

Synthesis, characterization and solvent dependent reversible binding of carbon monoxide to Ru(III) Schiff base complexes

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Abstract

Ruthenium(III) Schiff base complexes of the composition [RuLXY] where L=Schiff base, viz. bis(salicylaldehyde)-*o*-phenylenediimine (saloph), bis(salicylaldehyde)ethylenediimine (salen), bis(salicylaldehyde)diethylenetriimine (saldien) bis(piccolinaldehyde)-*o*-phenylenediimine (picoph), bis(piccolinaldehyde)ethylenediimine (picen), bis(piccolinaldehyde)diethylenetriimine (picdien); X = chloro(Cl⁻); Y = chloro(Cl⁻), imidazole (Im) or 2-methylimidazole (2-MeIm) were synthesized and characterized by various physicochemical methods. The reversible binding of carbon monoxide to the Ru(III) Schiff base complexes was carried out in DMF, CH₃CN, CH₃OH and CH₃COCH₃ at 10, 25 and 40 °C. The polarity of the solvents as well as the electron donating substituents on Schiff base complexes increase the affinity of the complexes for CO. The thermodynamic parameters ΔH° , ΔG° and ΔS° for the carbonylation of Schiff base complexes were evaluated.

Introduction

The proteins in haemoglobin and myoglobin play an important role in the discrimination reaction against the binding of CO relative to that of O₂ [1]. The distal histidine is thought to be responsible for the reduced CO affinities by steric, electronic and solvation effects [2, 3]. Several studies [4–6] have shown that the binding of O₂ and CO involves different activation barriers and rate determining steps. The pressure dependence of the overall equilibrium constant for the formation of MbO₂ and release of O₂ has also been envisaged. A number of experimental data [7] have shown a reversible transition between low affinity (T) and high affinity quaternary structures (R) in carbon monooxyhaemoglobin CO(Hb) and deoxy Hb, respectively. The photolysis of the heme CO adducts provides a means for studying the dynamic features of the quaternary structural transition. The optical absorption [8–10] and visible resonance Raman techniques [11–13] were helpful for structural elucidation following the photolysis of COHb.

Some insertion reactions [14] of CO in iron–carbon bonds of alkyl porphyrins generated from the reaction of alkyl halides with electronically produced low

valent iron porphyrins with the exception of benzyl derivatives have also been reported [14].

In continuation of our earlier work on solid state carbonyl [15] ruthenium(III) Schiff base complexes [16, 17] and their reversible binding with CO, we report in this paper the synthesis of a number of ruthenium(III) Schiff base complexes with variation of donor sites (N₂O₂, N₃O₂ and N₄). To explore the solvation effects on CO binding, the thermodynamic parameters ΔH° and ΔS° for the formation of these complexes were evaluated in solvents of different polarity. Variations were also made in the axial coordination of the complexes by chloro, Im and 2-MeIm groups in order to assess the CO affinity of these complexes with a change in the σ -donor ability of the axial ligands.

Experimental

Material and methods

RuCl₃·3H₂O (Johnson Matthey), diethylenetriamine, imidazole, 2-methylimidazole (Fluka) were of AR grade and were used as such. Salicylaldehyde, acetone, acetonitrile, methanol, dimethylformamide, pyridine 2-carboxyaldehyde and ethylenediamine were distilled prior to use. *o*-Phenylenediamine (alpha) was recrystallized twice from benzene. All sol-

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vents were of AR grade and purified further by the usual laboratory techniques. Doubly distilled deionized water was used whenever required. The complex $K_2[RuCl_5(H_2O)]$ [18] and the Schiff bases, saloph, salen, picoph, picen, saldien and picdien were prepared under oxygen free N_2/Ar atmosphere by known procedures [16, 17, 19]. The completion of reaction and homogeneity of the complexes were checked on silica gel coated glass thin layer chromatography plates.

Preparation of the complexes

bis(salicylaldehyde)-*o*-phenylenediiminatodichlororuthenate(III), $K[Ru(saloph)Cl_2]$ (1);

bis(salicylaldehyde)-*o*-phenylenediiminatochloroimidazolerothene(III), $[Ru(saloph)(Im)Cl]$ (2);

bis(salicylaldehyde)-*o*-phenylenediiminatochloro-2-methylimidazolerothene(III), $[Ru(saloph)(2-MeIm)Cl]$ (3);

bis(salicylaldehyde)ethylenediiminatodichlororuthenate(III), $K[Ru(salen)Cl_2]$ (4);

bis(salicylaldehyde)ethylenediiminatochloroimidazolerothene(III), $[Ru(salen)(Im)Cl]$ (5);

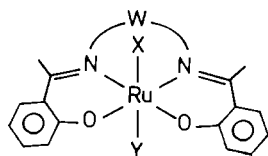
bis(salicylaldehyde)ethylenediiminatochloro-2-methylimidazolerothene(III), $[Ru(salen)(2-MeIm)Cl]$ (6);

bis(salicylaldehyde)diethylenetriiminatochlororuthene(III), $[Ru(saldien)Cl]$ (7);

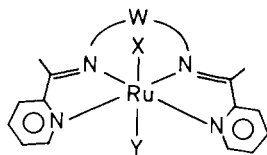
bis(picolinaldehyde)-*o*-phenylenediiminatodichlororuthene(III), $[Ru(picoph)Cl_2]Cl$ (8);

bis(picolinaldehyde)-*o*-phenylenediiminatochloroimidazolerothene(III), $[Ru(picoph)(Im)Cl]Cl_2$ (9);

bis(picolinaldehyde)-*o*-phenylenediiminatochloro-



Complex	W	X	Y
1, 2, 3	Saloph (C_6H_4)-	Cl^-	$Cl^-, Im, 2MeIm$
4, 5, 6	Salen (CH_2) ₂	Cl^-	$Cl^-, Im, 2MeIm$
13	Saldien- (C_2H_4)NH(C_2H_4)	N of W	Cl^-



Complex	W	X	Y
7, 8, 9	Picoph (C_6H_4)-	Cl^-	$Cl^-, Im, 2MeIm$
10, 11, 12	Picen (CH_2) ₂	Cl^-	$Cl^-, Im, 2MeIm$
14	Picdien (C_2H_4)NH(C_2H_4)	N of W	Cl^-

2-methylimidazolerothene(III), $[Ru(picoph)(2-MeIm)Cl]Cl_2$ (10);

bis(picolinaldehyde)ethylenediiminatodichlororuthenate(III), $[Ru(picen)Cl_2]Cl$ (11);

bis(picolinaldehyde)ethylenediiminatochloroimidazolerothene(III), $[Ru(picen)(Im)Cl]Cl_2$ (12);

bis(picolinaldehyde)ethylenediiminatochloro-2-methylimidazolerothene(III), $[Ru(picen)(2-MeIm)Cl]Cl_2$ (13);

bis(picolinaldehyde)diethylenetriiminatochlororuthene(III), $[Ru(picdien)Cl]$ (14).

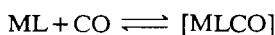
All the above mentioned complexes were synthesized by reported [15–17] procedures in N_2/Ar atmosphere.

Physical measurements

Microanalysis of the compounds was carried out by a Carlo Erba analysis instrument, model 1106 at CSMCRI, Bhavnagar. Molar conductivity was measured at room temperature on a Digisun Electronics conductivity bridge. IR spectra were recorded on Nicolet 200 SXV FT-IR spectrometer in nujol mulls/KBr. The electronic spectra were recorded on a Shimadzu UV-Vis recording model UV-160 spectrophotometer. Cyclic voltammograms were recorded with a Princeton Applied Research (PAR) instrument as described earlier [16, 17, 20]. The room temperature magnetic susceptibility of the complexes was determined by the Guoy method using $Hg[Co(SCN)_4]$ as calibrant, and experiment magnetic susceptibility was corrected for diamagnetism [21].

CO uptake measurements

In order to evaluate the equilibrium constant for carbonylation K_{CO} by UV-Vis spectrophotometry, solutions of the complexes were prepared in the concentration range 5×10^{-4} M in appropriate solvents like DMF CH_3CN , CH_3OH and $(CH_3)_2C=O$. The solvents were saturated with CO and solutions with different concentrations of dissolved CO were prepared by diluting the saturated solution with degassed solutions in the ratio 1:1, 1:2 and 1:3. The spectrum was recorded immediately at 10, 25 and 40 °C by monitoring the peak around ($\lambda_{max} = 405-570$ nm) and a constant value of absorbance was noted for each set. The solubility of CO in the solvents methanol, methyl cyanide, dimethyl formamide and acetone was measured separately at different temperatures. The reaction of the complexes with CO may be written as:



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

The equilibrium constant K_{CO} was calculated by reported methods [16, 17, 22].

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

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

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

Results and discussion

The elemental analysis and molar conductance of ruthenium(III) Schiff base complexes **1–14** with the general formulae [RuLXY] (where L = Schiff base; X = Cl⁻; Y = Cl⁻, Im, 2-MeIm) are in good accord with the suggested formulation of the complexes. All the complexes are paramagnetic with μ_{eff} in the range 1.97–2.06 BM indicating that the complexes are low spin Ru(III) species with a $(t_{2g})^5$ ground state configuration.

The broad ligational $\nu\text{O-H}$ band of the Schiff bases near 3380 cm^{-1} disappeared on complexation of the O-H to the metal ion. The $\nu(\text{C-O})$ band at 1280 cm^{-1} in the free Schiff bases was shifted slightly to lower wave number on coordination [23]. The strong azomethine $\nu(\text{H-C=N})$ band in the ligands in the range $1625\text{--}1635\text{ cm}^{-1}$ was shifted by $25\text{--}30\text{ cm}^{-1}$ towards lower energy on coordination indicating the coordination of the imine group to the metal ion. Thus the Schiff base ligand acts as a dianionic tetradentate or pentadentate ligand on coordination to the metal ion. The $\nu(\text{M-Cl})$ and $\nu(\text{M-N})$ bands were observed around 325 cm^{-1} in all the complexes. In the case of the complexes containing imidazole and 2-methylimidazole the bands corresponding to these groups were observed near 600 and 1000 cm^{-1} (Table 1).

Electronic spectra

The electronic spectra of all the complexes were recorded in DMF. The strong band near 300 ($\epsilon=5770$) and 350 ($\epsilon=25\,000$) nm are assigned to the ligational transitions in the azomethine group [15–17]. These bands undergo slight hypsochromic shifts on complexation. The bands in the range 470–490 nm were assigned to LMCT bands while the d-d bands lie near 900 nm. The presence of imidazole or 2-methylimidazole in the coordination sphere of the metal ion could not, however, be confirmed by electronic spectra of the complexes (Table 1) since the characteristic ligational peaks of

imidazole in the 300–310 nm region overlap with the ligational peaks of the Schiff bases.

The EPR studies of chloro complexes [15] of Ru(III) have shown the displacement of the axial Cl⁻ group in the Schiff base complexes by a solvent or CO. The lability of the chloro group is very important for catalysis of the complexes in carbonylation reactions [24]. The fact that the axial Cl⁻ in Schiff base complexes is readily displaced by CO is probably a consequence of the difference in the nature of the ligand bonding. Chloride ion is predominantly a σ -donor whereas CO is a π -acceptor. Consequently when d_{xz} and d_{yz} orbitals (assuming the z axis is directly towards Cl⁻ or CO) are occupied the $p\pi$ orbitals of Cl⁻ are unable to donate to ruthenium whereas CO can accept $d\pi$ density into its low lying empty π^* orbital giving more covalency to the Ru-CO bond.

This is due to the lower value of the orbital reduction factor for carbonyl complexes [15] than for chloro complexes. The π -acceptor capacity of CO depends on the oxidation state of the metal ion. Ru(III) complexes have a relatively weaker Ru-CO bond as compared to Ru(II) complexes because of the lower spin density available on ruthenium(III) $d\pi$ -orbitals to backdonation to CO. The Ru(III) carbonyl complexes are thus very reactive in nucleophilic reactions of CO.

Carbonylation studies

The equilibrium constant for carbonylation K_{CO} was evaluated by UV-Vis spectra of the complexes in DMF, CH₃CN, CH₃OH and (CH₃)₂C=O saturated with CO. The solutions with different concentrations of dissolved CO were then prepared by diluting the saturated solution of CO with the degassed solvents in the ratio of 1:1, 1:2 and 1:3. In all the complexes there is an increase in absorbance in the range ($\lambda_{\text{max}} = 405\text{--}570\text{ nm}$) with time. The electronic spectra of K[Ru(saloph)Cl₂] and [Ru(picoph)Cl₂]Cl in DMF saturated with CO are depicted in Figs. 1 and 2. A maximum increase in absorbance was observed at 471, 550 nm and assigned to the MLC_{Cl} band. Carbonylation of these complexes in the temperature range studied does not however cause a reduction of Ru(III) to Ru(II). This was confirmed by observation of the Ru(III)/Ru(II) couple in d.c. and differential pulse polarograms (DPP) of these complexes in solution saturated with CO gas in DMF at -0.210 to -0.480 V . The Ru(II)/Ru(I) peak was absent in the DPP of the couples. The reversible binding of CO in these complexes was confirmed by flushing nitrogen through the solution of these complexes which displaces CO. This displacement reflects on the lower stability of Ru(III) carbonyl species as

TABLE 1. UV-Vis data and selected IR bands for ruthenium Schiff base complexes

Complex	$\nu(\text{C-O})$ (cm^{-1})	$\nu(\text{C=N})$ (cm^{-1})		Imidazole peaks (cm^{-1})	λ_{max} (ϵ ($\text{M}^{-1} \text{cm}^2$))
		Azomethine	Aryl		
$\text{K}[\text{Ru}(\text{saloph})\text{Cl}_2]$ (1)	1265	1588			923(52), 485(4130), 368(8695), 333(10160), 275(12500)
$[\text{Ru}(\text{saloph})(\text{Im})\text{Cl}]$ (2)	1268	1590		620, 650, 1070	920(30), 483(3010), 365(6250), 333(8000), 275(12820)
$[\text{Ru}(\text{saloph})(2\text{-MeIm})\text{Cl}]$ (3)	1267	1591		611, 669, 1149	919(70), 488(3440), 374(5980), 333(6710), 270(12265)
$\text{K}[\text{Ru}(\text{salen})\text{Cl}_2]$ (4)	1260	1600			621(1120), 404(3630), 346(5770), 265(6620)
$[\text{Ru}(\text{salen})(\text{Im})\text{Cl}]$ (5)	1262	1595		620, 660, 1145	603(810), 459(1950), 386(3350), 346(4630), 265(5900)
$[\text{Ru}(\text{salen})(2\text{-MeIm})\text{Cl}]$ (6)	1265	1605		626, 673, 1150	624(1130), 376(4820), 322(6090), 265(10666)
$[\text{Ru}(\text{picoph})\text{Cl}_2]\text{Cl}$ (7)		1540	1606		473(7450), 318(25000), 266(13280)
$[\text{Ru}(\text{picoph})(\text{Im})\text{Cl}]\text{Cl}_2$ (8)		1555	1630	616, 658, 1148	472(4120), 319(25000), 266(9690)
$[\text{Ru}(\text{picoph})(2\text{-MeIm})\text{Cl}]\text{Cl}_2$ (9)		1540	1615	620, 670, 1140	472(11210), 338(24990), 269(21250)
$[\text{Ru}(\text{picen})\text{Cl}_2]\text{Cl}$ (10)		1532	1622		498(6710), 420(6040), 349(7990), 272(19840)
$[\text{Ru}(\text{picen})(\text{Im})\text{Cl}]\text{Cl}_2$ (11)		1543	1634	615, 660, 1150	498(8140), 368(11320), 274(11320)
$[\text{Ru}(\text{picen})(2\text{-MeIm})\text{Cl}]\text{Cl}_2$ (12)		1540	1625	620, 670, 1140	497(8140), 368(11320), 274(24990)
$[\text{Ru}(\text{saldien})\text{Cl}]$ (13)	1263	1601			473(1590), 331(3940), 266(7780)
$[\text{Ru}(\text{picdien})\text{Cl}]\text{Cl}_2$ (14)		1569	1620		506(5700), 362(6920), 270(16450)

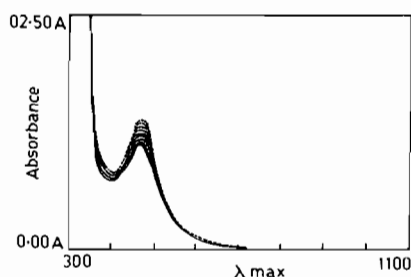


Fig. 1. The UV-Vis absorption spectral change during carbonylation of $K[Ru(\text{saloph})Cl_2]$ in DMF (1×10^{-3} M) with time: (—) soon after preparation, (---) after 4 h; in 15 min intervals at 303 K and path length $l=0.2$ cm.

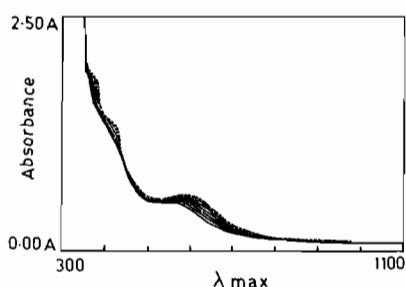


Fig. 2. The UV-Vis absorption spectral change during carbonylation of $[Ru(\text{picoph})Cl_2]Cl$ in DMF (1×10^{-3} M) with time: (—) soon after preparation, (---) after 4 h; in 15 min intervals at 303 K and path length $l=0.2$ cm.

compared to the very stable Ru(II) carbonyl complexes on the basis of the greater softness and lower electronegativity of Ru(II) as compared to Ru(III).

Solvation effect

The solute-solvent interaction [25] depends on the nature of both the solvent and solute in terms of dipolar interaction and dispersion forces. Solute induced modification of solvent-solvent interaction is due to structural changes produced in the solvent by creation of a cavity of a suitable size to incorporate the solute with consequent reorganization of the solvent molecule around the solute through hydrogen bonding. The discrimination in binding of CO depends on the polarity of the solvent as well as the electron donating substituent such as chloro, imidazole and 2-methylimidazole on the axial position of the Schiff base complexes.

The CO affinity of the Schiff base complexes as measured by the enthalpy of complex formation ΔH° is the lowest in DMF which is the most polar and maximum for the least polar solvent acetone. The affinities decrease in the order, acetone > methanol > CH_3CN > DMF which is the reverse of the order of polarity as well as the dielectric constant of the solvent. This observation is explained in terms of dipole-dipole interaction causing association of

the more polar solvent molecule around the complexes which weakens the CO affinity of the system. The solvation factor of the carbonylation reaction implies the difference of the free energy changes between solvated and non-solvated species. The solvation of the Ru(III)-Schiff base complexes implies a displacement of Cl^- from the coordination sphere of the metal ion as supported by EPR studies [15]. The solvent is then displaced by CO to form the carbonyl complex. In the case of a polar solvent the solvent is more strongly coordinated to the metal ion than CO, hence there is a reduction in the affinity of CO. Thus the CO affinity decreases from less polar to the more polar solvent (Table 2). The $P_{1/2}$ values obtained in several solvents are listed in Table 2. This trend is just the reverse for O_2 affinity of iron(II) porphyrins which increases with increase of solvent polarity [26]. The solvation effect of the Ru(III)-Schiff base complexes is similar to the flat chelated hemes that are more strongly solvated than the picket fence complexes [27], which is one of the factors for the higher discrimination of CO, K_{CO}/K_{O_2} in flat hemes as compared to the hydrophobic picket fence.

The equilibrium constant for the carbonylation reaction K_{CO} (Table 2) depends on the nature of the axial ligand and decreases in the order $Im > 2-MeIm > chloro$. This is due to the greater σ -donor capacities of imidazole and 2-methylimidazole as compared to chloro, causing an increase in electron density at the metal centre which in turn increases the $d\pi-p\pi$ backdonation from the metal ion to the coordinated CO, thereby increasing the stability of the corresponding complexes. In the case of 2-methylimidazole which is more basic than imidazole the stability is less than the imidazole complexes. This may be due to steric hindrance by the methyl group which predominates over the higher basicity of 2-methylimidazole [16, 17, 20]. The stability of the carbonyl complexes with respect to the equatorial ligand decreases in the order $saloph > picoph > saldien > picdien > salen > picen$.

The saloph complexes are in general more stable than the salen complexes [15]. The same trend was also observed in bis(naphthaldehyde)-*o*-phenylenediimine (naphoph) and bis(naphthaldehyde)-ethylenediimine (naphen) complexes [17]. This seems to be a structural effect of the doming in the case of saloph and naphoph complexes which increases the stability of the carbonyl complexes. Doming of the equatorial ligand also plays an important role in the dioxygen affinity of porphyrins [27-29].

The stability of these Ru(III) carbonyl complexes is about an order of magnitude lower than other Schiff base complexes already reported by us [16,

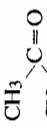
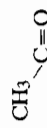
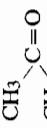
TABLE 2. Thermodynamic constants for carbon monoxide binding to ruthenium(III) Schiff base chloro complexes in different solvents

Complex	Solvents	T (°C)	Log K_{CO}	$P_{1/2}$ (torr)	ΔH° (kcal/mol)	ΔG° (kcal/mol)	ΔS° (e.u.)
K[Ru(saloph)Cl ₂] (1)	DMF	10	2.45 ± 0.01	0.53 ± 0.01	-7.67 ± 1	-2.76 ± 0.03	-16.44 ± 3
		25	2.03 ± 0.02	1.55 ± 0.07			
		40	1.88 ± 0.01	2.45 ± 0.05			
	CH ₃ CN	10	2.51 ± 0.01	0.28 ± 0.01	-7.97 ± 1	-2.80 ± 0.01	-17.34 ± 3
		25	2.06 ± 0.01	0.91 ± 0.02			
		40	1.90 ± 0.01	1.45 ± 0.03			
	CH ₃ OH	10	2.52 ± 0.01	0.33 ± 0.01	-8.35 ± 1	-2.81 ± 0.02	-18.05 ± 3
		25	2.07 ± 0.01	1.16 ± 0.03			
		40	1.91 ± 0.01	2.17 ± 0.05			
[Ru(saloph)(Im)(Cl)] (2)	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$	10	2.53 ± 0.01	0.29 ± 0.01	-8.72 ± 1	-2.83 ± 0.02	-19.76 ± 3
		25	2.08 ± 0.01	0.95 ± 0.02			
		40	1.92 ± 0.01	1.65 ± 0.04			
	DMF	10	2.60 ± 0.01	0.37 ± 0.01	-8.75 ± 1	-2.86 ± 0.01	-19.77 ± 3
		25	2.11 ± 0.01	1.30 ± 0.03			
		40	1.95 ± 0.03	2.27 ± 0.16			
	CH ₃ CN	10	2.63 ± 0.01	0.22 ± 0.01	-8.98 ± 0.5	-3.00 ± 0.01	-20.06 ± 1
		25	2.21 ± 0.01	0.63 ± 0.02			
		40	1.97 ± 0.01	1.23 ± 0.03			
CH ₃ OH	10	2.64 ± 0.01	0.24 ± 0.01	-9.24 ± 0.2	-3.03 ± 0.03	-20.83 ± 1	
	25	2.22 ± 0.01	0.81 ± 0.01				
	40	1.99 ± 0.01	1.00 ± 0.05				
[Ru(saloph)(2-MeIm)(Cl)] (3)	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$	10	2.67 ± 0.01	0.20 ± 0.01	-9.71 ± 1	-3.17 ± 0.03	-21.94 ± 3
		25	2.33 ± 0.01	0.53 ± 0.02			
		40	2.00 ± 0.01	1.37 ± 0.03			
	DMF	10	2.49 ± 0.01	0.48 ± 0.02	-7.93 ± 0.9	-2.81 ± 0.01	-17.32 ± 3
		25	2.06 ± 0.01	1.45 ± 0.04			
		40	1.90 ± 0.01	2.37 ± 0.05			
	CH ₃ CN	10	2.54 ± 0.01	0.26 ± 0.01	-8.27 ± 1	-2.83 ± 0.02	-18.20 ± 3
		25	2.08 ± 0.01	0.86 ± 0.02			
		40	1.93 ± 0.01	1.35 ± 0.03			
CH ₃ OH	10	2.59 ± 0.01	0.27 ± 0.01	-8.87 ± 0.03	-3.05 ± 0.01	-18.77 ± 2	
	25	2.21 ± 0.01	0.84 ± 0.03				
	40	1.94 ± 0.01	2.04 ± 0.04				
$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$	10	2.61 ± 0.01	0.23 ± 0.01	-8.97 ± 0.5	-3.01 ± 0.01	-19.99 ± 1	
	25	2.22 ± 0.01	0.69 ± 0.01				
	40	1.96 ± 0.02	1.51 ± 0.07				

K[Ru(salen)Cl ₂] (4)	DMF	10	1.99 ± 0.01	1.54 ± 0.04	-4.33 ± 0.6	-2.58 ± 0.01	-6.56 ± 1	
		25	1.89 ± 0.01	2.17 ± 0.05				
		40	1.67 ± 0.01	4.08 ± 0.08				
CH ₃ CN	10	2.03 ± 0.01	0.88 ± 0.02				-7.41 ± 2	
	25	1.90 ± 0.01	1.31 ± 0.04	-4.80 ± 0.6	-2.59 ± 0.01			
	40	1.68 ± 0.01	2.44 ± 0.06					
CH ₃ OH	10	2.06 ± 0.02	0.96 ± 0.05				-8.35 ± 1	
	25	1.91 ± 0.02	1.68 ± 0.07	-5.08 ± 0.4	-2.59 ± 0.01			
	40	1.69 ± 0.01	3.63 ± 0.07					
[Ru(salen)(Im)(Cl)] (5)	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$ DMF	10	2.11 ± 0.02	0.75 ± 0.04	-5.56 ± 0.4	-2.62 ± 0.01		-10.36 ± 1
		25	1.93 ± 0.01	1.35 ± 0.03				
		40	1.70 ± 0.01	2.77 ± 0.07				
CH ₃ CN	10	2.23 ± 0.02	0.88 ± 0.04				-13.35 ± 2	
	25	2.63 ± 0.01	1.57 ± 0.04	-6.74 ± 0.6	-2.76 ± 0.01			
	40	1.73 ± 0.01	3.50 ± 0.07					
CH ₃ OH	10	2.27 ± 0.01	0.50 ± 0.01				-13.72 ± 1	
	25	2.05 ± 0.01	0.92 ± 0.03	-6.88 ± 0.4	-2.79 ± 0.01			
	40	1.74 ± 0.01	2.12 ± 0.04					
[Ru(salen)(2-MeIm)Cl] (6)	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$ DMF	10	2.28 ± 0.01	0.57 ± 0.02	-7.25 ± 0.01	-2.81 ± 0.01		-14.79 ± 0.03
		25	2.05 ± 0.01	1.21 ± 0.02				
		40	1.75 ± 0.01	3.17 ± 0.05				
CH ₃ CN	10	2.36 ± 0.01	0.47 ± 0.01				-15.22 ± 2	
	25	2.07 ± 0.02	0.98 ± 0.05	-7.36 ± 0.5	-2.82 ± 0.02			
	40	1.77 ± 0.01	2.35 ± 0.03					
CH ₃ OH	10	2.21 ± 0.01	0.73 ± 0.02				-10.60 ± 3	
	25	2.01 ± 0.01	1.63 ± 0.02	-5.90 ± 0.4	-2.74 ± 0.01			
	40	1.71 ± 0.01	3.63 ± 0.07					
[Ru(picoph)Cl ₂]Cl (7)	CH ₃ CN	10	2.22 ± 0.01	0.56 ± 0.02	-6.16 ± 0.4	-2.75 ± 0.01		-11.40 ± 1
		25	2.02 ± 0.01	1.00 ± 0.02				
		40	1.73 ± 0.01	2.17 ± 0.05				
CH ₃ OH	10	2.23 ± 0.01	0.64 ± 0.02				-12.31 ± 1	
	25	2.03 ± 0.01	1.26 ± 0.03	-6.43 ± 0.3	-2.76 ± 0.01			
	40	1.74 ± 0.01	3.22 ± 0.10					
DMF	10	2.24 ± 0.01	0.55 ± 0.01				-13.15 ± 1	
	25	2.04 ± 0.01	1.11 ± 0.08	-6.69 ± 0.4	-2.79 ± 0.01			
	40	1.75 ± 0.01	2.44 ± 0.06					
DMF	10	2.29 ± 0.01	0.76 ± 0.02				-12.61 ± 0.7	
	25	2.03 ± 0.01	1.57 ± 0.04	-6.53 ± 0.2	-2.77 ± 0.01			
	40	1.80 ± 0.01	2.98 ± 0.04					

(continued)

TABLE 2. (continued)

Complex	Solvents	T (°C)	Log K_{CO}	$P_{1/2}$ (torr)	ΔH° (kcal/mol)	ΔG° (kcal/mol)	ΔS° (e.u.)	
[Ru(picoph)(Im)Cl]Cl ₂ (8)	CH ₃ CN	10	2.31 ± 0.01	0.46 ± 0.01				
		25	2.04 ± 0.01	0.95 ± 0.03	-6.72 ± 0.1	-2.78 ± 0.01	-13.22 ± 0.3	
		40	1.81 ± 0.01	1.75 ± 0.1				
	CH ₃ OH	10	2.32 ± 0.01	0.58 ± 0.07				
		25	2.05 ± 0.01	1.21 ± 0.02	-6.86 ± 0.1	-2.79 ± 0.01	-13.65 ± 0.4	
		40	1.82 ± 0.01	2.70 ± 0.07				
	CH ₃  C=O	10	2.37 ± 0.01	0.41 ± 0.01				
		25	2.07 ± 0.01	0.98 ± 0.03	-7.27 ± 0.2	-2.82 ± 0.01	-14.92 ± 0.7	
		40	1.83 ± 0.01	2.04 ± 0.04				
	DMF	10	2.39 ± 0.01	0.68 ± 0.09				
		25	2.09 ± 0.01	1.35 ± 0.03	-7.46 ± 0.2	-2.85 ± 0.01	-15.46 ± 1	
		40	1.84 ± 0.01	2.70 ± 0.07				
CH ₃ CN	10	2.41 ± 0.01	0.36 ± 0.01					
	25	2.10 ± 0.01	0.82 ± 0.02	-7.60 ± 0.1	-2.86 ± 0.01	-15.90 ± 0.1		
	40	1.85 ± 0.01	1.62 ± 0.04					
CH ₃ OH	10	2.44 ± 0.01	0.40 ± 0.01					
	25	2.11 ± 0.01	1.85 ± 0.02	-7.8 ± 0.2	-2.88 ± 0.01	-16.20 ± 0.4		
	40	1.86 ± 0.01	2.44 ± 0.06					
[Ru(picoph)(2-MeIm)Cl]Cl ₂ (9)	CH ₃  C=O	10	2.46 ± 0.02	0.33 ± 0.02				
		25	2.13 ± 0.01	0.85 ± 0.02	-8.01 ± 0.2	-2.90 ± 0.01	-17.14 ± 0.7	
		40	1.87 ± 0.01	1.86 ± 0.05				
	DMF	10	2.35 ± 0.01	0.66 ± 0.01				
		25	2.06 ± 0.01	1.54 ± 0.12	-7.06 ± 0.2	-2.81 ± 0.01	-14.25 ± 0.7	
		40	1.82 ± 0.01	2.85 ± 0.09				
	CH ₃ CN	10	2.37 ± 0.01	0.40 ± 0.01				
		25	2.07 ± 0.01	0.88 ± 0.02	-7.26 ± 0.1	-2.82 ± 0.01	-14.92 ± 0.5	
		40	1.83 ± 0.01	1.62 ± 0.04				
	CH ₃ OH	10	2.38 ± 0.01	0.45 ± 0.05				
		25	2.09 ± 0.01	1.10 ± 0.03	-7.45 ± 0.2	-2.85 ± 0.01	-15.46 ± 1	
		40	1.84 ± 0.01	2.50 ± 0.01				
CH ₃  C=O	10	2.40 ± 0.01	0.38 ± 0.01					
	25	2.11 ± 0.01	0.89 ± 0.02	-7.59 ± 0.2	-2.86 ± 0.1	-15.86 ± 0.7		
	40	1.84 ± 0.01	2.00 ± 0.04					
DMF	10	1.92 ± 0.01	1.81 ± 0.04					
	25	1.73 ± 0.01	3.17 ± 0.05	-4.31 ± 0.2	-2.35 ± 0.01	-6.52 ± 1		
	40	1.61 ± 0.01	4.65 ± 0.01					

[Ru(picen)Cl₂]Cl (10)

CH ₃ CN	10	1.93 ± 0.01	1.10 ± 0.03	-4.45 ± 0.3	-2.36 ± 0.01	-7.01 ± 1
	25	1.74 ± 0.01	1.90 ± 0.06			
	40	1.62 ± 0.01	2.77 ± 0.07			
CH ₃ OH	10	1.94 ± 0.01	1.26 ± 0.03	-4.59 ± 0.4	-2.35 ± 0.01	-7.512 ± 1
	25	1.75 ± 0.01	2.44 ± 0.06			
	40	1.63 ± 0.01	4.25 ± 0.09			
CH ₃ C=O CH ₃	10	1.96 ± 0.01	1.05 ± 0.03	-4.72 ± 0.02	-2.38 ± 0.01	-7.84 ± 0.7
	25	1.76 ± 0.01	2.02 ± 0.06			
	40	1.64 ± 0.01	3.17 ± 0.05			
DMF	10	2.15 ± 0.01	1.06 ± 0.02	-6.37 ± 1	-2.45 ± 0.01	-13.15 ± 3
	25	1.80 ± 0.01	2.70 ± 0.07			
	40	1.69 ± 0.01	3.85 ± 0.05			
CH ₃ CN	10	2.17 ± 0.01	0.63 ± 0.02	-6.50 ± 1	-2.48 ± 0.01	-13.48 ± 3
	25	1.82 ± 0.01	1.50 ± 0.03			
	40	1.70 ± 0.01	2.32 ± 0.06			
CH ₃ OH	10	2.22 ± 0.01	0.66 ± 0.02	-6.77 ± 1	-2.51 ± 0.01	-14.29 ± 3
	25	1.85 ± 0.01	1.92 ± 0.04			
	40	1.72 ± 0.01	3.38 ± 0.05			
CH ₃ C=O CH ₃	10	2.25 ± 0.01	0.54 ± 0.02	-6.91 ± 0.9	-2.54 ± 0.01	-14.66 ± 3
	25	1.87 ± 0.01	1.50 ± 0.08			
	40	1.74 ± 0.01	2.49 ± 0.06			
DMF	10	2.12 ± 0.01	1.14 ± 0.02	-6.30 ± 1	-2.41 ± 0.01	-13.05 ± 3
	25	1.78 ± 0.01	2.73 ± 0.03			
	40	1.66 ± 0.01	4.08 ± 0.08			
CH ₃ CN	10	2.14 ± 0.01	0.68 ± 0.02	-6.38 ± 1	-2.43 ± 0.01	-13.25 ± 3
	25	1.79 ± 0.01	1.70 ± 0.05			
	40	1.68 ± 0.01	2.44 ± 0.06			
CH ₃ OH	10	2.18 ± 0.01	0.72 ± 0.01	-6.58 ± 1	-2.45 ± 0.01	-13.85 ± 3
	25	1.81 ± 0.01	2.12 ± 0.04			
	40	1.69 ± 0.01	3.63 ± 0.07			
CH ₃ C=O CH ₃	10	2.21 ± 0.01	0.59 ± 0.01	-6.78 ± 1	-2.48 ± 0.01	-14.42 ± 3
	25	1.82 ± 0.01	1.75 ± 0.03			
	40	1.71 ± 0.01	2.74 ± 0.11			
DMF	10	2.35 ± 0.01	0.66 ± 0.02	-7.20 ± 1	-2.61 ± 0.01	-15.40 ± 3
	25	1.91 ± 0.01	2.08 ± 0.04			
	40	1.82 ± 0.01	2.85 ± 0.09			
CH ₃ CN	10	2.37 ± 0.01	0.40 ± 0.01	-7.33 ± 1	-2.63 ± 0.01	-15.77 ± 3
	25	1.93 ± 0.01	1.23 ± 0.03			
	40	1.83 ± 0.01	1.70 ± 0.05			

(continued)

TABLE 2. (continued)

Complex	Solvents	T (°C)	Log K_{Co}	$P_{1/2}$ (torr)	ΔH° (kcal/mol)	ΔG° (kcal/mol)	ΔS° (e.u.)	
[Ru(picdien)Cl] (14)	CH ₃ OH	10	2.38 ± 0.01	0.45 ± 0.01				
		25	1.94 ± 0.01	1.57 ± 0.04	-7.47 ± 1	-2.64 ± 0.01	-16.20 ± 3	
		40	1.84 ± 0.01	2.60 ± 0.01				
	$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$	10	2.42 ± 0.01	0.36 ± 0.01				
		25	1.96 ± 0.01	1.26 ± 0.03	-7.74 ± 1	-2.68 ± 0.01	-16.97 ± 3	
		40	1.85 ± 0.01	1.96 ± 0.04				
	DMF	10	2.05 ± 0.01	1.33 ± 0.02				
		25	1.82 ± 0.01	2.56 ± 0.06	-4.72 ± 0.2	-2.48 ± 0.01	-7.51 ± 1	
		40	1.70 ± 0.01	3.70 ± 0.08				
	CH ₃ CN	10	2.06 ± 0.01	0.82 ± 0.02				
		25	1.84 ± 0.01	1.51 ± 0.05	-4.85 ± 0.3	-2.51 ± 0.01	-7.85 ± 1	
		40	1.70 ± 0.01	2.32 ± 0.06				
CH ₃ OH	10	2.09 ± 0.01	0.89 ± 0.02					
	25	1.86 ± 0.01	1.88 ± 0.03	-5.12 ± 0.2	-2.54 ± 0.01	-8.65 ± 1		
	40	1.71 ± 0.01	3.50 ± 0.06					
$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{CH}_3 \end{array}$	10	2.11 ± 0.01	0.75 ± 0.01					
	25	1.88 ± 0.01	1.52 ± 0.04	-5.61 ± 0.2	-2.56 ± 0.01	-10.23 ± 0.8		
	40	1.72 ± 0.01	2.63 ± 0.07					

17]. The complexes exhibit discrimination towards CO binding, though the electronic effects of the axial and equatorial ligands are about the same. The lower stability of Ru(III) carbonyls seems to be due to a weak $d\pi-p\pi$ backbonding to CO in these complexes. The situation is therefore, the reverse of the Fe(II) porphyrins [27, 29] where CO exhibits a strong bonding to the metal ion. The discrimination against CO binding in Fe(II) porphyrins comes mostly from the steric effects such as the interaction of distal histidine in haemoglobin or the size of the pocket [29] containing the CO. In the Ru(III) carbonyls studied, the CO is reversibly bonded and is displaced by bubbling N_2 through the solution in contrast to the irreversible binding of CO in Fe(II) porphyrins [30].

The values of the thermodynamic parameters ΔG° , ΔH° and ΔS° associated with the equilibrium constant for carbonylation K_{CO} are in agreement with those reported earlier [16, 17]. The enthalpies are less exothermic and the entropies are less negative for saloph complexes than naphoph complexes which reflects on the weaker M-CO bond in the saloph complexes than those already reported by us [16, 17].

References

- 1 Y. Uemori and E. Kyuno, *Inorg. Chim. Acta*, **165** (1989) 115.
- 2 J. Kuriyan, S. Wilz, M. Karplus and G. A. Petsko, *J. Mol. Biol.*, **192** (1986) 133.
- 3 B. Luisi and K. Nagai, *Nature (London)*, **320** (1986) 555.
- 4 Q. H. Gibson, J. S. Olson, R. E. McKinnie and R. J. Rahlfs, *J. Biol. Chem.*, **261** (1986) 10228.
- 5 R. J. Rahlfs, J. S. Olson and Q. H. Gibson, *J. Biol. Chem.*, **263** (1988) 1803.
- 6 B. A. Springer, K. D. Egeberg, S. G. Sligar, R. J. Rahlfs, A. J. Mathews and J. S. Olson, *J. Biol. Chem.*, **264** (1989) 3057.
- 7 S. Kaminaka, T. Ogura and T. Kitagawa, *J. Am. Chem. Soc.*, **112** (1990) 23.
- 8 J. Hafrichter, J. H. Sommer, E. R. Henry and W. A. Eaton, *Proc. Natl. Acad. Sci. U.S.A.*, **80** (1983) 2235.
- 9 J. W. Petrich, J. L. Martin, D. Honde, C. Poyart and A. Orszag, *Biochemistry*, **26** (1987) 7914.
- 10 A. H. Reynolds and P. M. Rentzepis, *J. Biophys.*, **38** (1982) 15.
- 11 S. Dasgupta and T. G. Spiro, *Biochemistry*, **25** (1986) 5941.
- 12 T. W. Scott and J. M. Friedman, *J. Am. Chem. Soc.*, **106** (1984) 5677.
- 13 W. H. Woodruff and S. Farquharson, *Science*, **201** (1978) 831.
- 14 C. Gueutin, D. Lexa, M. Momenteau and J. M. Saveant, *J. Am. Chem. Soc.*, **112** (1990) 1874.
- 15 M. M. Taqui Khan, D. Srinivas, R. I. Kureshy and N. H. Khan, *Inorg. Chem.*, **29** (1990) 2320.
- 16 M. M. Taqui Khan, N. H. Khan, R. I. Kureshy, A. B. Boricha and Z. A. Shaikh, *Inorg. Chim. Acta*, **170** (1990) 213.
- 17 M. M. Taqui Khan, N. H. Khan, R. I. Kureshy and A. B. Boricha, *Inorg. Chim. Acta*, **174** (1990) 175.
- 18 E. E. Mercer and R. R. Buckley, *Inorg. Chem.*, **4** (1965) 1692.
- 19 M. M. Collman, R. K. Boggess, J. W. Hughes, L. T. Taylor, *Inorg. Chem.*, **20** (1981) 700.
- 20 M. M. Taqui Khan, Ch. Sreelatha, S. A. Mirza, G. Ramachandiraiah and S. H. R. Abdi, *Inorg. Chim. Acta*, **154** (1988) 103.
- 21 B. N. Figgis, J. Lewis, in J. Lewis and R. G. Wilkins (eds.), *Modern Coordination Chemistry*, Interscience, New York, 1960, p. 403.
- 22 N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81** (1959) 6138.
- 23 S. A. Patel and V. H. Kulkarni, *Polyhedron*, **3** (1984) 21.
- 24 M. M. Taqui Khan, S. B. Halligudi, S. Shukla and Z. A. Shaikh, *J. Mol. Catal.*, **57** (1990) 301.
- 25 J. Calalan, J. Gomez, A. Couto and J. Laynez, *J. Am. Chem. Soc.*, **112** (1990) 1678.
- 26 J. P. Collman, J. I. Brauman, I. R. Halbert and K. S. Suslick, *Proc. Natl. Acad. Sci., U.S.A.*, **73** (1976) 3333.
- 27 J. P. Collman, J. I. Brauman, L. J. Brent, J. L. Sissler, R. M. Morris and Q. M. Gibson, *J. Am. Chem. Soc.*, **105** (1983) 3052.
- 28 T. G. Traylor, N. Koga, L. A. Deonduff, *J. Am. Chem. Soc.*, **107** (1985) 6504.
- 29 R. D. Hancock, J. S. Weaveng and H. M. Margues, *J. Chem. Soc., Chem. Commun.*, (1989) 1176.
- 30 K. Kim, J. Fellenger, J. L. Sissler, J. Hugdahl, M. Cyr, J. P. Collman and J. P. Ibers, *J. Am. Chem. Soc.*, **111** (1989) 403.