

Synthesis, characterization, redox properties and reactivities of a group of phenolato complexes of ruthenium(III)

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Abstract—Seven complexes of the type $[Ru^{III}(PPh_3)_2(L)Cl_2]$ (where L = 8-quinolinolate, 4-methyl-2-(phenylazo)phenolate and salicylal-diminate anion) have been synthesized by the reaction of $[Ru(PPh_3)_3Cl_2]$ with HL. These complexes are one-electron paramagnetic and show rhombic ESR spectra in 1:1 dichloromethanetoluene at 77 K. In CH₂Cl₂ solution, these complexes show intense LMCT transitions in the visible region together with weak ligand-field transitions at lower energies. Each of these complexes shows a ruthenium(III)– ruthenium(II) reduction (-0.12 to -0.40 V vs SCE) and a ruthenium(III)–ruthenium(IV) oxidation (0.78– 0.88 V vs SCE) in acetonitrile solution. The potentials of the ruthenium(III)–ruthenium(II) reduction vary linearly with the nature of substituent in L. The $[Ru^{III}(PPh_3)_2(L)Cl_2]$ complexes react with bidentate chelating ligands (L' = 8-quinolinolate anion, 2,2'-bipyridine, 1,10-phenanthroline) to afford complexes of type [Ru (PPh_3)_2(L)(L')]^{*+}. These complexes are diamagnetic and show intense MLCT transitions in the visible region. The potential of the ruthenium(II)–ruthenium(III) couple in these complexes depend on the nature of both L and L'. Copyright © 1996 Elsevier Science Ltd

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The present work has developed from our interest in the chemistry of ruthenium in different coordination spheres [1]. We have observed that coordination of ruthenium by phenolate oxygen is very effective in stabilizing the higher oxidation states of this metal [2]. In this study, phenolic ligands of three different types have been used, which are 8-quinolinol (HQ, 1), 4methyl-2-(phenylazo)phenol (Hap, 2) and salicylaldimine (Hsal-R, 3). All these ligands (abbreviated in general as HL, where H stands for the acidic hydrogen) bind to a metal ion as bidentate N,O-coordinator via dissociation of the phenolic proton. It may be noted here that the ruthenium chemistry of these ligands has received relatively little attention [3-5]. Herein we report the synthesis and characterization of a group of complexes of type $[Ru^{III}(PPh_3)_2(L)Cl_3]$ and their spectroscopic and electron-transfer properties. Reactivity studies, involving the dissociation of Ru-Cl bonds, are also described.

EXPERIMENTAL

Materials

Commercial ruthenium trichloride, purchased from Arora Matthey, Calcutta, India was converted to RuCl₃·3H₂O by repeated evaporation with concentrated hydrochloric acid. Triphenylphosphine (PPh₃), triethylamine (Et₃N), 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and 8-quinolinol (HQ) were purchased from SD Fine Chemicals, Bombay, India. $[Ru(PPh_3)_3Cl_2]$ was prepared by following a reported procedure [6]. The salicylaldimine ligands were prepared by reacting equimolar amounts of salicylaldehyde and the respective amine in hot ethanol. The 4-methyl-2-(phenylazo)phenol ligand was prepared by coupling diazotized aniline with p-cresol. Purification of acetonitrile and dichloromethane and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported earlier [1a]. All other chemicals and solvents were reagent grade commercial materials and were used as received.

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Preparation of complexes

The seven $[Ru(PPh_3)_2(L)Cl_2]$ complexes were synthesized by using a general procedure. Yields varied in the range 80–90%. Specific details are given for one complex.

[Ru(PPh₃)₂(Q)Cl₂]. To a mixture of [Ru(PPh₃)₃Cl₂] (100 mg, 0.10 mmol) and 8-quinolinol (15 mg, 0.10 mmol) was added dichloromethane (40 cm³). The resulting solution was stirred for 30 min. The volume of the solvent was reduced by evaporation and hexane was added to it upon which [Ru¹¹¹(PPh₃)₂(Q)Cl₂] started separating out as a dark-coloured solid. This was collected by filtration, washed thoroughly with hexane and dried in air. The yield was 70 mg, 83%.

[Ru(PPh₃)₂(Q)₂]. To a solution of [Ru(PPh₃)₂ (Q)Cl₂] (100 mg, 0.12 mmol) and 8-quinolinol (17 mg, 0.12 mmol) in acetonitrile (40 cm³) was added triethylamine (24 mg, 0.24 mmol). The resulting solution was refluxed for 1 h upon which the colour of the solution changed from green to yellowish red. The solution was cooled and concentrated by evaporation. Ether was then added to the solution and [Ru (PPh₃)₂(Q₂)] separated out as a brown microcrystalline solid. It was filtered, washed with water and ethanol and dried in air. The yield was 95 mg, 87%.

[Ru(PPh₃)₂(ap)(phen)]ClO₄. To a solution of [Ru^{III} (PPh₃)₂(ap)Cl₂] (100 mg, 0.11 mmol) and 1,10-phenanthroline (22 mg, 0.11 mmol) in acetonitrile (40 cm³) was added triethylamine (22 mg, 0.22 mmol). The colour of the solution changed from green to yellowish red upon refluxing the solution for 1 h. The solution was then cooled to room temperature and a saturated aqueous solution of NaClO₄ (10 cm³) was added to it. [Ru^{III}(PPh₃)₂(ap)(phen)]ClO₄ precipitated as a dark solid, which was collected by filtration, washed with ice-cold water and dried *in vacuo* over P₄O₁₀. Recrystallization of this crude product from acetonitrile– toluene solution gave [Ru(PPh₃)₂(ap)(phen)]ClO₄ in the pure state. The yield was 75 mg, 60%.

 $[Ru(PPh_3)_2(sal-H)(bpy)]ClO_4$. This was prepared by following the same above procedure using $[Ru(PPh_3)_2(sal-H)Cl_2]$ and bpy instead of $[Ru(PPh_3)_2(ap)Cl_2]$ and phen, respectively.

Physical measurements

As described earlier [1a].

RESULTS AND DISCUSSION

Synthesis and characterization

The reaction of $[Ru(PPh_3)_3Cl_2]$ with an equimolar quantity of HL in dichloromethane solution at ambient temperature afforded the $[Ru(PPh_3)_2(L)Cl_2]$ complexes [eq. (1)] in good yields. In total seven complexes have been prepared using different phenolic ligands.

$$[Ru^{II}(PPh_3)_3Cl_2] + HL$$

$$\rightarrow [Ru^{III}(PPh_3)_2(L)Cl_2] + H^+ + e^- \quad (1)$$

It is interesting to note here that during the course of this synthetic reaction ruthenium undergoes a oneelectron oxidation. In view of the low ruthenium(III)– ruthenium(II) reduction potential in these complexes (*vide infra*) oxygen in the air appears to be the probable oxidant [7].

Elemental (C, H, N) analytical data (Table 1) confirm the compositions of these complexes. Magnetic susceptibility measurements show that these complexes are one-electron paramagnetic (Table 1), as expected for complexes of ruthenium(III) (low-spin d^5 , S = 1/2). The infrared spectra of these complexes contain many sharp bands of different intensities due to vibrations arising from the coordinated PPh₃, L and Cl⁻ and are therefore complex in nature. No attempt has been made to assign individual bands. However, comparison of the IR spectra of these $[Ru(PPh_3)_2(L)Cl_2]$ complexes with that of $[Ru(PPh_3)_3]$ Cl₂] shows that besides small shifts in frequencies. some vibrations are common in both the spectra (e.g. vibrations near 520, 540, 690 and 740 cm^{-1}) which are due to the common PPh₃ ligand. Some additional bands are observed in the spectra of the $[Ru(PPh_3)_2(L)Cl_2]$ complexes which are obviously due to the coordinated phenolic ligand L. Two sharp bands of medium intensity, observed in all the com-

Compound	Analytical data"			μeff	Electronic spectral data ^b	Cyclic-voltammetric data ^c $E_{298}^0, V(\Delta E_p, mV)$	
	%C	%H	%N	(BM)	$\hat{\lambda}_{max}$, nm (ϵ , M ⁻¹ cm ⁻¹)	Ru ^{11/111}	Ru ^{III/IV}
$[Ru(PPh_3)_2(Q)Cl_2]$	64.2 (64.3)	4.1	1.6	1.85	1800(42), 760(625) $425^{4}(3550), 390(4200)$	-0.40°	0.85′
[Ru(PPh ₃) ₂ (ap)Cl ₂]	64.6 (64.8)	4.5 (4.5)	3.0 (3.1)	1.92	1400(80), 625(370). 420(9400)	-0.22(120)	0.78′
$[Ru(PPh_3)_2(sal-OMe)Cl_2]$	65.1 (65.1)	4.4 (4.6)	1.5 (1.5)	1.95	667(2190), 515(3210)	-0.34(70)	0.847
$[Ru(PPh_3)_2(sal-Me)Cl_2]$	66.0 (66.2)	4.4 (4.6)	1.5 (1.6)	1.89	600(2530), 400 ^d (5170)	-0.30(60)	0.867
$[Ru(PPh_3)_2(sal-H)Cl_2]$	65.7 (65.9)	4.4 (4.5)	1.6 (1.6)	1.84	$1600^{d}(70), 660(2650), 390^{d}(5400), 340(6600)$	-0.27(60)	0.857
[Ru(PPh ₃) ₂ (sal-Cl)Cl ₂]	63.4 (63.5)	4.0 (4.2)	1.5 (1.5)	1.90	600(2950), 375(7570)	-0.24(70)	0.88'
$[Ru(PPh_3)_2(sal-NO_2)Cl_2]$	62.6 (62.8)	4.2 (4.2)	1.4 (1.5)	1.83	550(3230), 435(6900), 340(17575)	-0.12(70)	0.861
$[Ru(PPh_3)_2(sal-H)(bpy)]ClO_4^{g}$	65.7 (65.8)	4.4 (4.5)	3.8 (3.9)		$600^{d}(840), 425^{d}(2050)$	0.72(80)	
$[Ru(PPh_3)_2(ap)(phen)]ClO_4^{g}$	65.5 (65.6)	4.3 (4.4)	4.9 (5.0)		575 ^{<i>d</i>} (1580), 410(2950)	0.76(80)	

Table 1. Microanalytical, magnetic moment, electronic spectral and cyclic voltammetric data

"Calculated values are given in parentheses.

^b In dichloromethane solution.

^c Supporting electrolyte, TEAP (0.1 M); reference electrode, SCE; $E_{298}^0 = 0.5$ ($E_{pa} + E_{pc}$), where E_{pa} and E_{pc} are anodic and cathodic peak potentials; $\Delta E_p = E_{pa} - E_{pc}$; scan rate, 50 mV s⁻¹; solvent acetonitrole.

^d Shoulder.

 $^{e}E_{pc}$ value.

 $^{\prime}E_{\rm pa}$ value.

⁹ Electronic spectra recorded in acetonitrile solution.

plexes near 315 cm⁻¹ and 330 cm⁻¹, have been attributed to the v(Ru—Cl) stretching mode [8]. The infrared spectral data are therefore in good agreement with the compositions of these complexes.

The $[Ru(PPh_3)_2(L)Cl_2]$ complexes may exist in four geometrical isomeric forms. However, it is well known that complexes containing the Ru^{III}(PPh₃)₂ moiety prefers the trans geometry [3b, 9] and hence we assume a similar structure, with the two PPh₃ ligands trans to each other, for these [Ru(PPh₃)₂(L)Cl₂] complexes. In this geometry the two Ru-Cl bonds are non-equivalent and hence are expected to vibrate at different energies, as actually observed in the infrared spectra (vide supra). The $[Ru(PPh_3)_2(L)Cl_2]$ complexes are soluble in acetonitrile and dichloromethane producing green solutions. Conductivity studies in acetonitrile show that these complexes behave as non-electrolytes in solution, indicating that the chloride ligands do not dissociate in solution. Electronic spectra of these complexes have been recorded in dichlormethane solution. Spectral data are presented in Table 1 and selected spectra are shown in Fig. 1. All the seven complexes display two or three intense absorptions, one of which appears in the visible region while the others extend into the UV region. These are probably due to allowed metal-to-ligand charge-transfer transitions. A low-intensity absorption at lower energy is also displayed by all these complexes which is discussed below.

ESR spectra of three representative complexes, viz., $[Ru^{III}(PPh_3)_2(Q)Cl_2], [Ru^{III}(PPh_3)_2(sal-H)Cl_2]$ and [Ru^{III}(PPh₃)₂(ap)Cl₂] have been recorded in 1:1 dichloromethane-toluene solution at 77 K. A selected spectrum is shown in Fig. 2 and the q-values are given in Table 2. All the three complexes show rhombic spectra with three distinct *q*-values. The rhombicity of the spectra reflects the asymmetry of electronic environments around ruthenium in these complexes. Under the combined influence of this low-symmetry and spin-orbit coupling, the three t_2 -levels get well separated. Hence two electronic transitions (transition energies ΔE_1 and ΔE_2 ; $\Delta E_1 < \Delta E_2$) within these three levels are probable. These transition energies have been computed (Table 2) using the observed *g*-values : the g-tensor theory of low-spin d^5 complexes [10] and a reported method [11]. The ΔE_2 transitions in all these three complexes have indeed been observed close to the theoretically predicted values as a low-intensity absorption (Table 1, Fig. 1) whereas the ΔE_1 transitions fall in the IR region and could not be detected. The ESR spectral data therefore show that these ruthenium(III) complexes are significantly distorted



Fig. 1. Electronic spectra of $[Ru(PPh_3)_2(Q)Cl_2]$ (----) and $[Ru(PPh_3)_2(sal-H)Cl_2]$ (---) in dichloromethane solution.



Fig. 2. ESR spectrum of [Ru(PPh₃)₂(Q)Cl₂] in 1 : 1 dichloromethane-toluene at 77K.

from ideal octahedral geometry, which is understandable by simple examination of the coordination sphere consisting of three different P—Ru—P, N—Ru—Cl and O—Ru—Cl axes.

Cyclic voltammetric studies

Electron-transfer properties of the $[Ru(P-Ph_3)_2(L)Cl_2]$ complexes have been studied in acetonitrile solution (0.1 M TEAP) by cyclic voltammetry. A selected voltammogram is shown in Fig. 3



Fig. 3. Cyclic voltammogram of $[Ru(PPh_3)_2(Q)Cl_2]$ in acetonitrile solution (0.1 M TEAP) at a scan rate of 50 mV s⁻¹. The solute concentration was 10^{-3} M.

Table 2. ESR g values and derived energy parameters of ruthenium(III) complexes

Compound		g values ^a		Derived energy p	arameters (cm ⁻¹)
	g_1	g_2	g_3	ΔE_1	ΔE_2
$[Ru(PPh_3)_2(Q)Cl_2]$	2.7263	2.0985	1.6225	2300	5700
[Ru(PPh ₃) ₂ (sal-H)Cl ₂]	2.4508	2.2265	1.8424	3800	6400
$[Ru(PPh_3)_2(ap)Cl_2]$	2.3862	2.1962	1.8695	4100	6800

^a ESR spectra recorded in 1:1 dichloromethane--toluene at 77 K.

and voltammetric data are given in Table 1. All these complexes show a ruthenium(III)-ruthenium(II) reduction [eq. (2)] on the negative side of SCE and a ruthenium(III)-ruthenium(IV) oxidation [eq. (3)] on the positive side.

$$[\operatorname{Ru}^{III}(\operatorname{PPh}_{3})_{2}(L)\operatorname{Cl}_{2} + e^{-} \rightleftharpoons [\operatorname{Ru}^{II}(\operatorname{PPh}_{3})_{2}(L)\operatorname{Cl}_{2}]^{-}$$

$$(2)$$

$$[\operatorname{Ru}^{III}(\operatorname{PPh}_{3})_{2}(L)\operatorname{Cl}_{2}] \rightleftharpoons [\operatorname{Ru}^{IV}(\operatorname{PPh}_{3})_{2}(L)\operatorname{Cl}_{2}]^{+} + e^{-}$$

$$(3)$$

In $[Ru(PPh_3)_2(Q)Cl_2]$ both electron-transfer processes take place irreversibly at -0.40 V and 0.85 V, respectively, which indicates that in the NOP₂Cl₂ coordination sphere the +3 state of ruthenium is stable while the +2 and +4 states are not. The ruthenium(III)ruthenium(II) potential in this complex is 430 mV less than that in [Ru(PPh₃)₂(bpy)Cl₂] (0.39 V) [1a] which indicates that relative to bpy, 8-quinolinolate is a much better stabilizer of ruthenium(III). This is due to the recognized ability of phenolate oxygen to stabilize the higher oxidation states of ruthenium. In $[Ru(PPh_3)_2(ap)Cl_2]$, the ruthenium(III)-ruthenium(II) reduction and ruthenium(III)-ruthenium (IV) oxidation are observed at -0.22 V and 0.78 V respectively. In $[Ru(PPh_3)_2(sal-R)Cl_2]$ complexes the irreversible ruthenium(III)-ruthenium(IV) oxidation is observed near 0.85 V and remains virtually insensitive to the substituent R. However, the ruthenium(III)-ruthenium(II) reduction potential varies as R is varied. The plot of this reduction potential vs the Hammett substituent constant [12] of R is linear (Fig. 4) with $\rho = 0.20$ V [13]. This shows that ruthenium(III)-ruthenium(II) reduction potential in the [Ru(PPh₃)₂(sal-R)Cl₂] complexes can be finetuned by varying R in the salicylaldiminate ligand.

Reactivities

Solution electrical conductivity studies have shown (vide supra) that the chloride ligands of the [Ru $(PPh_3)_2(L)Cl_2$] complexes do not dissociate in solution. This indicates the strong bonding between trivalent

ruthenium and chloride ion. However, both the chloride ligands can be displaced from the coordination sphere under mild condition by bidentate chelating ligands (L'). Such reactivity studies have been restricted to only three representative complexes, viz. [Ru $(PPh_3)_2(Q)Cl_2$, $[Ru(PPh_3)_2(sal-H)Cl_2]$ and $[Ru(PPh_3)_2(sal-H)Cl_2]$ (ap)Cl₂]. Reaction of these complexes with another ligand (L') in the presence of NEt₃ affords new complexes of the type $[Ru(PPh_3)_2(L)(L')]^+$ [eq. (4)] in decent yields. Two types of L', monoanionic (8quinolinolate anion, Q) and neutral (2,2'-bipyridine, bpy; 1,10-phenanthroline, phen) have been used and three complexes [L = L' = Q; L = sal-H, L' = bpyand L = ap, L' = phen have been synthesized. Triethylamine primarily serves the function of a reducing agent for the ruthenium(III) complexes thereby facilitating the dissociation of the Ru(II)-Cl bond (formed due to the reduction) followed by the subsequent incorporation of the L' ligand. It is interesting to note here that ruthenium undergoes a one-electron reduction during the course of the synthetic reaction [eq. (4)].

$$[\operatorname{Ru}^{\operatorname{III}}(\operatorname{PPh}_3)_2(L)\operatorname{Cl}_2] \xrightarrow[\operatorname{EtoH/reflux}]{EtoH/reflux} [\operatorname{Ru}^{\operatorname{II}}(\operatorname{PPh}_3)_2(L)(L')]^+$$
(4)

The characterization data of these $[Ru(PPh_3)_2]$ (L)(L')⁺ complexes [14] are given in Table 1. Microanalytical data agree well with the compositions of these complexes. All the three complexes are diamagnetic, confirming the +2 oxidation state of ruthenium (low-spin d^6 , S = 0) in these complexes. IR spectra of the $[Ru(PPh_3)_2(L)(L')]^+$ complexes show many vibrations, some of which are also observed in the spectra of their respective precursors. Some additional bands are observed in the fingerprint region of the spectra of $[Ru(PPh_3)_2(L)(L')]^+$, which are obviously due to the new coordinated ligand L'. The v(Ru-Cl) vibrations observed in the spectra of the precursor complexes, are absent as expected. Intense bands are observed near 1100 cm⁻¹ and 620 cm⁻¹ in the spectra of [Ru(PPh₃)₂(sal-H)(bpy)]ClO₄ and $[Ru(PPh_3)_2(ap)(phen)]ClO_4$ due to the presence of ClO₄.



Fig. 4. Least-squares plot of E_{298}^0 values of the Ru^{II}/Ru^{III} couple vs σ .

The spectral and cyclic voltammetric properties of $[Ru(PPh_3)_2(Q)_2]$, synthesized by us from $[Ru(PPh_3)_2(Q)Cl_2]$, are virtually identical to those of the *trans*-*trans*-*trans* isomer of this complex reported earlier [3b]. Hence $[Ru(PPh_3)_2(Q)_2]$, synthesized by us, is assumed to have the completely *trans* geometry. The $[Ru(PPh_3)_2(sal-H)(bpy)]^+$ and $[Ru(PPh_3)_2(ap)(phen)]^+$ complexes can exist in only one geometrical isomeric form provided the two PPh_3 ligands are *trans*, as assumed in their respective precursors. The displacement of the two chloride ions from $[Ru(PPh_3)_2(L)Cl_2]$ by L' [eq. (4)] therefore takes place without any gross change of stereochemistry.

All the three $[Ru(PPh_3)_2(L)(L')]^+$ complexes are soluble in acetonitrile. Conductivity measurements show that in solution $[Ru(PPh_3)_2(sal-H)(bpy)]ClO_4$ and $[Ru(PPh_3)_2(ap)(phen)]ClO_4$ complexes behave as 1:1 electrolytes ($\Lambda_M = 140$ and 155 ohm⁻¹ cm² M⁻¹ respectively) while $[Ru(PPh_3)_2(Q)_2]$ is a non-electrolyte, as expected. Electronic spectra of these three complexes have been recorded in acetonitrile solution (Table 1). Each complex shows several intense absorptions in the visible region which are probably due to allowed metal-to-ligand charge-transfer transitions.

Redox properties of the $[Ru(PPh_3)_2(L)(L')]^+$ complexes have been studied in acetonitrile solution (0.1 M TEAP) by cyclic voltammetry. Voltammetric data are given in Table 1. A reversible ruthenium(II)ruthenium(III) oxidation is displayed by all three complexes, the potential of which varies as L and L' are varied. In [Ru(PPh₃)₂(sal-H)(bpy)]⁺, this oxidation takes place at 0.72 V, which is approximately 1 V more positive than that of the ruthenium(II)ruthenium(III) couple in [Ru(PPh₃)₂(sal-H)Cl₂]. This shows that replacement of two chloride ions by one bpy stabilizes the bivalent state of ruthenium to a great extent. A similar shift in the ruthenium(II)ruthenium(III) potential was observed in the pair: $[Ru(bpy)_2Cl_2]$, (0.30 V) [15] and $[Ru(bpy)_3]^{2+}$, (1.30 V) [16]. One quasi-reversible one-electron reduction is observed in $[Ru(PPh_3)_2(sal-H)(bpy)]^+$ at -1.39 V, which is assigned to the reduction of the coordinated bpy. Each bpy is expected to show two one-electron reductions [17]. The second one-electron reduction of bpy, which is expected to occur at much more negative potential, has not been observed due to solvent cutoff. In [Ru(PPh₃)₂(ap)(phen)]⁺, the ruthenium(II)ruthenium(III) couple appears at 0.76 V, which is again ~1 V more positive than that in $[Ru(PPh_3)_2]$ (ap)Cl₂], as in the previous case. The one-electron reduction of phen is observed as a quasi-reversible process in $[Ru(PPh_3)_2(ap)(phen)]^+$ at -1.43 V.

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