Inorganica Chimica Acta, *174* (1990) 175–184

Oxygenation and Carbonylation Studies of some Ruthenium(III) Schiff Base Complexes Containing Nitrogen and Oxygen as Donor Atoms. II

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(Received January 2, 1990)

Abstract

Synthesis and characterization of a series of ruthenium(III) Schiff base complexes of the type [$Ru^{III}LXY$] where L = Schiff base viz. bis(naphthaldehyde)-*o*-phenylenediimine (naphoph), bis(naphthaldehyde)ethylenediimine (naphen), bis(naphthaldehyde)propylenediimine (naphprop) and bis(naphthaldehyde)diethylenetriimine (naphdien); X = Cl and Y = Cl imidazole (Im) or 2-methylimidazole (2-MeIm) are reported. Elemental analysis, conductivity and IR studies of the complexes suggest an octahedral geometry around ruthenium. Magnetic moments of the complexes indicate a single unpaired electron in a low spin d^5 configuration. Oxygenation studies in DMF or THF solutions suggest the reversible binding of molecular oxygen to the ruthenium(III) complexes. EPR studies at liquid nitrogen temperature and UV–Vis measurements at room temperature support the formation of a Ru(IV) superoxo species [$Ru^{IV}L(O_2^{\cdot})^-Y$]. The EPR spectrum of the Ru(IV) superoxo complex at 77 K ($g_1 = 2.063$, $g_2 = 2.047$, $g_3 = 2.023$) is consistent with the odd electron occupying a highly localized antibonding π^* orbital of molecular oxygen. The reversible binding of O_2 and CO has been carried out in DMF at 10, 25 and 40 °C. The complexes show discrimination against the binding of CO over O_2 as evinced by values of K_{O_2} and K_{CO} in the complexes. The thermodynamic paramegers ΔH°, ΔG° and ΔS° for oxygenation and carbonylation reactions are evaluated.

Introduction

The reversible binding of molecular oxygen to transition metal complexes has received a great deal of attention in recent years [1–5]. Some of the synthetic systems reported to bind molecular oxygen reversibly are cobalt(II) complexes [5–8], where it has been demonstrated that a wide variety of ligand environment having donor atoms N_2O_2 [7, 8] and N_4 around the metal ion result in reversible coordination of dioxygen [7, 8]. Several other ions such as Fe(II) [9], Mn(II) [4, 10], Cu(I) [11] and Ni(II) [12] which have readily available multi-oxidation states were found to be most promising in oxygenation studies and occupied a key position in the development of dioxygen coordination chemistry. A systematic study on Co(II) complexes [13] has suggested that the type of ligand environment which can increase the electron density at the metal centre and the ease with which the metal ion can go to higher oxidation states are important factors effecting the stability of dioxygen complexes [14, 15]. Except for Co(II) Schiff base complexes the reversible oxygen binding capacity at ambient conditions is almost non-existent for other metal ions [4, 5].

Carbonyl complexes of some transitions metal ions especially those of ruthenium play an important role in homogeneous catalysis of carbonylation and oxo reactions [16–18]. Most of the work on metal carbonyls is restricted to metal ions in a lower oxidation state [19] which are stabilized by CO. The study of mixed ligand carbonyls of ruthenium in aquo medium is however restricted because of the hydrolytic tendencies [20, 21] of the metal ion. Reaction of $RuCl_3 \cdot xH_2O$ with CO in acidic medium [22] has been reported to give the octahedral [$RuCl_5(CO)$]$^{2-}$ ion for which EPR and MO studies have been carried out [23].

In continuation of our earlier work on oxygenation [24, 25] and carbonylation [26] of ruthenium(III) Schiff base complexes, we are reporting in this paper the synthesis and characterization of some ruthenium(III) Schiff base complexes of the type [$Ru^{III}LXY$] derived from the condensation of naphthaldehyde and amines where L = Schiff bases and Y = Cl, Im, 2MeIm. The reversible binding of O_2 and CO by these complexes was carried out in order to assess the difference in their dioxygen and CO affinities with the variation of the σ-donor capacity of the ligand coordinated to the metal ion. The complexes show a higher affinity for O_2 compared to CO,

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0020-1693/90/$3.50

$\log K_{CO} < \log K_{O_2}$. Such discrimination plays an important role in preventing poisoning by CO in hemoproteins [27–30]. In hemoglobin the distal effect of histidine produced by the globin chain is a major factor in discrimination. In the present complexes we believe that the effect may be partly due to the steric effect of the ligated naphthaldehyde moiety and partly due to the electronic effect of Ru^{3+}. The stability of the dioxygen and carbonyl complexes varies in the order naphoph > naphdien > naphprop > naphen in the equatorial ligands and Im > 2-MeIm > Cl for the axial ligands. The enthalpy and entropy of formation of dioxygen complexes are more negative than those for carbonyl complexes.

Experimental

$RuCl_3 \cdot 3H_2O$ (Johnson and Mathey), naphthaldehyde (Aldrich), ethylenediamine, imidazole, 2-methylimidazole (Fluka) and orthophenylenediamine (Alpha) were recrystallized twice from benzene before use. The Schiff bases bis(naphthaldehyde)-*o*-phenylenediimine (naphoph), bis(naphthaldehyde)-ethylenediimine (naphen), bis(naphthaldehyde)-propylenediimine (naphprop), bis(naphthaldehyde)-diethylenetriimine (naphdiene) were prepared according to known procedures [31]. All the complexes were prepared under oxygen free atmosphere. The progress of the reaction was checked by TLC from time to time.

Preparation of Complexes

Bis(naphthaldehyde)-o-phenylenediiminatodichlororuthenate(III), K[Ru(naphoph)Cl₂] (1); bis(naphthaldehyde)ethylenediiminatodichlororuthenate(III), K[Ru(naphen)Cl₂] (2); bis(naphthaldehyde)propylenediiminatodichlororuthenate(III), K[Ru(naphprop)Cl₂] (3)

Hot ethanolic solutions (1.0 mmol) of the above ligands were added to 1.0 mmol of $K_2[RuCl_5(H_2O)]$ in 1:1 M:L ratio. The reaction mixture was refluxed up to 10–25 h in argon atmosphere. After completion of the reaction as checked by TLC the solution was filtered in argon atmosphere and the filtrate concentrated to about 10 ml. The complexes were precipitated from the filtrate by diethyl ether or ethyl acetate and recrystallized from ethyl acetate and dried *in vacuo*. Yield 65%. Complex **1** is dark brown, **2** and **3** are dark green in colour.

Bis(naphthaldehyde)-o-phenylenediiminatochloroimidazoleruthenium(III), [Ru(naphoph)(Im)Cl] (4); bis(naphthaldehyde)-o-phenylenediiminatochloro-2-methylimidazoleruthenium(III), [Ru(naphoph)(2-MeIm)Cl] (5); bis(naphthaldehyde)ethylenediiminatochloroimidazoleruthenium(III), [Ru(naphen)(Im)Cl] (6); bis(naphthaldehyde)ethylenediiminatochloro-2-methylimidazoleruthenium(III), [Ru(naphen)(2-MeIm)Cl] (7); bis(naphthaldehyde)propylenediiminatochloroimidazoleruthenium(III), [Ru(naphprop)(Im)Cl] (8); bis(naphthaldehyde)-propylenediiminatochloroimidazoleruthenium(III) [Ru(naphprop)(2-MeIm)Cl] (9)

These complexes were synthesized from their parent dichloro complexes **1**–**3**. After the completion of the synthesis of the dichloro complexes, the axial base ligand was added in a 1:1 molar ratio of axial base to the complexes to the reaction mixture which was further refluxed for 8–10 h and the completion of the reaction checked by TLC. The compounds were isolated and recrystallized as described for the preparation of complexes **1**–**3**. Yield 60%.

Bis(naphthaldehyde)diethylenetriiminatochlororuthenium(III) [Ru(naphdien)Cl] (10)

Bis(naphthaldehyde)diethylenetriimine (1.0 mmol) was dissolved in ethanol and mixed with $K_2[RuCl_5(H_2O)]$ 1.0 mmol in 1:1 metal to ligand ratio. The reaction mixture was refluxed for 5–6 h in argon atmosphere. After completion of the reaction the product was filtered washed with ethanol and recrystallized in dry diethyl ether and ethyl acetate. The complex was dried *in vacuo*. Yield 63%.

Physical Measurements

Microanalyses of the complexes were done by a Carlo Erba Analyzer model 1106. Molar conductance was measured at room temperature on a Digisun Electronics conductivity bridge. The IR spectra were recorded on Nicolet 200 SXV FT-IR spectrometer in nujol mulls/KBr. Electronic spectra were recorded on a Shimadzu UV–Vis recording spectrophotometer model 160. Cyclic voltammograms, d.c. polarograms and differential pulse polarograms were recorded with a Princeton Applied Research (PAR) instrument as described earlier [26]. The magnetic moment measurements were done at 298 K by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant and experimental susceptibilities were corrected for diamagnetism. The EPR spectra was recorded on a Bruker Scientific X-band spectrometer (ESP-300) using a 100 KHz field modulation and the values determined calibrated with DPPH powder ($g = 2.0036$).

Oxygen Uptake Measurements

The kinetics of oxygenation of all Schiff base complexes was investigated by oxygen absorption technique in DMF at 10, 25 and 40 °C with the help of a manometric set-up [24–26]. The solubility of dioxygen was also measured separately in DMF at these three temperatures. The vapour pressure of the solvent was negligible over the temperature employed in this investigation. From the stoichiometry of the reaction determined by dioxygen uptake and the corrected partial pressure of dioxygen at equilibrium, the oxygenation constant K_{O_2} as defined by eqn. (1) was calculated [14].

$$ML + O_2 \rightleftharpoons MLO_2 \qquad (1)$$

$$K_{O_2} = \frac{[MLO_2]}{[ML][O_2]}$$

The $P_{1/2}$ value (equilibrium O_2 pressure at half saturation) was calculated by the expression

$$P_{1/2} = \frac{K_h}{K_{O_2}}$$

where K_h = Henry's law constant given by the reciprocal of the solubility of O_2 in the medium at 1 atm. at a particular temperature.

CO Uptake Measurements

In order to calculate equilibrium constant K_{CO} by UV–Vis spectrophotometry, the solution of the complexes was prepared in the concentration range of about 5×10^{-4} M in DMF saturated with CO by varying the concentration of CO in the range 1:1, 1:2 and 1:3 with respect to the degassed DMF. The spectrum was recorded immediately at 10, 25 and 40 °C by monitoring the peaks around (λ_{max} = 406–560 nm) and a constant value of absorbance was noted for each set. The solubility of CO was also measured separately in DMF at varying temperatures. The reaction of the complexes with CO may be written as

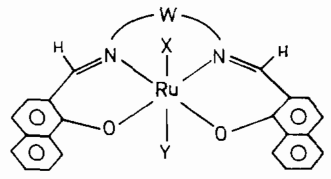
$$ML + CO \rightleftharpoons MLCO$$

$$K_{CO} = \frac{[MLCO]}{[ML][CO]}$$

The equilibrium constant K_{CO} was calculated by the reported method [32].

Results and Discussion

The analytical data of the solid ruthenium(III) Schiff base complexes along with their conductivity results in DMF are given in Table 1. The data are consistent with the formation of octahedral ruthenium(III) complexes with the general composition [RuLXY], where L = Schiff base, X = Cl and Y = Im or 2-MeIm. Millimolar solutions of the complexes 1–3 in DMF are 1:1 electrolytes while *trans*-substituted imidazole or 2-methylimidazole complexes are non-electrolytes. The magnetic moments μ_{eff} of the complexes are in the range 1.97–2.08 BM which confirms the complexes to be of the paramagnetic spin paired $4d^5$ system.



Complexes		W	X	Y
1,2,3	Naphoph	(C_6H_4)-	Cl	Cl, Im, 2MeIm
4,5,6	Naphen	$(CH_2)_2$-	Cl	Cl, Im, 2MeIm
7,8,9	Naphprop	$(CH_2 \cdot CH \cdot CH_3)$-	Cl	Cl, Im, 2Me Im
10	Naphdien	$(C_2H_2)NH(C_2H_2)$-	N of W	Cl, Im, 2Me Im

IR Spectra

The IR spectra of the Schiff base ligands showed a broad band near 3380 cm^{-1} due to ν(O–H). This band disappeared on complexation with ruthenium. The band due to ν(C–O) at 1280 cm^{-1} in the free ligands was slightly shifted to lower wave number on coordination [33]. A strong band in the range 1625–1635 cm^{-1} assigned to the azomethine group (H–C=N) in the free ligand was shifted by 10 to 20 cm^{-1} towards lower frequency in the complexes. This not only suggests the coordination of the azomethine N to the metal ion but also the participation of the Schiff base ligand in a dianionic tetradentate or pentadentate coordination mode. The ν(M–Cl) bands were more intense than the ν(M–N) bands and were observed around 325 cm^{-1} in all the complexes. In the case of complexes involving imidazole and 2-methylimidazole the bands corresponding to Im and 2-MeIm groups were observed near 600 and 1000 cm^{-1}, respectively (Table 2).

The electronic spectra of all the Schiff base complexes were recorded in DMF. The strong band near 300 nm is assigned to $\pi \rightarrow \pi^*$ transitions from the benzene ring and the double bond of the azomethine groups. The band at 350 nm is due to the $n\pi^*$ transition of non-bonding electrons present in the nitrogen of the azomethine group. This band on complexation undergoes hypsochromic shift. The bands in the range 470–490 nm were assigned to LMCT bands.

All the complexes are paramagnetic and thus EPR active. The EPR spectrum of the complex K[Ru(naphoph)Cl_2] shown in Fig. 1(a) as DMF/THF frozen glass solution at 77 K exhibited three g features at g_1 = 2.310, g_2 = 2.162, g_3 = 1.849 corresponding to a Ru(III) octahedral system with an unpaired electron occupying the d_{xy} orbital of the t_2 level [34–36].

The above experimental data support the formation of octahedral ruthenium Schiff base complexes with tervalent ruthenium. The Schiff bases naphen, naphprop and naphoph participate as tetradentate ligands with coordinating atoms N_2O_2 occupying the

TABLE 1. Analytical data and molar conductance of ruthenium(III) Schiff base complexes

No.	Complex	Analysis[a] (%)				Ω_M (ohm^{-1} cm^2 mol^{-1})
		C	H	N	Cl	
1	K[Ru(naphoph)Cl$_2$]	53.50 (53.84)	2.20 (2.60)	4.20 (4.28)	11.00 (11.20)	80
2	[Ru(naphoph)(Im)Cl]	56.43 (56.83)	3.40 (3.88)	9.35 (9.81)	5.90 (5.22)	10
3	[Ru(naphoph)(2-MeIm)Cl]	59.98 (60.70)	3.45 (3.82)	8.20 (8.84)	5.00 (5.60)	09
4	K[Ru(naphen)Cl$_2$]	49.50 (50.00)	3.01 (3.14)	4.30 (4.85)	12.02 (12.14)	65
5	[Ru(naphen)(Im)Cl]	56.25 (56.79)	3.30 (3.89)	9.30 (9.80)	6.10 (6.21)	15
6	[Ru(naphen)(2-MeIm)Cl]	56.89 (57.01)	4.00 (4.14)	9.35 (9.95)	5.65 (6.00)	08
7	K[Ru(naphprop)Cl$_2$]	50.32 (50.84)	3.10 (3.41)	4.45 (4.74)	11.85 (12.02)	73
8	[Ru(naphprop)(Im)Cl]	57.32 (57.10)	4.15 (4.46)	9.20 (9.54)	5.40 (5.97)	07
9	[Ru(naphprop)(2-MeIm)Cl]	57.25 (57.98)	4.25 (4.69)	9.15 (9.32)	5.20 (5.83)	06
10	[Ru(naphdien)Cl]	57.00 (57.19)	4.00 (4.24)	6.96 (7.69)	6.10 (6.50)	12

[a] Calculated values are given in parentheses.

TABLE 2. IR stretching frequencies and UV–Vis data of ruthenium(III) Schiff base complexes

No.	Complex	ν(C–O) (cm^{-1})	ν(C=N) (cm^{-1})	ν(M–Cl) (cm^{-1})	Imidazole peaks (cm^{-1})	λ_{max} (ϵ (M^{-1} cm^{-2}))
1	K[Ru(naphoph)Cl$_2$]	1265	1600	325		495(4835), 405(4200), 370(6250), 302(2030)
2	Ru(naphoph)(Im)Cl]	1270	1595	320	618, 650, 1068	485(4785), 400(4190), 372(6255), 300(12030)
3	[Ru(naphoph)(2-MeIm)Cl]	1260	1605	325	610, 668, 1149	490(4780), 404(4185), 375(6322), 302(12035)
4	K[Ru(naphen)Cl$_2$]	1250	1600	324		495(4800), 402(4195), 371(6253), 300(12020)
5	Ru(naphen)(Im)Cl	1265	1590	325	619, 660, 1143	495(4825), 404(4190), 368(6252), 305(12032)
6	Ru(naphen)(2-MeIm)Cl	1260	1600	325	625, 670, 1149	493(4930), 404(4195), 373(6249), 300(12040)
7	Ru(naphprop)Cl$_2$	1270	1605	325		490(4820), 400(4200), 370(6255), 305(12010)
8	Ru(naphprop)(Im)Cl	1265	1610	324	618, 670, 1150	493(4802), 402(4199), 370(6253), 302(12035)
9	Ru(naphprop)(2-MeIm)Cl	1275	1605	325	615, 660, 1142	492(4830), 405(4195), 369(6253), 302(12030)
10	Ru(naphdien)Cl	1250	1600	325		490(4828), 404(4190), 370(6252), 300(12035)

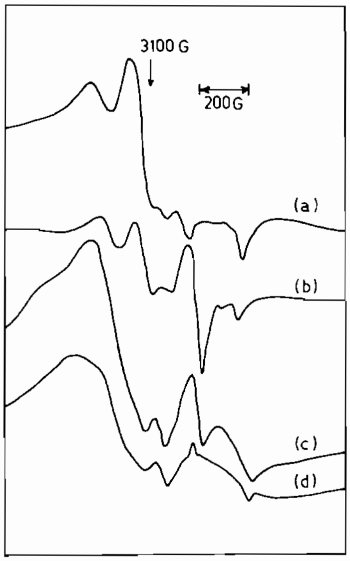


Fig. 1. X-band EPR spectra of K[Ru(naphoph)Cl_2] at 77 K in THF: (a) unoxygenated, (b) oxygenated, $t = 0$ min; (c) solution of (b) at $t = 6$ h; (d) solution of (b) at 15 h.

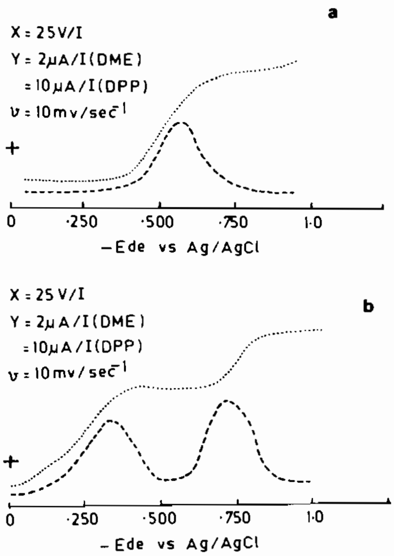


Fig. 2. Polarogram and differential pulse polarogram of K[Ru(naphoph)Cl_2] (1 mM) solution at 25 °C in DMF solvent using tetrabutyl ammonium perchlorate as supporting electrolyte: (a) under nitrogen, (b) under oxygen.

basal plane of the Ru(III) octahedron while naphdien coordinates as a pentadentate ligand with the coordinating atoms N_3O_2 and with the bridging nitrogen of the two imine groups occupying one of the axial positions of the octahedron.

Oxygenation Studies

Oxygen uptake measurement by the manometric technique shows that complexes **1**–**10** take up one mole of oxygen per mole of the complex which supports a 1:1 stoichiometry of metal ion to dioxygen in the complexes. Oxygenation of the complexes results in the reversible oxidation of Ru(III) to a formal Ru(IV) oxidation state with the reduction of O_2 to superoxide ion O_2^-. The formation of Ru(IV) in the oxygenated solution was confirmed by electrochemical studies (Table 3). The cyclic voltammetry, DC polarograms and differential pulse polarograms of the complex were recorded in N_2 as well as in O_2 atmosphere. The Ru(III)/Ru(II) redox couple observed under N_2 atmosphere lies in the range −0.430 to −0.701 V versus Ag/AgCl for all the complexes (Fig. 2(a)). However, when the same solutions were flushed with oxygen two waves appeared (Fig. 2(b)), one in the range −0.210 to −0.378 V which is assigned to the Ru(IV)/Ru(III) couple and the other in the range −0.708 to 0.762 V due to reduction of dissolved molecular oxygen ($O_2 + e^- \rightarrow O_2^-$) [37]. The Ru(III)/Ru(II) couple is masked under the O_2/O_2^- reduction. By flushing nitrogen for 15 to 20 min through the oxygenated solutions, the waves

TABLE 3. Polarographic data for Ru(III) Schiff base complexes in DMF ($E_{1/2}$ V vs. Ag/AgCl)

No.	Complex	Fresh solution under N_2	Oxygenated solution under O_2	
		Ru(III)/(II)	Ru(IV)/(III)O_2^-	Ru(III)/(II)O_2^- [a]
1	K[Ru(naphoph)Cl_2]	−0.552	−0.345	−0.724
2	[Ru(naphoph)(Im)Cl]	−0.606	−0.378	−0.750
3	[Ru(naphoph)(2-MeIm)Cl]	−0.576	−0.368	−0.724
4	K[Ru(naphen)Cl_2]	−0.504	−0.315	−0.720
5	[Ru(naphen)(Im)Cl]	−0.575	−0.347	−0.750
6	[Ru(naphen)(2-MeIm)Cl]	−0.551	−0.315	−0.708
7	K[Ru(naphprop)Cl_2]	−0.551	−0.343	−0.730
8	[Ru(naphprop)(Im)Cl]	−0.630	−0.375	−0.709
9	[Ru(naphprop)(2-MeIm)Cl]	−0.605	−0.365	−0.717
10	[Ru(naphdien)Cl]	−0.543	−0.336	−0.715

[a] The currents of this couple are catalyzed by O_2 in solution and overlapped with the O_2/O_2^- couple.

due to Ru(IV)/Ru(III) and O_2/O_2^- disappeared with the appearance of the Ru(III)/Ru(II) couple at the same potential as was observed for the parent complexes under nitrogen, indicating the reversible binding of molecular oxygen to ruthenium(III) Schiff base complexes. The UV–Vis spectra of the complexes were recorded as a function of time in DMF/THF solutions after passing O_2 for 10 min. Such a spectrum for $K[Ru(naphoph)Cl_2]$ in DMF is shown in Fig. 3. Soon after passing oxygen through the solution, two new bands were observed at 545 and 410 nm which were assigned to LMCT bands of superoxo ion to Ru(IV). This behaviour was also reported by Chen and Martell [14]. EPR spectra of the complexes in oxygenated THF further support the formation of Ru(IV)–superoxo species. Representative EPR spectra of $K[Ru(naphoph)Cl_2]$ in THF at liquid nitrogen temperature (before and after oxygenation) are shown in Fig. 1. On oxygenation, the lines due to the parent Schiff base complexes partially disappeared and three new g features at $g_1 = 2.063$, $g_2 = 2.047$ and $g_3 = 2.026$ characteristic of the superoxo group appeared. The observed g values are in agreement with those reported earlier [38, 39] for the superoxo ion.

The g values of the superoxide anion indicate that the unpaired electron resides on the oxygen π^* orbitals having a little admixture of the metal d orbitals. The rhombic nature of the g tensor suggests that the Ru–O_2 fragment is non-linear. Oxygenation of the Ru(III)–Schiff base complex, therefore, takes place by transferring an electron from ruthenium +3 state to O_2 which is reduced to the superoxide anion and ruthenium is oxidized to a formal +4 state.

The Ru(IV) superoxo complex $[RuL(O_2)^-Y]$ is stable at liquid nitrogen temperature and slowly loses O_2 at room temperature to form the Ru(III) Schiff base complex. The deoxygenation is complete at room temperature in 15 h when the superoxo complex is completely converted back to the parent complex. The conversion was monitored by observing a change in the intensity of the superoxo signals. This confirms the reversibility of O_2 uptake.

The EPR lines of the parent complex, obtained after conversion are broad due to the presence of uncoordinated dissolved oxygen. The coexistence of resonance due to chloro and superoxo complexes indicate the following equilibrium between these two complexes in solution

$$[\mathrm{RuLXY}] \underset{-O_2}{\overset{+O_2}{\rightleftharpoons}} [\mathrm{Ru^{IV}L(O_2)^-Y}] + X^-$$

The Ru(IV) superoxo complexes obtained from $K[Ru(naphoph)Cl_2]$ are long lived (15 h) as compared to those from $K[Ru(saloph)Cl_2]$ [40] (20–30 min) indicating that the number of aromatic rings is one of the factors responsible for the stability of the dioxygen complex. Isolation of the dioxygen complexes as solids was not successful due to their instability at room temperature.

Carbonylation Studies

The UV–Vis spectra of complexes **1**–**10** were recorded in DMF saturated with CO by varying the concentration of CO in the ratio 1:1, 1:2 and 1:3 with respect to degassed DMF. In all the cases there is an increase in absorbance in the range (λ_{max} = 406–560 nm) with time. In naphoph complexes, however, a new peak appeared at 555 nm (ϵ 4192) which may be assigned to the MLCT band of Ru(III) → CO (Fig. 4). Carbonylation of the complexes however does not result in the reduction of Ru(III) to Ru(II) as confirmed by the observation of the Ru(III)/Ru(II) couple in DC and differential pulse polarograms of the solutions at −0.325 to −0.570 complexes. The Ru(II)/Ru(I) peak was absent in the DPP of the couple. The reaction with CO is reversible and CO can be displaced by flushing N_2 through the solution of the complexes. This explains the relatively low

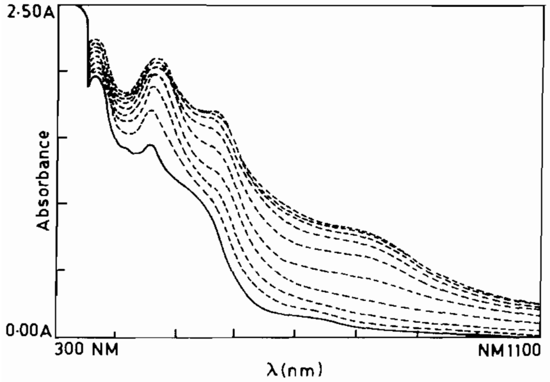


Fig. 3. The UV–Vis absorption spectral changes during carbonylation of $K[Ru(naphoph)Cl_2]$ in DMF (1×10^{-3} M) with time (——) soon after preparation (- - - -) after 4 h in 15 min interval at 303 K and path length l = 0.2 cm.

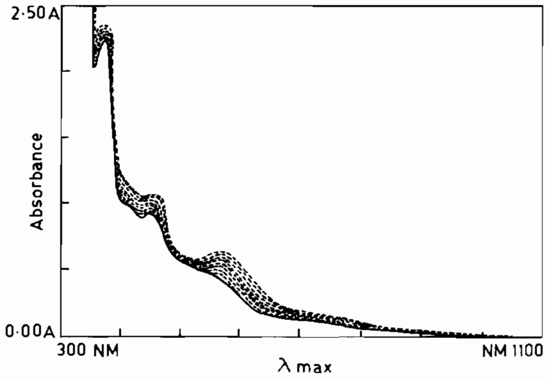


Fig. 4. The UV–Vis absorption spectral changes during carbonylation of $K[Ru(naphoph)Cl_2]$ in DMF (1×10^{-3} M) with time (——) soon after preparation (- - - -) after 4 h in 15 min interval at 303 K and path length l = 0.2 cm.

stability of the Ru(III) carbonyl complexes as compared to Ru(II) carbonyl complexes which are much more stable due to greater softness and lower electronegativity of Ru(II) as compared to Ru(III). The values of K_{O_2} and K_{CO} (Tables 4 and 5) depend on the nature of the axial ligand and decrease in the order Im > 2-MeIm > Cl. The higher stability of imidazole and 2-methylimidazole complexes is due to the greater σ-donor capacities of these ligands as compared to chloride. These σ-donor axial ligands cause an increase in electron density at the metal centre which in turn increases the dπ–pπ backdonation from the metal ion to coordinated O_2 or CO increasing thereby the stability of the corresponding complexes. In the case of 2-methylimidazole which is more basic than imidazole the values of $\log K_{O_2}$ and $\log K_{CO}$ are lower than those of the imidazole complexes. This is due to the steric hindrance by the methyl group which predominates over the greater σ-basicity of 2-methylimidazole [26].

The stability of the dioxygen and carbonyl complexes with respect to the equatorial ligand decrease in the order naphoph > naphdien > naphprop > naphen. The naphoph complexes are more stable than other Schiff base ligands [26]. The same trend was also observed in the saloph, bis(salicylaldehyde)-*o*-phenylenediimine complexes which are more stable than salen, bis(salicylaldehyde)ethylenediimine complexes [40]. The naphoph dioxygen complexes have a higher stability than the saloph complexes. The stability of the dioxygen complexes thus seems to increase with an increase in the number of aromatic rings in the Schiff base ligand. This seems to be a structural effect of the doming in the case of naphoph and saloph complexes which increases the stability of the dioxygen and carbonyl complexes. Doming of the equatorial ligand also plays an important role in the dioxygen affinity of porphyrins [27–29].

The stabilities of the carbonyl complexes of Ru(III) (Table 5) are about an order of magnitude

TABLE 4. Thermodynamic constant for dioxygen binding to ruthenium(III) Schiff base complexes in DMF at 1 atm.

No.	Complex	t (°C)	$\log K_{O_2}$	$P_{1/2}$ (Torr)	ΔH° (kcal mol^{-1})	ΔG° (kcal mol^{-1})	ΔS° (e.u.)
1	K[Ru(naphoph)Cl_2]	10	3.64 ± 0.08	0.049 ± 0.003	−20 ± 2	−4.1 ± 0.1	−53 ± 7
		25	3.06 ± 0.06	0.15 ± 0.02			
		40	2.12 ± 0.08	1.41 ± 0.26			
2	[Ru(naphoph)(Im)Cl]	10	3.97 ± 0.13	0.06 ± 0.005	−23 ± 2	−4.5 ± 0.2	−62 ± 7
		25	3.31 ± 0.17	0.09 ± 0.03			
		40	2.25 ± 0.07	1.04 ± 0.17			
3	[Ru(naphoph)(2-MeIm)Cl]	10	3.77 ± 0.15	0.026 ± 0.01	−21 ± 3	−4.5 ± 0.1	−55 ± 10
		25	3.33 ± 0.08	0.08 ± 0.01			
		40	2.20 ± 0.07	1.03 ± 0.34			
4	K[Ru(naphen)Cl_2]	10	2.78 ± 0.14	0.25 ± 0.09	−15 ± 2	−3.2 ± 0.1	−39 ± 6
		25	2.35 ± 0.08	0.75 ± 0.15			
		40	1.67 ± 0.08	3.9 ± 0.86			
5	[Ru(naphen)(Im)Cl]	10	3.31 ± 0.03	0.07 ± 0.01	−18 ± 1	−3.7 ± 0.1	−48 ± 3
		25	2.71 ± 0.11	0.33 ± 0.08			
		40	1.95 ± 0.06	1.91 ± 0.47			
6	[Ru(naphen)(2-MeIm)Cl]	10	3.05 ± 0.10	0.14 ± 0.03	−16 ± 1	−3.4 ± 0.2	−43 ± 3
		25	2.49 ± 0.18	0.58 ± 0.22			
		40	1.85 ± 0.13	2.71 ± 0.78			
7	K[Ru(naphprop)Cl_2]	10	3.15 ± 0.10	0.11 ± 0.02	−18 ± 1	−3.5 ± 0.2	−50 ± 4
		25	2.59 ± 0.14	0.44 ± 0.14			
		40	1.78 ± 0.10	3.13 ± 0.73			
8	[Ru(naphprop)(Im)Cl]	10	3.55 ± 0.25	0.05 ± 0.02	−21 ± 4	−3.8 ± 0.2	−60 ± 13
		25	2.76 ± 0.21	0.26 ± 0.2			
		40	1.91 ± 0.1	2.3 ± 0.6			
9	[Ru(naphprop)(2-MeIm)Cl]	10	3.55 ± 0.15	0.04 ± 0.01	−19 ± 3	−3.9 ± 0.1	−50 ± 10
		25	2.87 ± 0.23	0.25 ± 0.12			
		40	2.05 ± 0.07	1.6 ± 0.20			
10	[Ru(naphdien)Cl]	10	3.45 ± 0.13	0.05 ± 0.02	−20 ± 3	−4.05 ± 0.1	−54.5 ± 10
		25	2.97 ± 0.17	0.19 ± 0.07			
		40	1.96 ± 0.06	2.0 ± 0.24			

TABLE 5. Thermodynamic constants for carbon monoxide binding to ruthenium(III) Schiff base chloro complexes in DMF at 10, 25 and 40 °C

No.	Complex	t (°C)	$\log K_{CO}$	ΔH° [a] (kcal mol^{-1})	ΔG° [b] (kcal mol^{-1})	ΔS° (e.u.)
1	K[Ru(naphoph)Cl$_2$]	10	2.55 ± 0.01	−6	−3.2	−11 ± 1
		25	2.31 ± 0.02			
		40	2.07 ± 0.02			
2	[Ru(naphoph)(Im)Cl]	10	2.58 ± 0.03	−8	−3.3 ± 0.02	−15 ± 3
		25	2.41 ± 0.02			
		40	1.99 ± 0.02			
3	[Ru(naphoph)(2-MeIm)Cl]	10	2.55 ± 0.02	−7	−3.1 ± 0.05	−14 ± 1
		25	2.26 ± 0.03			
		40	2.02 ± 0.02			
4	K[Ru(naphen)Cl$_2$]	10	2.24 ± 0.02	−5	−2.8 ± 0.01	−7 ± 3
		25	2.05 ± 0.01			
		40	1.87 ± 0.08			
5	[Ru(naphen)(Im)Cl]	10	2.36 ± 0.02	−6	−2.8 ± 0.02	12 ± 3
		25	2.05 ± 0.02			
		40	1.89 ± 0.09			
6	[Ru(naphen)(2-MeIm)Cl]	10	2.28 ± 0.01	−6	−2.7	11 ± 3
		25	2.01 ± 0.02			
		40	1.84 ± 0.12			
7	K[Ru(naphprop)Cl$_2$]	10	2.26 ± 0.02	−6	−2.7	11 ± 3
		25	2.00 ± 0.01			
		40	1.81 ± 0.09			
8	[Ru(naphprop)(Im)Cl]	10	2.34 ± 0.03	−7	−2.7	13 ± 4
		25	2.02 ± 0.02			
		40	1.84 ± 0.10			
9	[Ru(naphprop)(2-MeIm)Cl]	10	2.30 ± 0.02	−6	−2.8	12 ± 3
		25	2.05 ± 0.05			
		40	1.85 ± 0.09			
10	[Ru(naphdien)Cl]	10	2.31 ± 0.02	−6	−2.8	10 ± 2
		25	2.06 ± 0.04			
		40	1.87 ± 0.07			

[a] Accurate upto ±1 kcal/mol. [b] Correct upto ±0.1 kcal/mol.

lower than those of the dioxygen complexes though the electronic effects of the axial and equatorial ligand are about the same for the carbonyl and dioxygen complexes. The complexes thus exhibit discrimination towards CO binding. The lower stability of the Ru(III) carbonyls seems to be predominantly due to a decrease in the dπ–pπ backbonding of CO in these complexes. The situation is, therefore, the reverse of the Fe(II)–porphyrins [27, 28] where O_2 exhibits a stronger bonding to the metal ion than CO. The discrimination against CO binding in Fe(II)–porphyrins comes mostly from the steric effects such as the interaction of distal histidine in hemoglobin or the size of the pocket [29] containing the CO or the O_2 group [29]. In the Ru(III) carbonyls CO is reversibly bonded to the metal ion and is displaced by bubbling N_2 through the solution, in contrast to the irreversible binding of CO in Fe(II)–porphyrins [27, 30].

The thermodynamic parameters ΔG°, ΔH° and ΔS° associated with $\log K_{O_2}$ are given in Table 4. These values are in agreement with those reported for other Ru(III) Schiff base dioxygen complexes [26, 41]. The enthalpies are highly exothermic and the entropies are fairly negative. From Table 4, it is ascertained that ΔH° is maximum for the naphoph imidazole complex which reflects on the highest metal–oxygen bond strength of this complex in the series.

The thermodynamic parameters ΔH°, ΔS° and ΔG° for the formation of carbonyl complexes in Table 5 reflect the same trend with the change of axial and equatorial ligands as the dioxygen complexes (Table 4). The enthalpy values which are a

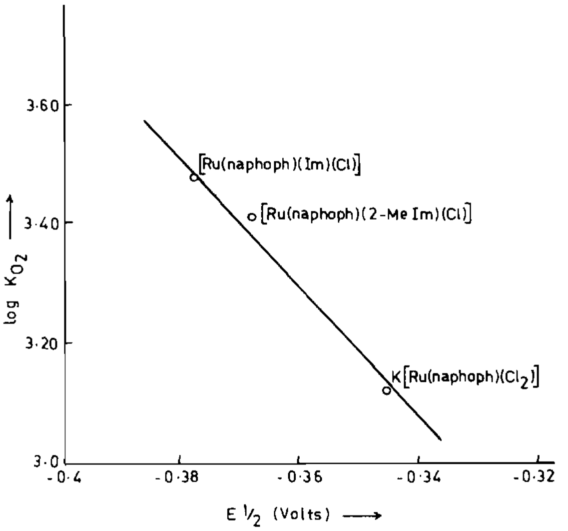


Fig. 5. Correlation of log K_{O_2} (25 °C) with Ru(IV) → Ru(III) peak potentials for superoxo complexes 1–3.

measure of the metal ligand bond strength are more endothermic (more positive) in carbonyl complexes as compared to dioxygen complexes reflecting on a weaker M–CO bond strength in these carbonyls. The entropies are about -7 ± 3 to -15 ± 3 e.u. more positive than the dioxygen complexes indicating a comparatively lower [26] loss of vibrational and rotational degree of freedom of CO on coordination as compared to O_2.

A good correlation has been drawn between the $\log K_{O_2}$ and $E_{1/2}$ values of the Ru(IV)/Ru(III) couple in the dioxygen complexes as depicted in Fig. 5. This correlation reflects on the ease of oxidation of Ru(III) → Ru(IV) as the redox potential of the Ru(IV)/Ru(III) couple is shifted to more negative values. This negative shift depends on an increase in charge density on the metal ion by the equatorial and axial ligands. In such cases, the transfer of electron density from metal to dioxygen becomes easier resulting in a stabilization of the dioxygen complexes and the coordination of a formal superoxide ion to a formal Ru(IV) ion. A similar trend was observed between $E_{1/2}$ values of the Co(III)/Co(II) couple and the $\log K_{O_2}$ values for a series of Co(II) Schiff base complexes [41].

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