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Synthesis and Characterization of some Ruthenium(V) Oxo Complexes of the Schiff Base, Bis(salicylaldehyde)-*o*-phenylenediamine, with Appended Cl^-, Imidazole and 2-Methylimidazole: the First Examples of Stable Oxo Complexes via Direct Oxygenation

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Abstract

Oxygenation of ruthenium(III) Schiff base complexes of the composition $K[Ru^{III}(Saloph)Cl_2]$ and $[Ru^{III}(Saloph)XCl]$ (Saloph = bis(salicylaldehyde)-*o*-phenylenediamine; X = imidazole (Im), 2-methylimidazole (2-MeIm)) with molecular oxygen gives the oxo derivatives of the composition, $[Ru^V(Saloph)X(O)]^+$ (X = Cl, Im or 2-MeIm). The oxo complexes were also synthesized by the reaction of $[Ru^{III}(Saloph)XCl]$ with PhIO or H_2O_2. The complexes thus obtained were characterized by analytical data, molar conductance, magnetic susceptibility, spectroscopic and electrochemical methods. Kinetics of the oxygenation reaction have also been investigated.

Introduction

Ever since the initial discovery by Tsumaki [1] that Schiff base complexes of Co(II) are oxygen carriers, there has been a continued interest in this property of Co(II) [2], Mn(II) [3], Fe(II) [4] and Cu(I) [5] complexes. Co(II) complexes have been widely used for oxygenation studies after the historical discovery of Calvin that Co(II) salen, 'Salcomine' [6, 7] was an oxygen carrier. Recently the 3-fluorosalicylaldehyde derivative, 'fluomine' [8] was found to be very useful in the separation of O_2 and N_2. Although several reports [9–13] have been published on platinum group metal Schiff base complexes, the studies are very much limited compared to the wealth of information on 3d transition metal Schiff base complexes [14–16].

Recently, several ruthenium(III) complexes of aminopolycarboxylic acids that exhibit reversible coordination with dioxygen were reported [17–19]. The ruthenium(III) Schiff base complexes, however, have not received much attention except for a few reports [10–12] on ruthenium(II) complexes with coordinated π-acidic groups such as PPh_3 and CO. Such complexes, however, show no reactivity towards molecular oxygen. With a view to developing new catalysts for oxidation reactions, we have synthesized simple ruthenium(III) Schiff base complexes with Cl, Im or MeIm as axial ligands. The kinetics of the oxidation of cyclohexene by molecular oxygen catalyzed by these complexes was reported elsewhere [20, 21]. These results have indicated that these complexes show catalytic activity comparable with that of Ru(III)–EDTA systems [22–24] in the oxidation of unsaturated hydrocarbons. The present work is confined to the synthesis and characterization of some Ru(V) oxo complexes $[Ru^V(Saloph)(X)(O)]$ obtained from the oxidation of $[Ru^{III}(Saloph)(X)Cl]$ systems (X = Cl, imidazole, 2-methylimidazole). The kinetics and mechanism of the oxidation of $[Ru^{III}(Saloph)(X)Cl]$ to $[Ru^V(Saloph)(X)(O)]$ have been investigated. These Ru(V) oxo complexes have relevance in catalysis and oxygen atom transfer reactions of the analogous unstable Fe(V)–oxo complexes in cytochrome P-450 oxidase [25, 26]. Though many oxo complexes of ruthenium have been obtained by indirect methods [27, 28], these complexes constitute the first series of stable Ru(V)–oxo complexes obtained directly from molecular oxygen.

Experimental

$RuCl_3 \cdot 3H_2O$ (Johnson and Mathey) was used as supplied. *o*-Phenylenediamine (Alpha Chemicals) was twice recrystallized from benzene. Salicylaldehyde was distilled prior to use. Imidazole (Im), 2-methylimidazole (2-MeIm) (Fluka Chemicals) and H_2O_2 (30% BDH) were of analytical grade and were used as such. All solvents used were of analytical grade and purified further by the established laboratory techniques [29] before use. Doubly distilled deionized

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water was used wherever necessary. The complex K$_2$[RuCl$_5$(H$_2$O)] [30], iodosyl benzene [31] and the Schiff base, bis(salicylaldehyde)-*o*-phenylenediamine-(Saloph-H$_2$) [32] were prepared according to literature procedures.

Preparation of Complexes

K[Ru(Saloph)Cl$_2$] (1), [Ru(Saloph)XCl] (X = Im, 2; 2-MeIm, 3)

These complexes were prepared as reported in a previous communication [21]. Physical properties and elemental analysis of the complexes are given in Table I.

[Ru^V(Saloph)X(O)]Cl (X = Cl, 4; Im, 5; 2-MeIm, 6)

These complexes were obtained by the following methods.

(a) Complex **1**, **2** or **3** (0.5 mmol) was dissolved in 20 ml of DMF and then stirred overnight under constant bubbling of oxygen. The products were precipitated by the addition of ether. The purity of the complexes were checked by TLC. Yield 57–60%.

(b) Complex **1**, **2** or **3** (0.5 mmol) was dissolved in 20 ml of 1:1 water–dioxane/DMF and then treated with 7 ml of 0.097 M H$_2$O$_2$ solution at room temperature. The reaction mixture was stirred for 6 h and the desired product then obtained by evaporating the solvent under vacuum and precipitation by ether. The purity of the complexes was checked by TLC. Yield 60–65%.

(c) Complex **1**, **2** or **3** (0.5 mmol) was dissolved in 20 ml of 1:1 water–dioxane/DMF, iodosyl benzene (0.5 mmol) was added in small fractions and the solution stirred for 6 h. The iodobenzene thus liberated was extracted with diethyl ether. The solution was evaporated almost to dryness and diethyl ether added to get the solid product. Yield 55–60%.

The microanalytical data of complexes **4**–**6** are given in Table I.

Physical Measurements

Microanalysis of the compounds was carried out at Australian Mineral Department Laboratory, Australia. Molar conductance was measured at room temperature on Digisun Electronics Conductivity Bridge. The room temperature magnetic susceptibility of the complexes was determined by Gouy method using Hg[Co(SCN)$_4$] as calibrant and experimental magnetic susceptibilities were corrected for diamagnetism [33]. The IR spectra were recorded on a Beckman Acculab 10 spectrometer in the range 4000–600 cm^{-1} and on a Perkin-Elmer 621 spectrometer in the range 600–200 cm^{-1} in Nujol mulls. Absorption spectra were recorded with a Shimadzu UV–Vis recording spectrophotometer model UV-160. Cyclic voltammograms were recorded with Princeton Applied Research (PAR) instrument as described earlier [19]. The kinetics of oxygenation was investigated using oxygen absorption technique [21].

Results and Discussion

Complexes **1**–**6** are light to dark brown in colour and highly stable in the solid state. The electrical conductivity of a freshly prepared solution of **1** (Table 1) corresponds to a 1:1 electrolyte whereas complexes **2** and **3** are found to be non-electrolytes. The conductivity values of 2 and 3 increase with time

TABLE I. Elemental Analysis, Conductivity and Magnetic Susceptibility Data

Complex	Analysis: found (calc.) (%)				M (mhos cm^{-2} mol^{-1})	μ_{eff} (BM)
	C	H	N	Cl		
1 K[Ru(Saloph)Cl$_2$]	44.7 (45.7)	3.0 (2.6)	5.2 (5.3)	13.0 (13.5)	115^a	1.97
2 [Ru(Saloph)ImCl]	52.9 (53.1)	3.5 (3.6)	10.4 (10.8)	6.6 (6.8)	53^a	2.02
3 [Ru(Saloph)(2-MeIm)Cl]	53.3 (54.0)	3.3 (3.7)	10.2 (10.5)	6.2 (6.6)	45^a	2.06
4 [Ru(Saloph)Cl(O)]	49.9 (51.4)	2.7 (3.0)	5.4 (6.0)	7.1 (7.60)	52^b	1.99
5 [Ru(Saloph)Im(O)]Cl	50.1 (51.7)	3.1 (3.4)	9.2 (10.5)	6.1 (6.6)	90^b	2.01
6 [Ru(Saloph)(2-MeIm)(O)]Cl	51.0 (52.4)	3.2 (3.8)	9.3 (10.2)	5.7 (6.4)	64^b	2.02

^{a}In methanol. ^{b}In dimethyl formamide.

TABLE II. UV–Vis and Selected IR Bands

Complex	Selected IR bands				λ_{max} (ϵ (M^{-1} cm^{-2}))
	ν(C=N)	ν(C–O)	ν(Ru–Cl)	ν(Ru–O)	
1 K[Ru(Saloph)Cl_2]	1588	1225	325		923w(52), 485b(4130), 368b(8695), 333sh(10160), 275s(12500)
2 [Ru(Saloph)ImCl]	1590	1238	328		920w(30), 483b(3010), 365(6250), 333sh(8000), 275s(12820)
3 [Ru(Saloph)(2-McIm)Cl]	1591	1237	346		919w(70), 488b(3440), 374b(5980), 333sh(6710), 270s(12265)
4 [Ru(Saloph)Cl(O)]	1588	1230	319	785	545(2865), 460s(4560), 367(5050), 336sh(5360), 269s(10160)
5 [Ru(Saloph)Im(O)]Cl	1592	1232		825	751b(2875), 463s(5170), 339sh(6100), 268s(8900)
6 [Ru(Saloph)(2-MeIm)(O)]Cl	1591	1234		819	610(2672), 470(5195) 333sh(6782), 270s(122265)
2a [Ru(Saloph)Im(O_2^-)]$^{+\,a}$					553b(3770), 455b(4910), 368b(6850), 333sh(9000), 275s(15090)

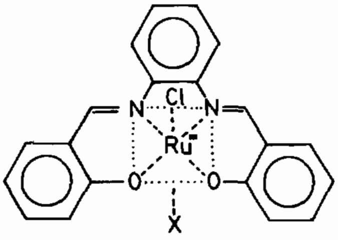
[a] Oxygenated solution of **2** in DMF after 2 h; s, strong; sh, shoulder; b, broad; w, weak.

indicating the lability of Cl^- ion in the complexes. The IR data of **1**–**6** are given in Table II with their assignments. All the complexes show the usual ligational bands of coordinated Saloph. Negative shifts observed in the ν(C=N) and ν(C–O) bands compared to the free ligand clearly indicate the coordination [34] of both azomethine and phenolic oxygen to the Ru(III) ion. The far-IR spectrum of complex **1** exhibits only one intense band at 325 cm^{-1} due to the ν(Ru–Cl) stretching mode indicative of *trans* configuration of chlorides [35]. Complexes **2** and **3** also show a band in the region 320–350 cm^{-1} due to the ν(Ru–Cl) mode along with the imidazole oriented bands.

The UV–Vis spectral data are summarized in Table II. All the bands are undoubtedly charge transfer in origin except a band around 900 nm which can be assigned to a forbidden ligand field transition. In the UV region an intense band at ~275 nm with a shoulder at 333 nm which are also present in the free ligand are assigned [10] to intra ligand π(Saloph) → π^*(Saloph) transitions. A moderately intense band at 485 nm can be attributed to the CT transition of the chloride ion [36]. Complexes **1**–**3** show magnetic moments in the range 1.92 to 2.06 BM at room temperature which are in the region expected for a low spin d^5 system.

The polarograms of **1**–**3** give two anodic waves between +0.2 to −0.15 V whose diffusion currents are dependent on the chloride ion concentration in solution. These waves are assigned to coordinated chloride. The Ru(III)/Ru(II) redox couple is observed in complexes **1**–**3** at −0.686, −0.701 and −0.655 V, respectively and is irreversible in nature. Such large negative values are expected for the Ru(III)/Ru(II) couple because of the presence of electron rich donors in the axial position. The values become even more negative for an appended imidazole in complex **2**. The lowering of the value in **3** may be because of the steric effect of the axial-2-methylimidazole.

Based on the above evidences together with the analytical data, the geometry of complexes **1**–**3** can be assigned as shown in Scheme 1.



Scheme 1. X = Cl, **1**; Im, **2**; 2-MeIm, **3**.

Interaction of **1**–**3** with molecular oxygen in DMF/water–dioxane mixture gave the oxo–Ru(V) complexes **4**–**6** respectively. Based on the conductivity values complex **4** is a non-electrolyte and complexes **5** and **6** are 1:1 electrolytes. The IR spectra of **4**–**6** give an intense band around 785–825 cm^{-1} (Fig. 1b and c) corresponding to the ν(Ru=O) stretch [28, 37]. This band is absent in complexes **1**–**3**; representative spectrum of complex **2** is given in Fig. 1a for comparison. As expected the ν(Ru=O) frequency in **5** and **6** is shifted to higher values as compared to **4** (785 cm^{-1}) by coordination of imidazole and 2-methylimidazole in the axial position, indicative of a strengthening of the ν(Ru=O) bond by σ-donation from the axial group. The

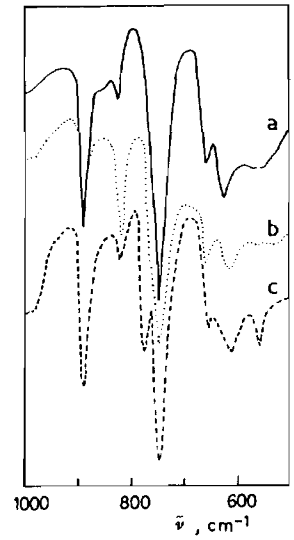


Fig. 1. Infrared spectra of representative unoxygenated and oxygenated complexes in 1000–500 cm^{-1} region: (a) [Ru(Saloph)(Im)Cl] (**2**); (b) [Ru(Saloph)(Im)O] (**5**); (c) [Ru(Saloph)Cl(O)] (**4**).

ligational IR modes of complexes **4**–**6** are similar to those of **1**–**3** indicating that the Saloph and imidazole units remain intact in the oxidation process. Complex **4** exhibits ν(Ru–Cl) at 319 cm^{-1}. This mode is absent in complexes **5** and **6**.

On oxygenation, complexes **1**–**3** showed similar spectral changes as described herewith for complex **2** as an example. On oxygenation of solution of **2** in DMF, two new bands appeared at 455 and 553 nm which disappear on flushing nitrogen through the solution. These spectral changes are attributed to the coordination of O_2 to Ru(III) in **2** to form a Ru(IV) superoxo complex of composition, [Ru^{IV}(Saloph)Im(O_2^-)]$^+$ (**2a**). These two new bands at 455 and 553 nm are assigned to LMCT and MLCT bands of the coordinated superoxo group in **2a**, respectively. Stoichiometric studies of oxygen absorption also indicated that one mole of oxygen is absorbed per mole of the complex in **2a** thereby suggesting the formulation of **2a** as a Ru(IV) superoxo complex. On ageing of the solution of **2a**, the intensity of the band at 455 nm increases with the shift to 463 nm whereas the intensity of the 365 and 553 nm bands decrease with the appearance of two isobestic points at 418 and 525 nm (Fig. 2). These changes support the conversion of **2a** into a stable Ru(V)–oxo species **5** which is isolated from the solution after 12 h and is characterized by comparing its UV–IR and electrochemical data with the samples synthesized by the reaction of **2** with PhIO/H_2O_2. Complexes **1** and **3** gave the oxo complexes **4** and **6**, respectively in a similar manner. The new bands observed in **4**–**6** at 460, 463 and 470 nm, respectively are assigned to O(π^*) → t_{2g} Ru(V) transition. The ligand field transitions are observed in these complexes as low intensity bands in the region 545–721 nm.

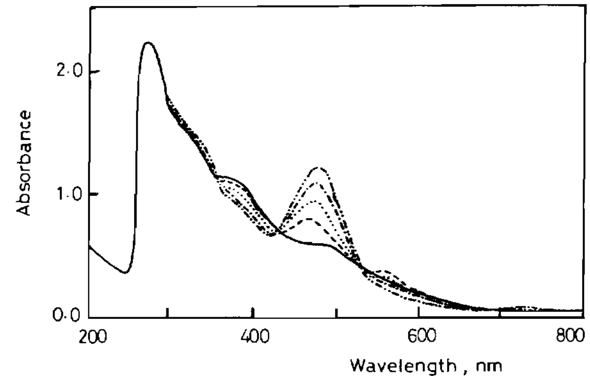


Fig. 2. The UV–Vis absorption spectral changes during oxygenation of [Ru(Saloph)(Im)Cl] (1 mM) in DMF with time; (——) soon after preparation; (– – –) after 6 h; (······) 12 h; (–·–) 24 h; (–··–) 96 h at t = 303 K and path length (l) = 0.2 cm.

Based on the kinetic studies the following mechanism is proposed for the formation of Ru(V) oxo complexes **4**–**6** from **1**–**3**, respectively.

$$\underset{\mathbf{1\text{–}3}}{[\mathrm{Ru^{III}(Saloph)XCl}]} \overset{K_1}{\rightleftharpoons} \underset{\mathbf{1a\text{–}3a}}{[\mathrm{Ru^{IV}(Saloph)X(O_2^-)}]} \quad (1)$$

$$\underset{\mathbf{1a\text{–}3a}}{[\mathrm{Ru^{IV}(Saloph)X(O_2^-)}]} \xrightarrow{k} \underset{\mathbf{4\text{–}6}}{[\mathrm{Ru^{V}(Saloph)X(O)}]} + 1/2O_2 \quad (2)$$

The formation constant K_1 for the superoxo complexes **1a**–**3a** were determined directly from the equilibrium oxygen absorption method as described by Chen and Martell [38]. The rate constant k was obtained by the spectrophotometric method by following the increase in the intensity of the bands at 460, 463 and 470 nm (Fig. 3). The data is tabulated in Table III The values reflect the effect of the axial ligand on the stability of the dioxygen complexes. The oxygenation constant K_1 increases from **1** to **2** which is expected as the imidazole is more σ-basic than chloride. The presence of a σ-basic imidazole in the axial position increases the electron density at the metal centre and facilitates the formation of the superoxo species by an electron transfer to dioxygen [38]. In the case of **3**, although 2-MeIm is more basic than imidazole, the K_1 value was found to be lower than **2**. This may be due to the steric hindrance by the methyl group in 2-MeIm which seems to predominate in reducing the value of K_1 in **3** in contrast to its basicity.

The formation of superoxo complexes in the equilibrium step K_1 is further supported by the electro-

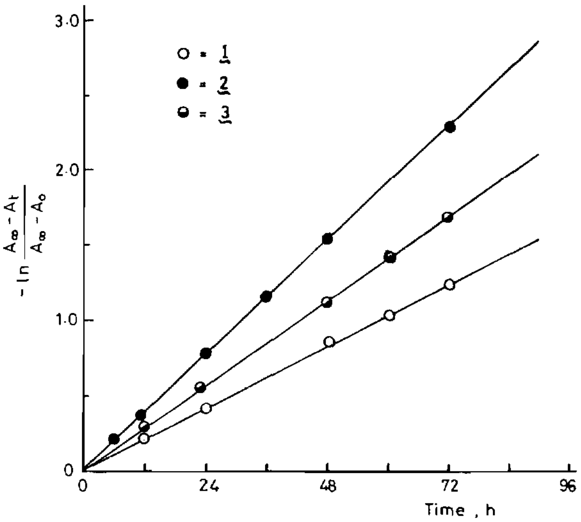


Fig. 3. First order rate constant plot for the reaction $[Ru^{IV}(Saloph)(X)(O_2^-)] \rightarrow [Ru^{V}(Saloph)(X)O] + 1/2O_2$ in DMF at 303 K.

TABLE III. Equilibrium Constant and Rate Constant Data for the Oxygenation of Complexes 1–3 in DMF at 303 K

Complex	$\log K_1$	$k \times 10^4$ (min^{-1})
1 $K[Ru^{III}(Saloph)Cl_2]$	2.34	2.83
2 $[Ru^{III}(Saloph)(Im)Cl]$	3.04	5.27
3 $[Ru^{III}(Saloph)(2\text{-}Me\text{-}Im)Cl]$	2.76	3.89

chemical studies of the oxygenated solutions of 1–3. The oxygenated solutions of 1–3 show three cathodic waves, two at –0.243 and –0.420 V in 1, –0.277 and –0.482 V in 2, –0.293 and –0.584 V in 3 and the third at –0.760 V in all the complexes. The first wave in the range –0.243 to –0.293 V is assigned to the redox couple Ru^{IV}/Ru^{III}. The second redox step in the range –0.420 to –0.585 V is assigned to the Ru(III)/Ru(II) couple. The third step at a more negative potential –0.760 V is assigned to a reversible one electron reduction of oxygen to superoxide [39]. On ageing of the solution the total diffusion currents of the first two reduction steps are shifted to more negative potentials, accompanied by a decrease in the O_2/O_2^- wave. The electrochemical reactions of 1–3 oxygenated solution can thus be written as follows

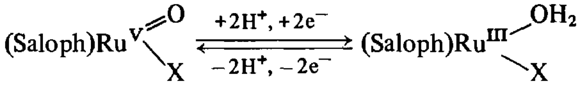
$$[Ru^{IV}(Saloph)X(O_2^-)] + e \xrightarrow{-0.243 \text{ to } 0.293\ V} [Ru^{III}(Saloph)X(O_2^-)] \quad (3)$$

$$[Ru^{III}(Saloph)(O_2^-)X] + e \xrightarrow{-0.420 \text{ to } -0.542\ V} [Ru^{II}(Saloph)X] + O_2^- \quad (4)$$

$$O_2 + e \xrightarrow{-0.760\ V} O_2^- \quad (5)$$

A direct evidence for the formation of the Ru(V) oxo species in step (2) is the cyclic voltammetric studies of complexes 4–6 obtained by direct oxygenation and their comparison with the authentic samples prepared by the reactions of 1–3 with PhIO or H_2O_2. The cyclic voltammogram of complex 4 in the presence and absence of 0.1 M $HClO_4$ in 1:1 water–dioxane ($\mu = 0.1$ M $NaClO_4$) is shown in Fig. 4. In the presence of 0.1 M $HClO_4$ the Ru(V)/Ru(III) couple appears at +0.418 V. The $E_{1/2}$ value of the above couple (Fig. 5) shifts linearly with pH in the range 0.0 to 4.5 pH with a gradient of 60–70 mV/pH. These studies could not be extended to higher pH values because of the decomposition of the complexes at higher pH. The peak to peak separation of the Ru(V)/Ru(III) couple is about 30–35 mV which is sufficient for a two electron redox process. The CV is reproduced upon the repetitive scannings indicating the quasi-reversible nature of Ru(V)/Ru(III) couple.

The pH dependence of the Ru^{V}/Ru^{III} couple of complexes 4–6 at lower pH 0.0–4.5 suggests the electron proton reaction as shown below



$$(Saloph)Ru^{V}(=O)(X) \underset{-2H^+,\,-2e^-}{\overset{+2H^+,\,+2e^-}{\rightleftharpoons}} (Saloph)Ru^{III}(OH_2)(X)$$

X = Cl, Im, 2-MeIm.

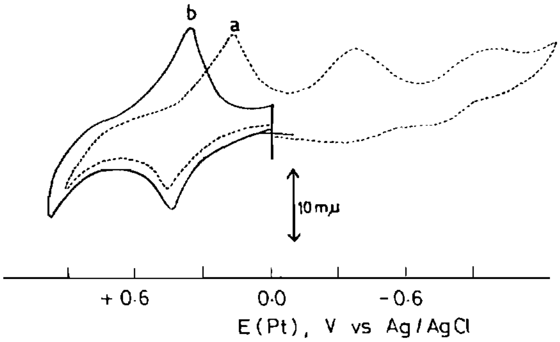


Fig. 4. CV of [Ru(Saloph)Cl(O)] (1 mM) in 1:1 water–dioxane (a) at its own pH 4.5 and (b) pH 1.18; $\mu = 0.1$ M $NaClO_4$ at 25 °C. Scan rate (ν) at 100 mV/s.

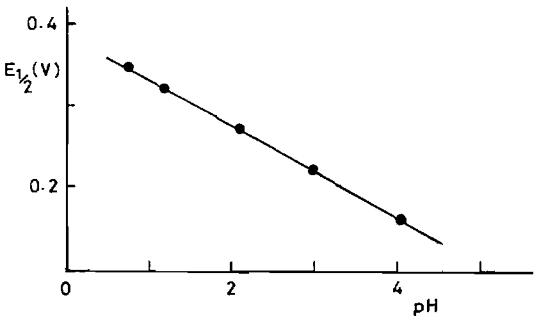
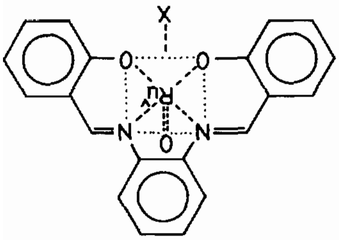


Fig. 5. Plot of $E_{1/2}$ *vs.* pH for the Ru(V)/Ru(III) couple in [Ru(Saloph)Cl(O)].

The Ru(III)/Ru(II) redox couple for complexes **4–6** is observed at the Pt electrode in the absence of 0.1 M $HClO_4$ at −0.720, −0.815 and −0.710 V, respectively. These values are slightly shifted to negative values as compared to the values of the Ru^{III}/Ru^{II} couple in complexes **1–3**.

The magnetic susceptibility of **4–6** in the solid state give the values of 1.99, 2.01 and 2.02 BM, respectively corresponding to Ru(V) with spin paired $(t_{2g})^3$ configuration. Based on the information, Scheme 2 is proposed for complexes **4–6**.



Scheme 2. X = Cl, **4**; Im, **5**; 2-MeIm, **6**.

The rate constants for decomposition of the superoxo complexes **1a–3a** to **4–6** are tabulated in Table III. These constants decrease in the same order as that of the decrease in stability of the superoxo complexes, *i.e.* **2**, **3**, **1**. The rate of decomposition of **3** and **2** is more than that of **1**, which shows the inductive effect of the imidazole group in stabilizing complexes **5** and **6**. The rate of decomposition of superoxo to the oxo species also reflects the thermodynamic stability of the oxo complex. This can be roughly measured by the ν(Ru=O) stretching frequency which is 825, 819 and 785 cm^{-1} for **1–3**, respectively.

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