ₂ Ru) (1113.63)	72	85	55.18 (55.00)	3.71 (3.98)	1.32 (1.25)
[RuBr ₂ (PPh ₃) ₂ (o-val-o-toldn)] (C ₅₁ H ₄₄ NO ₂ P ₂ Br ₂ Ru) (1024.51)	62	75	59.53 (59.79)	4.39 (4.32)	1.22 (1.36)
$[RuCl_{2}(PPh_{3})_{2}(o-val-m-toldn)] \\ (C_{51}H_{44}NO_{2}P_{2}Cl_{2}Ru) (936.83)$	70	92	65.16 (65.38)	4.59 (4.73)	1.56 (1.49)
$[RuCl_{2}(AsPh_{3})_{2}(o-val-m-toldn)] \\ (C_{51}H_{44}NO_{2}As_{2}Cl_{2}Ru) (1024.73)$	72	90	59.51 (59.77)	4.55 (4.32)	1.28 (1.36)
$ \begin{array}{ } [RuBr_2(AsPh_3)_2(o\text{-val-m-toldn})] \\ (C_{51}H_{44}NO_2As_2Br_2Ru) (1113.63) \end{array} $	68	96	55.23 (55.00)	3.83 (3.98)	1.12 (1.25)
$[RuBr_2(PPh_3)_2(o-val-m-toldn)] (C_{51}H_{44}NO_2P_2Br_2Ru) (1024.51)$	60	91	59.67 (59.79)	4.18 (4.32)	1.40 (1.36)

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

Table I. Continued					
$[RuCl_2(PPh_3)_2(o-val-p-toldn)]$	74	95	65.13	4.56	1.58
$(C_{51}H_{44}NO_2P_2C_1R_u)$ (936.83)			(65.38)	(4.73)	(1.49)
$[\operatorname{RuCl}_2(\operatorname{AsPh}_3)_2(o\operatorname{-val}_p\operatorname{-toldn})]$	70	110	59.51	4.45	1.38
$(C_{51}H_{44}NO_2AS_2Cl_2Ru)$ (1024.73)			(59.77)	(4.32)	(1.30)
$\begin{bmatrix} [RuBr_2(AsPh_3)_2(o-val-p-toldn)] \\ (C_1U_1) \\ (C_2U_2) \\ (D_1) \\ (D_2) \\ $	70	90	54.87	3.82	1.36
(C31H44NO2AS2BI2RU) (1113.03)			(55.00)	(3.76)	(1.25)
$[\operatorname{RuBr}_2(\operatorname{PPh}_3)_2(o\operatorname{-val}-p\operatorname{-toldn})]$	65	98	59.54	4.15	1.17
$(C_{51}\Pi_{44}NO_{2}r_{2}Dr_{2}Ru)(1024.51)$			(39.79)	(4.32)	(1.30)

Table II. Spectroscopic Data of the Ligands and their Ru(III) Complexes

Compound	v(C = N)	v(C-O)	v(O – H)	λ _{max} (ε)	
H-o-val-aniline	1620 vs	1260 s	3320 s	-	
H-o-val-o-toldn	1620 vs	1255 s	3320 s	-	
H-o-val-m-toldn	1620 vs	1260 s	3320 s		
H-o-val-p-toldn	1630 vs	1270 s	3315 s	<u>.</u>	
[RuCl ₂ (PPh ₃) ₂ (o-val-aniline)]	15 8 6 vs	1306 s	-	670 (935), 364 (1856), 272 (3658)	
[RuCl2(AsPh3)2(0-val-aniline)]	1578 vs	1311 s	-	680 (945), 370 (1908), 320 (3780)	
[RuBr2(AsPh3)2(0-val-aniline)]	1585 vs	1313 s	-	675 (1090), 370 (4320), 330 (4518)	
[RuBr2(PPh3)2(o-val-aniline)]	1580 vs	1310 s	-	690 (980), 380 (2154), 320 (3925)	
[RuCl2(PPh3)2(0-val-o-toldn)]	1594 vs	1310 s	-	670 (1076), 375 (1985), 325 (4097)	
[RuCl2(AsPh3)2(0-val-0-toldn)]	1603 vs	1311 s	-	665 (1238), 380 (1976), 330 (4136)	
[RuBr2(AsPh3)2(0-val-0-toldn)]	1604 vs	1311 s	-	680 (1014), 390 (1987), 330 (3995)	
[RuBr2(PPh3)2(0-val-0-toldn)]	1586 vs	1307 s	-	648 (1120), 392 (1992)	
[RuCl ₂ (PPh ₃) ₂ (o-val-m-toldn)]	1590 vs	1310 s	-	680 (955), 390 (2128), 330 (3945)	
[RuCl ₂ (AsPh ₃) ₂ (o-val-m-toldn)]	1594 vs	1310 s	-	670 (1405), 385 (1850), 325 (4816)	
[RuBr ₂ (AsPh ₃) ₂ (o-val-m-toldn)]	1590 vs	1310 s	-	670 (1416), 380 (1845), 325 (4927)	
[RuBr2(PPh3)2(o-val-m-toldn)]	1595 vs	1312 s	-	680 (973), 380 (1956), 330 (3988)	
[RuCl2(PPh3)2(o-val-p-toldn)]	1585 vs	1310 s	-	620 (940), 380 (1850), 335 (4008)	
[RuCl2(AsPh3)2(0-val-p-toldn)]	1579 vs	131 1 s	-	670 (920), 385 (1836), 325 (3635)	
[RuBr2(AsPh3)2(0-val-p-toldn)]	1599 vs	1312 s	-	675 (1083), 380 (1970), 325 (4078)	
[RuBr2(PPh3)2(0-val-p-toldn)]	1584 vs	1312 s	-	665 (1225), 375 (1975), 320 (3915)	

v in cm⁻¹; λ_{max} in nm; ε in dm³ mol⁻¹ cm⁻¹; vs - very strong; s - strong.

RESULTS AND DISCUSSION

Stable ruthenium(III) complexes of the general formula $[RuX_2(EPh_3)_2(L)]$ (X = Cl, Br; E = P, As; LH = bidentate Schiff bases derived from the condensation of *o*-vanillin with aniline, *o*-toluidine, *m*-toluidine or *p*-toluidine) were obtained from the reactions of $[RuX_3(EPh_3)_3]$ or $[RuBr_3(PPh_3)_2(MeOH)]$ with the respective Schiff bases in 1 : 1 molar ratio in benzene in the presence of triethylamine as shown below in Fig. 2.



 $(R = C_6H_5, 2-CH_3C_6H_4, 3-CH_3C_6H_4 \text{ and } 4-CH_3C_6H_4; X = Cl, Br; E = P, As)$

Fig. 2. Formation of the New Ruthenium(III) Complexes

All the complexes are green in colour and stable to air and light. The analytical data obtained for the new complexes (Table I) agree very well with the proposed molecular formula. In all of the above reactions, the Schiff bases behave as uninegative bidentate ligands by replacing a molecule of triphenylphosphine or triphenylarsine or methanol and a chloride or bromide ion, from the starting complexes.

IR Spectra

The IR spectra of the free Schiff bases were compared with those of the ruthenium complexes to study the binding mode of the Schiff base ligands to ruthenium metal ion in the complexes. A band at 1620 cm⁻¹ is observed in the free Schiff bases, which is characteristic of the azomethine (>C=N) group. If the nitrogen atom from the azomethine group of the Schiff bases coordinates to the metal ion, there should be a reduction in electron density in the azomethine link leading to lowering of the >C=N frequency. In the Schiff base complexes, this band is slightly shifted to the lower frequency side and is observed at 1580-1605 cm⁻¹. This clearly indicates the coordination of the Schiff bases through the azomethine nitrogen.^{28,29} A high-intensity band around 1255-1270 cm⁻¹ in the Schiff bases is due to the phenolic C-O stretching. In the complexes the C-O stretching vibrations appear at a slightly higher value, at 1305-1315 cm⁻¹, confirming the other coordination through the phenolic oxygen atom.^{28,30} This is further supported by the disappearance of the broad v(O-H) band in the 3315-3320 cm⁻¹ region in the complexes. In addition to the above absorptions, other characteristic bands due to triphenylphosphine and arsine were also present in the spectra of the ruthenium complexes.

Electronic Spectra

The ground state of ruthenium(III) is ${}^{2}T_{2g}$ and the first excited doublet levels in the order of increasing energy are ${}^{2}A_{2g}$ and ${}^{2}A_{1g}$ which arise from the $t_{2g}{}^{4}$ $e_{g}{}^{1}$ configuration.³¹ In most of the ruthenium(III) complexes, the UV and visible spectra show only charge transfer bands.³² Since, in a d⁵ system and especially in ruthenium(III) which has relatively high oxidising properties, the charge transfer bands of the type $L_{\pi y} \rightarrow$ t_{2g} are prominent in the low-energy region which obscure the weaker bands due to d - d transitions. It is thus difficult to assign conclusively the bands of ruthenium(III) complexes which appear in the visible region. The electronic spectra of all the complexes in dichloromethane showed three bands in the region 800-200 nm (Table II). The bands in the region 680-645 nm have been assigned to the ${}^{2}T_{2g} \rightarrow {}^{2}A_{2g}$ transition which is in confirmity with the assignment made for similar other octahedral ruthenium(III) complexes.^{33,34} The other bands in the region 392-322 nm have been assigned to charge transfer transitions. The electronic spectra of all the complexes indicate an octahedral environment around the ruthenium(III) ion.

EPR Spectra

The room temperature solid state EPR spectra of some powdered ruthenium(III) complexes have been recorded at X-band frequencies. All of the new complexes showed a single isotropic line with g values in the range 1.76-1.94. Isotropic lines of this type are usually observed either due to the intramolecular spin exchange which can broaden the lines or owing to the occupancy of the unpaired electron in a degenerate orbital. The nature and pattern of the EPR spectra suggest an almost perfect octahedral environment around the ruthenium ion in the complexes^{33,35,36} and there is no hyperfine interactions with any other nuclei present in the complexes.

Magnetic Measurements

The magnetic susceptibility measurements have been carried out for some of the new complexes and the values lie between 1.7-1.9 B.M. These values do indicate the presence of one unpaired electron confirming a low-spin t_{2g}^{5} configuration and a +3 oxidation state for ruthenium in all of the complexes.

Cyclic Voltammetry

The redox behaviour of some of the compounds in acetonitrile has been examined at a glassy carbon working electrode using cyclic voltammetry. The results are given in Table III. The potentials of the Schiff base complexes are characterised by well-defined waves in the range 0.62 to 0.80 V (oxidation) and -0.22 to -0.53 V (reduction) *versus* a saturated calomel electrode. As the ligands are inactive at the potential range concerned (+1.0 to 1.0 V), the redox waves are assigned to the metal-centred Ru(III)-Ru(II) and Ru(IV)-Ru(III) couples. All of the complexes exhibit one reversible oxidation couple and an

RUTHENIUM(III) COMPLEXES

Complex			Ru(III)-Ru(II)		
-	$E_{pa}(V)$	$E_{pc}(V)$	E _f (V)	$\Delta E_p(mV)$	$E_{pc}(V)$
[RuCl ₂ (PPh ₃) ₂ (o-val-aniline)]	0.80	0.74	0.77	60	-0.43
[RuCl2(AsPh3)2(o-val-aniline)]	0.62	0.56	0.59	60	-0.53
[RuCl2(PPh3)2(o-val-o-toldn)]	0.68	0.62	0.65	60	-0.29
[RuBr2(AsPh3)2(o-val-o-toldn)]	0.71	0.63	0.67	80	-0.22
[RuBr2(PPh3)2(o-val-m-toldn)]	0.72	0.63	0.67	90	-0.27
[RuCl2(AsPh3)2(o-val-p-toldn)]	0.66	0.60	0.63	60	-0.25
[RuBr2(AsPh3)2(o-val-p-toldn)]	0.73	0.65	0.69	80	-0.33

Table III. Cyclic Voltammetric Data^a for some Ru(III) Complexes

^a Supporting electrolyte: [NBu₄]ClO₄ (0.05 M); concentration of the complex: 0.001 M; scan rate: 100 mV sec⁻¹; All the potentials are referenced to SCE; $E_f = 0.5(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.

irreversible reduction peak. The peak-to-peak separation (ΔEp) for the oxidation couples {Ru(IV)-Ru(III)} is found to be 60-90 mV which is characteristic of a singlestep, one-electron transfer process and that the oxidation processes are reversible. The reduction processes {Ru(III)-Ru(II)} for all the complexes exhibit irreversible cyclic voltammograms. These observations indicate that the charge transfer process for the Ru(III)-Ru(II) couple in general is not as rapid as for the Ru(IV)-Ru(III) couple. Hence, it is clear that the present ligand system is ideally suitable for stabilising the higher oxidation state of ruthenium ions.

If the two phosphines or arsines are trans to each other, they should compete for the same d orbitals of the central metal ion. Because of this trans influence³⁷, it should be possible to replace one of the phosphine or arsine by a ligand with different π -bonding ability. When the Schiff base complexes are reacted with pyridine in dichloromethane at around 70 – 80 °C, the following reaction takes place. This indicates trans-diphosphine geometry for the new ruthenium(III) Schiff base complexes.

 $[RuX_2(EPh_3)_2(L)] + py \rightarrow [RuX_2(EPh_3)(L)(py)] + EPh_3$ (X = Cl, Br; E = P, As; LH = bidendate Schiff bases)

Compound*	% of Inhibition		
	Aspergillus niger	Fusarium Sp.	
H-o-val-aniline	14	21	
[RuCl ₂ (PPh ₃) ₂ (o-val-aniline)]	27	29	
[RuBr ₂ (PPh ₃) ₂ (o-val-aniline)]	24	30	
H-o-val-m-toldn	20	18	
[RuCl ₂ (PPh ₃) ₂ (o-val-m-toldn)]	34	25	
$[RuBr_2(PPh_3)_2(o-val-m-toldn)]$	40	32	
H-o-val-p-toldn	16	19	
[RuCl ₂ (PPh ₃) ₂ (o-val- p-toidn)]	30	27	
[RuBr ₂ (PPh ₃) ₂ (o-val-p-toldn)]	32	32	

Table IV. Fungicidal Activity Data for some Ru(III) Complexes

*Concentration of the test solution is 400 µg mL⁻¹.

Biocidal Activity

The antifungal activity of some of the complexes and that of the free Schiff bases have been screened by the Agar plate technique.³⁸ Seven-day-old cultures of *Aspergillus niger* and *Fusarium* Sp. were used as test organisms which were grown on a potato-dextrose agar medium. The concentration of the complexes taken for the studies was of the order of 400 μ g mL⁻¹. The percentage inhibition was calculated as [(C-T)100]/C, where C is the average diameter of fungal growth (in cm) on the control plate and T is the average diameter of fungal growth (in cm) on the test plate.

From the fungicidal activity data (Table IV), we observed that the ruthenium(III) complexes have more toxicity against the fungus species than the free Schiff bases. This is explained by Tweedy's chelation theory,³⁹ according to which chelation reduces the polarity of the central metal atom mainly because of partial sharing of its positive charge with the ligand. Consequently, this favours the permeation of the complexes through the lipid layer of cell membrane. Furthermore, the mode of action of the compounds may involve the formation of hydrogen bonds through the azomethine (>C = N) group present in these complexes with the active centres of cell constituents of the fungi resulting in the interference with normal cell process.⁴⁰



$$(R = C_6H_5, 2-CH_3C_6H_4, 3-CH_3C_6H_4 \text{ and } 4-CH_3C_6H_4; X = Cl, Br; E = P, As)$$

Fig. 3. Proposed Structure of the Ruthenium(III) Complexes

Based on the analytical, spectroscopic data (IR, electronic, EPR), and electrochemistry, the following tentative octahedral structure has been proposed for all of the new complexes.

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