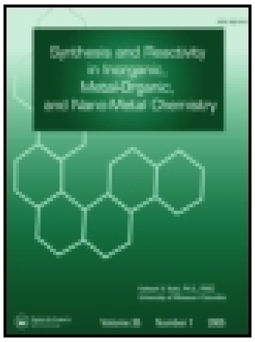

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2′-HYDROXYCHALCONATE COMPLEXES OF Ru(III) CONTAINING TRIPHENYLPHOSPHINE OR TRIPHENYLARSINE

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ABSTRACT

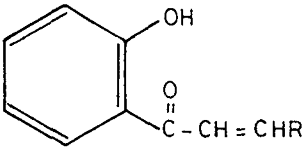
Mixed ligand complexes of ruthenium(III) with 2′-hydroxychalcones and triphenylphosphine or triphenylarsine as ligands have been synthesised. The new complexes were characterized on the basis of analytical, spectral (IR, electronic, magnetic moment and EPR) and electrochemical data and are formulated as $[RuX_2(L)(EPh_3)_2]$ (where X = Cl or Br; E = P or As; HL = 2′-hydroxychalconate). An octahedral structure has been tentatively proposed for the complexes.

INTRODUCTION

Several low-spin d^5 complexes of second and third row transition metal ions with phosphines and arsines as ligands have been reported in the literature[1-6]. However, only a few ruthenium(III) complexes with a tertiary arsine as one of the ligands are known[7-10]. Though mixed ligand complexes of Ru(III) containing β-diketones and other related ligands have been reported[11-13], the reactions of 2'-hydroxychalcones with ruthenium(III) complexes were not studied. In view of the growing interest of mixed ligand complexes as catalysts[14-16], we report in this paper the synthesis and characterization of some stable ruthenium(III) complexes containing the anion of 2'-hydroxychalcones as one of the ligands, the structure of the latter are shown in Fig. 1.

EXPERIMENTAL

All the reagents used were of Analar grade. Solvents were purified and dried according to standard procedures[16a]. The analyses of carbon and hydrogen were performed at the R & D Laboratory, Hindustan Photo Film Industry, Udhagamandalam, India. Infrared spectra were recorded in KBr pellets with a Perkin-Elmer 597 spectrophotometer in the range 4000-200 cm^{-1}. Electronic spectra of the complexes were recorded in methylene chloride with a Hitachi Perkin-Elmer model 20/200 spectrophotometer and room temperature EPR spectra of powdered samples were recorded with a Bruker ER-200D-SRC EPR spectrometer internally calibrated with diphenylpicrylhydrazyl (DPPH) at x-band frequencies. The magnetic susceptibility measurements were carried out on an EG & G-PARC vibrating sample magnetometer at room temperature. Melting points were determined using a Mettler FP51 instrument and are uncorrected. The cyclic voltammetric studies were carried out in acetonitrile using a glassy carbon working electrode and all the potentials were referenced to a saturated calomel electrode (SCE).



where R = C_6H_5; [HL^1 = $H\text{-}C_{15}H_{11}O_2$]
R = 4-(MeO)C_6H_4; [HL^2 = $H\text{-}C_{16}H_{13}O_3$]
R = 3,4-$(MeO)_2C_6H_3$; [HL^3 = $H\text{-}C_{17}H_{15}O_4$]

Fig. 1. Structure of the 2'-Hydroxychalcones HL

The starting complexes $[RuCl_3(PPh_3)_3]$[2], $[RuCl_3(AsPh_3)_3]$[17], $[RuBr_3(PPh_3)_2(MeOH)]$[4], $[RuBr_3(AsPh_3)_3]$[10] and the chalcones[18] were prepared according to the literature methods.

Preparation of 2'-Hydroxychalcone Ligands (HL)

Preparation of HL^1. The ligand HL^1 was prepared by condensing benzaldehyde (1.32 g, 0.25 mol) with 2-hydroxyacetophenone (1.74 g, 0.25 mol) in the presence of 50 mL alcoholic sodium hydroxide solution (20%). After 24h stirring, the product was precipitated by adding concentrated hydrochloric acid, filtered and recrystallized from ethanol.

Yield: 2.1 g (74.5%) M.P. 86°C (lit. m.p. 88-9°C)

Preparation of HL^2. The ligand HL^2 was prepared by condensing 4-methoxybenzaldehyde (1.74 g, 0.25 mol) with 2-hydroxyacetophenone (1.74 g, 0.25 mol) in the presence of 50 mL alcoholic sodium hydroxide solution (20%). After 24h stirring, the product was precipitated by adding concentrated hydrochloric acid, filtered and recrystallized from ethanol.

Yield: 2.6 g (82.0%) M.P. 92°C (lit. m.p. 93-4°C)

Preparation of HL³. The ligand HL^3 was prepared by condensing 3,4-dimethoxybenzaldehyde (2.07 g, 0.25 mol) with 2-hydroxyacetophenone (1.74 g, 0.25 mol) in the presence of 50 mL alcoholic sodium hydroxide solution (20%). After 24h stirring, the product was precipitated by adding concentrated hydrochloric acid, filtered and recrystallized from ethanol.

Yield: 2.70 g (76.2%) M.P. 119°C (lit. m.p. 121°C)

Preparation of Complexes of the Type $[RuCl_2(L)(EPh_3)_2]$ (HL = 2′-hydroxychalconates; E = P or As)

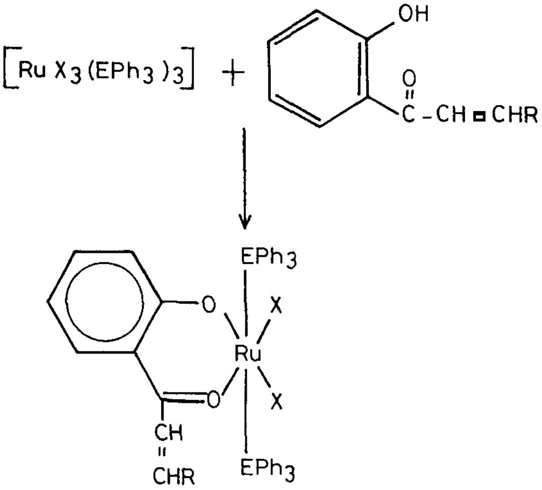
To a solution of $[RuCl_3(PPh_3)_3]$ or $[RuCl_3(AsPh_3)_3]$ (0.150 - 0.170 g, 0.125 mmol) in benzene (20 mL) the appropriate 2′-hydroxychalcone (0.125 mmol) was added (molar ratio Ru complex : 2′-hydroxychalcone is 1:1). The resulting solution was refluxed on a water bath for about 4h. After concentrating the solution to about 3 mL, the product was precipitated by the addition of a small quantity of petroleum ether (b.p. 60-80°C). The product was filtered and washed with the same solvent and recrystallized from CH_2Cl_2/petroleum ether (b.p. 60-80°C) mixture, the ratio of which is 20:80.

Preparation of Complexes of the Type $[RuBr_2(L)(EPh_3)_2]$ (HL = 2′-hydroxychalconates; E = P or As)

These complexes were prepared as described above by reacting $[RuBr_3(PPh_3)_2MeOH]$ or $[RuBr_3(AsPh_3)_3]$ with the various 2′-hydroxychalcones in 1:1 molar ratio.

RESULTS AND DISCUSSION

Air and light stable complexes of the general formula $[RuX_2(L)(EPh_3)_2]$ (where X = Cl or Br; HL = 2'-hydroxychalconates; E = P or As) were obtained from the reactions of $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$, $[RuBr_3(PPh_3)_2MeOH]$ or $[RuBr_3(AsPh_3)_3]$ with the respective chalcones in 1:1 molar ratio in benzene by the equation shown below.



X = Cl or Br; E = P or As; R = C_6H_5, 4-(MeO)C_6H_4, 3,4-$(MeO)_2C_6H_3$

In all the reactions, the chalcones behave as an uninegative bidentate chelating ligand similar to β-diketones by replacing one of the halide ions and a molecule of triphenylphosphine, arsine or methanol from the starting complexes. The analytical data given in Table I for the new complexes agree very well with the above molecular formula.

Table I. Analytical Data of New Ru(III) complexes

No.	Complex	Empirical formula (formula weight)	Colour	M.P.(°C)	Yield (%)	Elemental Analysis (%) Found (Calc.) Carbon	Hydrogen
1.	$[RuCl_2(L^1)(PPh_3)_2]$	$RuCl_2P_2C_{51}H_{41}O_2$ (919.48)	Brown	125	62	66.32 (66.61)	4.91 (4.45)
2.	$[RuCl_2(L^1)(AsPh_3)_2]$	$RuCl_2As_2C_{51}H_{41}O_2$ (1007.32)	Brown	160-62°C	65	61.20 (60.80)	4.12 (4.07)
3.	$[RuBr_2(L^1)(PPh_3)_2]$	$RuBr_2P_2C_{51}H_{41}O_2$ (1008.38)	Brown	154	60	60.42 (60.74)	4.01 (4.06)
4.	$[RuBr_2(L^1)(AsPh_3)_2]$	$RuBr_2As_2C_{51}H_{41}O_2$ (1096.22)	Brown	135	61	55.47 (55.87)	3.95 (3.74)
5.	$[RuCl_2(L^2)(PPh_3)_2]$	$RuCl_2P_2C_{52}H_{43}O_3$ (949.49)	Red brown	182	67	65.92 (65.77)	4.38 (4.53)
6.	$[RuCl_2(L^2)(AsPh_3)_2]$	$RuCl_2As_2C_{52}H_{43}O_3$ (1037.33)	Yellow brown	132-35	70	60.53 (60.20)	4.45 (4.15)
7.	$[RuBr_2(L^2)(PPh_3)_2]$	$RuBr_2P_2C_{52}H_{43}O_3$ (1038.39)	Red brown	151-53	62	60.45 (60.14)	4.61 (4.14)
8.	$[RuBr_2(L^2)(AsPh_3)_2]$	$RuBr_2As_2C_{52}H_{43}O_3$ (1126.23)	Brown	142	60	55.80 (55.45)	4.20 (3.82)
9.	$[RuCl_2(L^3)(PPh_3)_2]$	$RuCl_2P_2C_{53}H_{45}O_4$ (979.50)	Brown	162	65	65.25 (64.99)	5.02 (4.59)
10.	$[RuCl_2(L^3)(AsPh_3)_2]$	$RuCl_2As_2C_{53}H_{45}O_4$ (1067.34)	Yellow brown	120	68	59.50 (59.64)	4.35 (4.22)
11.	$[RuBr_2(L^3)(PPh_3)_2]$	$RuBr_2P_2C_{53}H_{45}O_4$ (1068.40)	Red brown	108-10	70	59.87 (59.58)	3.84 (4.21)
12.	$[RuBr_2(L^3)(AsPh_3)_2]$	$RuBr_2As_2C_{53}H_{45}O_4$ (1156.24)	Brown	135	64	55.41 (55.05)	3.51 (3.89)

IR Spectra

The important infrared frequencies of the new ruthenium(III) complexes are given in Table II. The intense band observed around 1620-1630 cm^{-1} in the IR spectra of free ligands due to $\nu_{C=O}$ has been shifted to lower wave number in the spectra of the complexes suggesting the coordination of the chalcones to the ruthenium ion through the carbonyl oxygen[19]. The phenolic C-O stretching absorption of the free ligands occurs as a doublet in the region 1330-1360 cm^{-1}. But in the spectra of the complexes, this band shows a bathochromic shift of 5-20 cm^{-1} and appears as a singlet. Based upon these facts, it is inferred that both the carbonyl and phenolic oxygen atoms are involved in the coordination of the chalcones to the ruthenium ion in all of these complexes. The absorption due to $\nu_{C=C}$ appears as a separate band in some complexes and in other complexes it could not be identified because of its possible merger with the strong $\nu_{C=O}$ band[20,21]. Another very intense band observed in the region 1540-1570 cm^{-1} in the free ligands is assigned to the phenylalkene vibration and is shifted to lower wave numbers by 10-20 cm^{-1} in the complexes[22]. All other characteristic bands due to triphenylphosphine, arsine and the chalcones were present in the expected region.

Electronic Spectra

The electronic spectra of all the complexes in methylene chloride solution showed two bands in the region 390 - 260 nm. The ground state of Ru(III) (t_{2g}^5 configuration) is $^2T_{2g}$ and the first excited doublet levels

Table II. Infrared and Electronic Spectral Data of the New Ruthenium(III) Complexes (ν in cm^{-1})

No.	Complex	$\nu_{C=O}$	$\nu_{C=C}$	$\nu_{Ph-C=C}$	ν_{C-O}	λ_{max}(nm)
1.	$[RuCl_2(L^1)(PPh_3)_2]$	1600	-	1520	1370	340, -
2.	$[RuCl_2(L^1)(AsPh_3)_2]$	1610	1580	1540	1380	360, 270
3.	$[RuBr_2(L^1)(PPh_3)_2]$	1600	1575	1530	1365	340, 280
4.	$[RuBr_2(L^1)(AsPh_3)_2]$	1600	-	1530	1370	360, 280
5.	$[RuCl_2(L^2)(PPh_3)_2]$	1600	-	1520	1360	390, -
6.	$[RuCl_2(L^2)(AsPh_3)_2]$	1600	1580	1540	1380	380, 260
7.	$[RuBr_2(L^2)(PPh_3)_2]$	1600	1570	1530	1360	380, 280
8.	$[RuBr_2(L^2)(AsPh_3)_2]$	1600	1580	1535	1370	375, 260
9.	$[RuCl_2(L^3)(PPh_3)_2]$	1600	-	1530	1370	390, 270
10.	$[RuCl_2(L^3)(AsPh_3)_2]$	1610	1570	1530	1380	380, 270
11.	$[RuBr_2(L^3)(PPh_3)_2]$	1600	-	1535	1375	390, 275
12.	$[RuBr_2(L^3)(AsPh_3)_2]$	1600	1570	1530	1370	380, 270

in increasing order of energy are $^2A_{2g}$ and $^2T_{1g}$ which arise from the $t_{2g}{}^4$ $e_g{}^1$ configuration[23]. In most of the ruthenium(III) complexes the UV and visible spectra show only charge transfer bands[24]. Hence, the above bands with very high extinction coefficients are assigned to charge transfer transitions. These are very characteristic of octahedral Ru(III) complexes and, hence, an octahedral geometry has been proposed tentatively for all the new complexes.

Magnetic Moments

The magnetic moments of the complexes $[RuBr_2(L^1)(PPh_3)_2]$ and $[RuCl_2(L^2)(PPh_3)_2]$ were measured at room temperature using a vibrating sample magnetometer and diamagnetic corrections were applied. The values are 1.74 BM and 1.81 BM, respectively, corresponding to one unpaired electron indicating a low-spin d^5 configuration for the ruthenium(III) ion in these complexes. The observed magnetic moment values also indicate that the chalcones are strong field ligands[19].

EPR Spectral Studies

The room temperature EPR spectra for some of the new ruthenium(III) complexes were recorded. All the complexes exhibit spectra characteristic of an axially symmetric low-spin d^5 system with $g_\perp$ around 2.28 - 2.49 and $g_\parallel$ around 2.02 - 2.30 (Table III). For an octahedral field with tetragonal distortion $g_x = g_y \neq g_z$ and, therefore, two different 'g' values indicate tetragonal distortion in these complexes. However, four of the complexes (no.s, 3, 6, 7 and 8) showed only one signal around 2.26 - 2.30 indicating a

Table III. EPR Spectral Data of Some Ruthenium(III) Complexes

No.	Complex	g_1	g_2	g_3	$\langle g \rangle^*$
1.	$[RuCl_2(L^1)(PPh_3)_2]$	2.28	2.28	2.02	2.19
2.	$[RuCl_2(L^1)(AsPh_3)_2]$	2.43	2.43	2.26	2.37
3.	$[RuCl_2(L^2)(PPh_3)_2]$	-	2.27	-	2.27
4.	$[RuCl_2(L^2)(AsPh_3)_2]$	2.46	2.46	2.25	2.39
5.	$[RuBr_2(L^2)(AsPh_3)_2]$	2.49	2.49	2.30	2.43
6.	$[RuCl_2(L^3)(PPh_3)_2]$	-	2.26	-	2.26
7.	$[RuBr_2(L^3)(PPh_3)_2]$	-	2.26	-	2.26
8.	$[RuBr_2(L^3)(AsPh_3)_2]$	-	2.30	-	2.30

$$\langle g \rangle^* = [\frac{1}{3} g_1^2 + \frac{1}{3} g_2^2 + \frac{1}{3} g_3^2]^{1/2}$$

very high symmetry around the ruthenium atom. Such isotropic lines are usually observed either due to the intermolecular spin exchange which can broaden the EPR lines or due to the occupancy of the unpaired electron in a degenerate orbital. The observed 'g' values are similar to those observed for other octahedral ruthenium(III) complexes[11,25-27].

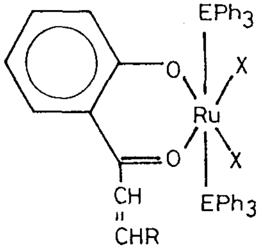
Cyclic Voltammetric Studies

Cyclic voltammetric studies were carried out for some of the new ruthenium(III) complexes in acetonitrile at a glassy carbon working electrode at the scan rate of 100 mVs^{-1}. The redox processes observed for these complexes within the potential limits of +1.0 V to -1.0 V are metal centered only. Cyclic voltammograms of all the complexes showed reversible redox couples. The oxidation and reduction potentials of all the complexes are characterised by well defined waves with E_f values in the range 0.63 V to 0.7 V (Ru^{IV} - Ru^{III}) and -0.27 V to -0.39 V (Ru^{III} - Ru^{II}) vs. a saturated calomel electrode (SCE) (Table IV). The observed electrochemical data of these complexes showed a reversible redox couple with a peak to peak separation value (ΔE_p) ranging from 60 to 100 mV, characteristic of a single step, one electron transfer process, which is similar to that observed for other ruthenium(III) complexes[28-30]. Since there is not much variation in the ligand system used in this study, the observed redox potentials did not change appreciably. Hence, it is concluded from the electrochemical data that the present ligand system is suitable for stabilizing the ruthenium ion in its higher oxidation state.

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

Complex	$Ru^{IV}-Ru^{III}$				$Ru^{III}-Ru^{II}$			
	Epa(V)	Epc(V)	E_f(V)	Ep(mV)	Epc(V)	Epa(V)	E_f(V)	Ep(mV)
$[RuCl_2(L^1)(PPh_3)_2]$	0.66	0.60	0.63	60	-0.32	-0.40	-0.36	80
$[RuBr_2(L^1)(PPh_3)_2]$	0.76	0.66	0.71	100	-0.24	-0.30	-0.27	60
$[RuBr_2(L^1)(AsPh_3)_2]$	0.69	0.61	0.65	80	-0.25	-0.32	-0.29	70
$[RuCl_2(L^2)(AsPh_3)_2]$	0.67	0.61	0.64	60	-0.36	-0.42	-0.39	60
$[RuBr_2(L^2)(AsPh_3)_2]$	0.68	0.62	0.65	60	-0.32	-0.38	-0.35	60
$[RuBr_2(L^3)(PPh_3)_2]$	0.71	0.65	0.68	60	-0.29	-0.35	-0.32	60

[a] Supporting electrolyte: $[NBu_4]ClO_4$ (0.05 mol); all potentials are referenced to SCE; $E_f = 0.5(Epa+Epc)$, where Epa and Epc are the anodic and cathodic peak potentials, respectively. Scan rate 100 mVS^{-1}.



X = Cl or Br; E = P or As; R = C_6H_5, 4-(MeO)C_6H_4 or 3,4-$(MeO)_2C_6H_3$

Fig. 2. Suggested Structure of the Complexes

Based on the analytical, spectroscopic and electrochemical data, the following octahedral structure (Fig. 2) has been tentatively proposed for the new Ru(III) complexes.

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