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Synthesis, Characterization, Electrochemistry, Catalytic and Biological Activities of Ruthenium(III) Complexes with Tridentate ONO Donar Schiff Base Ligands

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New hexa-coordinated ruthenium(III) complexes of the type $[RuX(EPh_3)_2(L)]$ (E = P or As: X = C1 or Br; L = dibasic tridentate Schiff base derived from the condensation of salicyloyl hydrazide with acetone, ethyl methyl ketone and salicyaldehyde) have been synthesized by the reaction of equimolar amounts of $[RuX_3(EPh)_3]$ or $[RuBr_3(PPh_3)_2(MeOH)]$ and Schiff base in benzene. The resulting complexes have been characterized by analytical, spectral (IR, electronic and EPR), magnetic moment and cyclic voltammetry. An octahedral structure has been tentatively proposed. All the complexes have exhibited catalytic activity for the oxidation of benzyl alcohol, cyclohexanol and cinnamyl alcohol in the presence of N-methylmorpholine-N-oxide as co-oxidant. All the new complexes were found to be active against bacteria such as *E. coli*, *Pseudomonas*, *Salmonella typhi* and *Staphylococcus aureus*. The activity was compared with standard streptomycin.

Key Words: Schiff base, Ru(III) Complex, Catalytic activity, Antimicrobial activity.

INTRODUCTION

Schiff bases and their metal complexes have been found to possess significant-biological activities[1]. Schiff base complexes continue to attract many researchers because of its wide application in the field of agriculture as pesticides and in medicine with their highly effective antibacterial and anticoagulant activities[2-6]. Hydrazones, simple as well as substituted ones are potential organic ligands for metals usually from the transition groups forming chelates. These compounds constitute and important class owing to their coordinating capability, analytical and industrial potentiality and biological activity[7-9].

Transition metal complexes with oxygen and nitrogen donor Schiff bases are of particular interest because of their ability to possess unusual configurations[10,11]. Schiff bases can accommodate different metal centers involving various coordination modes allowing successful synthesis of homo and hetero metallic complexes with varied stereochemistry[12]. The chemistry of ruthenium Schiff base complexes has a

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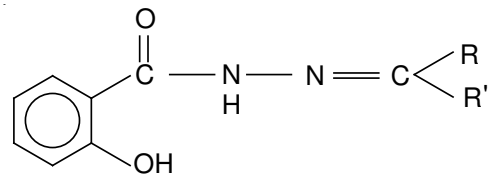
strong role in bioinorganic chemistry and redox enzyme systems[13]. Ruthenium Schiff base complexes have been used as catalysts for the oxygenation reactions, dioxygen carriers and oxygen activators[14-18] and enantioselective and asymmetric catalysis[19,20]. The chiral Ru complex catalysts for asymmetric reactions such as aziridination[21-23], Diels-Alder reactions[24] cyclopropanation[25], have received promising results. Having these all in our mind, we have interested to prepare a single complex having good catalytic and medicinal properties. Here, we describe the synthesis, spectral characterization, electrochemistry, catalytic and biological activities of ruthenium(III) Schiff base complexes containing triphenylphosphine/arsine. The general structure of Schiff base ligands used in the present work is given in Fig. 1.



R	R^1	Abbreviation
CH_3	CH_3	H_2ASH
CH_3	CH_2CH_3	H_2ESH
H	C_6H_4OH	H_2SSH

Fig. 1. Structure of the ligands

EXPERIMENTAL

All the reagents used were of analar or chemically pure grade. Solvents were purified and dried according to the standard procedures. $RuCl_3 \cdot 3H_2O$ purchased from Loba chemie, was used without further purification. The analyses of carbon, hydrogen and nitrogen were performed at the Central Drug Research Institute, Lucknow, India. IR Spectra of the complexes were recorded in KBr pellets with a Shimadzu 8000 FT-IR spectrophotometer in the 4000-400 cm^{-1} range. The electronic spectra were recorded in CH_2Cl_2 solution with Perkin-Elmer 20/200 spectrophotometer in the 800-200 nm range. EPR spectra of the powdered samples were recorded on a Bruker E-112 Varian model instrument in X-band frequencies at room temperature. Magnetic susceptibilities were recorded on EG and G-PARC vibrating sample magnetometer. The cyclic voltametric studies were carried out with BAS CV-27 model electro chemical analyzer in acetonitrile solution using a glassy carbon working electrode and the potentials were referenced to saturated calomel electrode.

Procedure: The starting complexes $[RuCl_3(PPh_3)_3]$[26], $[RuCl_3(AsPh_3)_3]$[27], $[RuBr_3(AsPh_3)_3]$[28], $[RuBr_3(PPh_3)_2(MeOH)]$[29] and the ligands[30] were prepared according to the literature procedures.

Preparation of new ruthenium(III) complexes: All the reactions were carried out under strictly anhydrous conditions. The Schiff bases (0.26-0.28 g, 0.01 mmol) were added to a solution of $[RuX_3(EPh_3)_3]$ (0.99-1.13 g; 0.01 mmol) (E = P or As, X = Cl or Br) or $[RuBr_3(PPh_3)_2(MeOH)]$ (0.98-1.12 g, 0.01 mmol) in 1:1 molar ratio in benzene (25 cm^3) and the mixture was refluxed for 6 h. The resulting dark colour solution was concentrated to about 3 cm^3. The complexes were precipitated by the addition of a small quantity of petroleum ether (60-80 °C). They were filtered, washed with petroleum ether (60-80 °C) and recrystallized from CH_2Cl_2/ petroleum ether and dried *in vacuo*.

Catalytic activity studies[31]: To a solution of alcohol (1 mmol) in CH_2Cl_2 (20 cm^3), N-methyl morpholine-N-oxide (3 mmol) and ruthenium(III) complex (0.01 mmol) were added. The solution was stirred for 3 h at room temperature. The mixture was evaporated to dryness and extracted with light petroleum (60-80 ºC). The combined light petroleum extracts were filtered and evaporated to give the corresponding aldehyde or ketone, which was then quantified as 2,4-dinitro phenylhydrazone derivative.

Antibactrial studies[32]: The ligands and their Ru(III) complexes have been tested for *in vitro* growth inhibitory activity against bacteria *Escherichia coli*, *Pseudomonas aeruginosa*, *Salmonella typhi*, *Salmonrlla typhi* and *Staphylococcus aureus*. The test organisms were grown on nutrient agar medium in Petri plates. The compounds to be tested were dissolved in DMSO to a concentration of 0.25, 0.50 and 1.00 %. They were soaked in filter paper discs of 5 mm diameter and 1 mm thickness. These discs were placed on the already seeded plates and incubated at 35 ± 2 ºC for 24 h. The diameter of the inhibition zone around each disc was measured after 24 h. Streptomycin was used as a standard.

RESULTS AND DISCUSSION

Stable ruthenium(III) complexes of general formula $[RuX(EPh_3)_2(L)]$ (E = P or As; X = C1 or Br: L = dibasic tridentate Schiff base ligands) have been prepared by the reaction of equimolar amounts of $[RuX_3(EPh_3)_3]$ or $[RuBr_3(PPh_3)_2(MeOH)]$ and Schiff base in benzene.

$$[RuX_3(EPh_3)_3] \text{ or } [RuBr_3(PPh_3)_2(MeOH)] + HL \xrightarrow[\text{Reflux, 6 h}]{\text{Benzene}} [RuX(EPh_3)_3(L)] + 2HX + EPh_3$$

All the complexes are reddish orange and soluble in common organic solvents. The analytical data obtained for the new complexes (Table-1) agree very well with the proposed molecular formulae. In all the above reactions, the Schiff bases behave as binegative tridentate ligands.

IR Spectra: The IR spectra of the free ligands were compared with those of the new complexes in order to confirm the coordination of hydrazones to the ruthenium metal. The IR spectrum of free ligands showed a band in the 1260-1270 cm^{-1} region for phenolic ν(C-O) stretching. On complexation, this band shifts to higher frequency

1320-1308 cm^{-1} indicating phenolic oxygen is coordinated to the ruthenium metal[33]. In the case of free Schiff base ligands, the absorption due to ν(C=N) appears in the 1620-1600 cm^{-1} region and this band is shifted to the lower region in the spectra of the complexes showing the coordination of the azomethine nitrogen to the meral[34]. The C=O group in the free ligands exhibits a band at 1662 cm^{-1}. This absorption has been shifted to lower frequencies (1560-1535 cm^{-1}) on complex formation, indicating a considerable change in bond order and strong metal-to-oxygen bonds[35-37]. The appearance of a new band at 1620 cm^{-1} was diagnostic for the >C=N-N=C< group indicating the transformation of the carbonyl group to its enolic form through keto-enol tautomerism and subsequent coordination of the enolic oxygen to the metal after deprotonation[38]. In addition, all the complexes show a new band at 1520 cm^{-1} characteristic of the ν(NCO) vibration[39,40].

TABLE-1
ANALYTICAL, IR (cm^{-1}), ELECTRONIC SPECTRAL DATA OF Ru(III) COMPLEXES

Complex	m.p. (ºC)	Calcd./(found.) %			ν(C=N)	ν(C-O)	ν(NCO)	T_{max}
		C	H	N				
$[RuCl(PPh_3)_2(ASH)]$	132	64.94 (64.53)	4.70 (4.64)	3.29 (3.27)	1635	1308	1537	690, 325, 240
$[RuCl(PPh_3)_2(ESH)]$	137	65.27 (65.24)	4.86 (4.79)	3.24 (3.20)	1595	1302	1533	683, 375, 247
$[RuCl(PPh_3)_2(SSH)]$	139	68.27 (68.18)	4.81 (4.84)	3.06 (3.12)	1610	1305	1550	595, 360, 246
$[RuCl(AsPh_3)_2(ASH)]$	129	59.35	4.30	3.01	1610	1310	1531	665, 246
$[RuCl(AsPh_3)_2(ESH)]$	131	59.74 (59.71)	4.44 (4.52)	2.96 (2.92)	1597	1306	1535	675, 350, 247
$[RuCl(AsPh_3)_2(SSH)]$	137	62.77 (62.79)	4.42 (4.61)	2.81 (2.90)	1633	1303	1541	690, 365, 250
$[RuBr(AsPh_3)_2(ASH)]$	130	56.67 (56.68)	4.10 (4.19)	2.87 (2.85)	1621	1310	1536	603, 370, 235
$[RuBr(AsPh_3)_2(ESH)]$	134	57.08 (57.07)	4.25 (4.21)	2.83 (2.80)	1630	1305	1530	595, 368, 230
$[RuBr(AsPh_3)_2(SSH)]$	138	60.11 (60.18)	4.28 (4.21)	2.69 (2.69)	1607	1302	1543	598, 230
$[RuBr(PPh_3)_2(ASH)]$	141	61.74	4.47	3.13	1628	1308	1530	640, 375, 236
$[RuBr(PPh_3)_2(ESH)]$	144	62.11 (62.13)	4.62 (4.59)	3.08 (3.07)	1635	1302	1537	675, 359, 246
$[RuBr(PPh_3)_2(SSH)]$	145	65.13 (65.18)	4.59 (4.50)	2.92 (2.89)	1625	1309	1548	595, 238

Electronic spectra: The electronic spectra showed two to three bands in the 230-690 nm region. The ground state of ruthenium(III) is $^2T_{2g}$ and the first excited doublet levels, in order to increasing energy are $^2A_{2g}$ and $^2T_{1g}$ which arises from $t^5{}_{2g}$ $e^1{}_g$ configuration[41]. In the most of the ruthenium(III) complexes the electronic spectra showed only charge transfer bands[42]. The band in the 690-595 nm region have been

assigned to the d-d transition, which is in conformity with assignments made for the similar ruthenium(III) complexes[43,44]. Other bands in the 375-230 nm region have been assigned to the charge transfer transitions[45]. In general the electronic spectra of the all the complexes are characteristic of an octahedral environment around ruthenium(III) ions.

Magnetic moments: The magnetic moments for some of the complexes have been measured at room temperature using a vibration sample magnetometer. The values obtained in the 1.90-1.96 BM range corresponding to one unpaired electrons, suggesting a low spin t^5_{2g} configuration for ruthenium(III) ion in pseudo-octahedral environment[46].

EPR Spectra: The room temperature spectra of powdered samples were recorded at X-band frequencies. The g values of the complexes are listed in Table-2. All the complexes showed a single isotropic resonance with a "g" value in the range 2.12-2.35 ranges. The isotropic lines of this type usually observed are either due to the intermolecular spin exchange, which may be broaden the lines or to the occupancy of the unpaired electron in the degenerate orbital. The nature and pattern of the EPR spectra suggests an almost perfect octahedral environment around the ruthenium ion in these complexes[47,48].

TABLE-2
EPR SPECTRAL DATA AND MAGNETIC MOMENTUM OF Ru(III) COMPLEXES

Complex	g_x	g_y	g_z	g^a	μ_m
$[RuCl(PPh_3)_2(ASH)]$	2.12	2.12	2.12	2.12	1.9
$[RuCl(PPh_3)_2(ESH)]$	2.15	2.15	2.15	2.15	n
$[RuCl(PPh_3)_2(SSH)]$	2.26	2.26	2.26	2.26	1.92
$[RuCl(AsPh_3)_2(ASH)]$	2.32	2.32	2.32	2.32	n
$[RuCl(AsPh_3)_2(ESH)]$	2.20	2.20	2.20	2.20	n
$[RuCl(AsPh_3)_2(SSH)]$	2.35	2.35	2.35	2.35	1.95
$[RuBr(AsPh_3)_2(ASH)]$	2.25	2.25	2.25	2.25	n
$[RuBr(AsPh_3)_2(ESH)]$	2.35	2.35	2.35	2.35	n
$[RuBr(AsPh_3)_2(SSH)]$	2.18	2.18	2.18	2.18	1.96
$[RuBr(PPh_3)_2(ASH)]$	2.30	2.30	2.30	2.30	n
$[RuBr(PPh_3)_2(ESH)]$	2.35	2.35	2.35	2.35	1.95
$[RuBr(PPh_3)_2(SSH)]$	2.26	2.26	2.26	2.26	1.96

$g^a = [1/2 (g_x^2 + g_v^2 + g_z^2)]^{1/2}$, n = not recorded.

Cyclic voltammetric studies: Cyclic voltametric studies were performed for some of the complexes in acetonitrile at a glassy-carbon working electrode. The oxidations and reductions of some complexes are achieved by well defined waves with E_f values in the range from-0.075 to - 0.195 and 0.150-0.500 V, respectively. The redox processes observed for these complexes are metal centered only. Most of the complexes showed reversible couples with peak-to-peak separation values (ΔEp) ranging from 138-390 mV indicating a single step one-electron transfer process[49,50] (Table-3).

TABLE-3
CYCLIC VOLTAMETRIC DATA OF SOME Ru(III) COMPLEXES

Complex	Ru(IV)-Ru(III)				Ru(III)-Ru(II)			
	Epa (V)	Epc (V)	E_f (V)	ΔEp (mV)	Epa (V)	Epc (V)	E_f (V)	ΔEp (mV)
$[RuCl(PPh_3)_2(ASH)]$	0.600	0.400	0.500	200	-0.300	-0.020	-0.160	320
$[RuCl(PPh_3)_2(ESH)]$	0.500	0.200	0.350	300	-0.100	-0.050	-0.075	150
$[RuCl(PPh_3)_2(SSH)]$	–	–	–	–	-0.250	-0.120	-0.185	270
$[RuCl(AsPh_3)_2(SSH)]$	0.200	0.100	0.150	100	-0.100	-0.080	-0.090	180
$[RuCl(AsPh_3)_2(ESH)]$	0.500	0.300	0.400	200	-0.180	-0.100	-0.140	280
$[RuCl(AsPh_3)_2(ASH)]$	0.300	0.100	0.200	200	-0.200	-0.190	-0.195	390
$[RuBr(AsPh_3)_2(SSH)]$	–	–	–	–	-0.200	-0.050	-0.125	250

Working electrode: glassy carbon electrode : reference electrode: Ag-AgCl electrode; Supporting electrolyte: $[NBu_4]ClO_4$ (0.05 M); scan rate: 100 mVs^{-1}: E_f = (Epa + Epc), where Epa and Epc are anodic and cathodic potentials, respectively.

Catalytic activity: The ruthenium(III) complexes were found to exhibit catalytic yield and comparable to those reported for similar ruthenium(III) complexes[51] (Table-4). The relatively higher product yield obtained for the oxidation of cinnamyl alcohol as compared to benzyl alcohol is due to the presence of the unsaturation in cinnamyl alcohol[52]. The relatively higher product yield obtained for the oxidation of benzyl alcohol as compared to cyclohexanol is due to the fact that the α-CH moiety of benzyl alcohol is more acidic[53]. It has also been found that triphenylphosphine complexes posses higher catalytic activity than triphenylarsine complexes[54]. This may be due to the higher donor ability of the arsine ligand compared to the phosphine ligand.

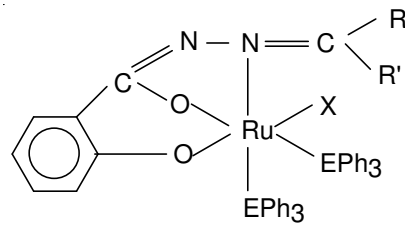
Antibacterial activity: The results showed that the ruthenium chelates are more toxic compared to their parent ligands against the same microorganisms under identical conditions (Table-5). The toxicity of ruthenium chelates increases on increasing the concentration[55]. The increase in the antibacterial activity of metal chelates may be due to the effect of the metal ion on the normal cell process. A possible mode of the toxicity increase may be considered in light of Tweed's chelation theory[56]. Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor groups and possible π-electron delocalization over the whole chelate ring. Such chelation could enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layers of cell membrane. Furthermore, the mode of action of the compounds may involve in the formation of a hydrogen bond through the azomethine (>C=N) group with the active centers of cell constituents, resulting in interference with the normal cell processes[57]. Though the complexes possess activity, it could not reach the effectiveness of the standard drug streptomycin. The variation in the effectiveness of the different compounds against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells[58,59].

TABLE-4
CATALYTIC OXIDATION OF ALCOHOLS BY Ru(III) COMPLEXES

Complex	Substrate	Product*	Yield**	Turnover
	Benzyl alcohol	A	70.40	72.53
$[RuCl(PPh_3)_2(ASH)]$	Cyclohexanol	K	65.71	67.36
	Cinnamyl acohol	C	7321	75.41
	Benzyl alcohol	A	70.83	72.65
$[RuCl(AsPh_3)_2(ESH)]$	Cyclohexanol	K	66.01	68.21
	Cinnamyl acohol	C	73.58	75.92
	Benzyl alcohol	A	70.50	74.71
$[RuCl(AsPh_3)_2(SSH)]$	Cyclohexanol	K	67.21	69.52
	Cinnamyl acohol	C	74.67	76.58
	Benzyl alcohol	A	60.71	62.57
$[RuCl(AsPh_3)_2(ASH)]$	Cyclohexanol	K	58.17	60.69
	Cinnamyl acohol	C	63.27	65.50
	Benzyl alcohol	A	60.83	62.91
$[RuCl(AsPh_3)_2(ESH)]$	Cyclohexanol	K	56.21	58.50
	Cinnamyl acohol	C	63.50	65.60
	Benzyl alcohol	A	62.71	64.93
$[RuCl(AsPh_3)_2(SSH)]$	Cyclohexanol	K	57.13	59.53
	Cinnamyl acohol	C	64.58	66.99
	Benzyl alcohol	A	71.32	73.53
$[RuCl(AsPh_3)_2(ASH)]$	Cyclohexanol	K	66.27	68.17
	Cinnamyl acohol	C	74.57	76.73
	Benzyl alcohol	A	61.53	62.47
$[RuCl(AsPh_3)_2(ASH)]$	Cyclohexanol	K	56.28	58.56
	Cinnamyl acohol	C	64.18	66.37
	Benzyl alcohol	A	75.51	74.75
$[RuCl(AsPh_3)_2(SSH)]$	Cyclohexanol	K	67.19	69.28
	Cinnamyl acohol	C	78.28	80.63
	Benzyl alcohol	A	62.17	64.52
$[RuCl(AsPh_3)_2(SSH)]$	Cyclohexanol	K	57.26	59.69
	Cinnamyl acohol	C	68.53	70.82

*A = Benzaldehyde; K = Cyclohexanone; E = Cinnamaldehyde. **Yields based on substrate.

Based on the analytical, spectral and electrochemical data, an octahedral structure (Fig. 2) has been proposed for all the ruthenium(III) complexes.



(E = P or As; X = C1 or Br; R = H or CH_3: R^1 = CH_3, CH_2CH_3 or C_6H_4OH)

Fig. 2. Structure of Ru(III) complexes

TABLE-5
ANTIMICROBIAL ACTIVITY OF LIGANDS AND Ru(III) COMPLEXES

Ligand/complex	*E. coli* (%)			*Pseudomonas* (%)			*S. typhi* (%)			*S. aureus* (%)		
	0.25	0.50	1.00	0.25	0.50	1.00	0.25	0.50	1.00	0.25	0.50	1.00
H_2ASH	9	11	12	11	12	14	10	12	13	8	11	13
[RuCl(PPh_3)$_2$(ASH)]	10	13	14	13	15	16	12	14	16	10	13	15
[RuCl($AsPh_3$)$_2$(ASH)]	12	13	16	12	14	18	11	15	19	12	14	20
[RuCl($AsPh_3$)$_2$(ASH)]	13	15	18	13	16	20	14	17	20	13	16	17
[RuBr($AsPh_3$)$_2$(ASH)]	14	16	20	14	17	19	12	15	18	14	16	19
H_2ESH	10	11	12	12	12	15	12	13	14	10	12	14
[RuCl(PPh_3)$_2$(ESH)]	12	14	17	13	15	17	14	17	19	12	14	19
[RuCl($AsPh_3$)$_2$(ESH)]	13	15	18	14	16	19	15	17	18	13	15	19
[RuBr(PPh_3)$_2$ (ESH)]	14	15	19	15	17	20	14	16	17	14	17	20
[RuBr($AsPh_3$)$_2$(ESH)]	14	17	20	16	18	19	15	17	19	12	14	17
H_2SSH	12	13	14	12	15	16	10	12	13	9	11	13
[RuCl(PPh_3)$_2$(SSH)]	14	15	17	13	16	19	12	14	16	10	12	14
[RuCl($AsPh_3$)$_2$(SSH)]	14	17	19	17	18	20	13	15	17	11	13	16
[RuBr(PPh_3)$_2$(SSH)]	15	18	20	18	20	20	14	17	19	12	14	17
[RuBr($AsPh_3$)$_2$(SSH)]	16	18	19	14	17	19	14	15	18	14	17	18
Streptomycin	22	23	28	21	27	29	20	21	25	20	22	24

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