# DIOXYGEN AFFINITIES OF SOME RUTHENIUM(III) SCHIFF BASE COMPLEXES

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**Abstract**—The synthesis and dioxygen affinities of some ruthenium(III) Schiff base complexes in DMF solution in the presence of different axial bases are reported. The ligands used are bis(salicylaldehyde)ethylenediimine (salen), bis(salicylaldehyde)diethylenetriimine (saldien), bis(picolinaldehyde)-o-phenylenediimine (picoph), bis(picolinaldehyde)ethylenediimine (picen) and bis(picolinaldehyde)diethylenetriimine (picdien). The axial ligands employed are chloride (Cl$^-$), imidazole (Im) and 2-methylimidazole (2-MeIm). From the oxygenation constants it is found that electron donating substituents on the Schiff bases increase the affinity for dioxygen. Equilibrium dioxygen uptake measurements at 278, 288 and 303 K provide values of $\Delta H^\circ$ and $\Delta S^\circ$ of oxygenation that fall in the range −6.1 to −13.3 kcal mol$^{-1}$ for $\Delta H^\circ$ and −10 to −31 cal deg$^{-1}$ mol$^{-1}$ for $\Delta S^\circ$. The dioxygen adducts of Ru$^{III}$ were characterized by electrochemistry, UV–vis, IR and EPR techniques as Ru$^{IV}$ superoxo complexes.

The study of complexes capable of reversible binding of molecular oxygen, known as oxygen-carriers, has received a great deal of interest.[1–14] Such systems are utilized biologically in the transport and storage of molecular oxygen.[1–14] In general chelating ligands which are good σ-donors increase the electron density on the metal ion, facilitating dioxygen binding. Hence the dioxygen carriers so far studied mainly include metal complexes of Schiff bases,[15–17] porphyrins[18–20] and macrocyclic ligands.[21] The binding of molecular oxygen to a metal centre involves a "formal" oxidation of the metal by one or two electrons with a simultaneous reduction of the coordinated dioxygen to a superoxo or peroxo species. For this reason metal ions such as Mn$^{II}$,[12] Co$^{II}$,[14] Fe$^{II}$,[3] Cu$^{I}$[22] and Ni$^{II}$,[23] which have readily available variable oxidation states, form dioxygen complexes with wide variations of geometry and coordination number. Among these, the complexes of Co$^{II}$ with tetra- and penta-dentate Schiff bases have attracted much attention as a means of separation of oxygen from air.[23] Very recently, the dioxygen affinities of Co$^{II}$ Schiff base complexes in the presence of a variety of axial bases were reported.[24]

We have recently reported the dioxygen affinities of Ru$^{III}$ Schiff base complexes prepared from bis(salicylaldehyde)-o-phenylenediimine (saloph),[25] naphthaldehyde and various amines.[26] In continuation of earlier work on the synthesis of homogeneous catalysts for oxygen atom transfer reactions, we report here the synthesis of a number of analogous Ru$^{III}$ Schiff base complexes with a variation of the donor sites (N$_2$O$_2$, N$_3$O$_2$, N$_4$ and N$_5$) and their oxygenation studies. The ligands used are salen, saldien, picoph, picen and picdien. Variations were also made in the axial coordination of the complexes in order to assess the difference in dioxygen affinities with a change in the σ-donor ability of the axial ligands.

## EXPERIMENTAL

### Synthesis

The complexes K[Ru(salen)Cl$_2$] (**1**), [Ru(salen)(Im)Cl] (**2**), [Ru(salen)(2-MeIm)Cl] (**3**), [Ru(picoph) Cl$_2$]Cl (**4**), [Ru(picoph)(Im)Cl]Cl$_2$ (**5**), [Ru(picoph)

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(2-MeIm)Cl]Cl$_2$ (**6**), [Ru(picen)Cl$_2$]Cl (**7**), [Ru(picen)(Im)Cl]Cl$_2$ (**8**), [Ru(picen)(2-MeIm)Cl]Cl$_2$ (**9**), [Ru(saldien)Cl] (**10**) and [Ru(picdien)Cl]Cl$_2$ (**11**) were prepared and characterized according to the reported procedures.[26]

oxygen by complexes **1–11** was measured with the help of a manometric set-up.[26] The values of equilibrium constants for oxygenation as log $K_{O_2}$ for all the complexes along with the thermodynamic parameters ($\Delta H^\circ$ and $\Delta S^\circ$) are listed in Table 1.

*Oxygen uptake measurements*

The oxygenation studies were conducted for a millimolar concentration of the complexes in DMF at 278, 288 and 303 K. Absorption of molecular

*Physical measurements*

Electronic spectra of complexes in DMF solutions were recorded on a Shimadzu UV–vis spectrometer (model UV-160). IR spectra were recorded

Table 1. Thermodynamic constants for dioxygen binding to Ru$^{III}$ Schiff base complexes in DMF at 1 atm

| Complex | Temperature (K) | log $K_{O_2}{}^a$ | $\Delta H^{\circ b}$ (kcal mol$^{-1}$) | $\Delta G^{\circ b}$ (kcal mol$^{-1}$) | $\Delta S^{\circ b}$ (eu) |
|---|---|---|---|---|---|
| K[Ru(salen)Cl$_2$] (**1**) | 278 | 2.71 | | | |
| | 288 | 2.48 | | | |
| | 303 | 2.10 | −9.4(0.5) | −2.9 | −21(2) |
| [Ru(salen)(Im)Cl] (**2**) | 278 | 3.42 | | | |
| | 288 | 3.15 | | | |
| | 303 | 2.71 | −11.0(0.5) | −3.8 | −24(2) |
| [Ru(salen)(2-MeIm)Cl] (**3**) | 278 | 3.01 | | | |
| | 288 | 2.77 | | | |
| | 303 | 2.38 | −9.8(0.4) | −3.3 | −21(2) |
| [Ru(picoph)Cl$_2$]Cl (**4**) | 278 | 2.78 | | | |
| | 288 | 2.54 | | | |
| | 303 | 2.14 | −9.9(0.5) | −3.1 | −23(2) |
| [Ru(picoph)(Im)Cl]Cl$_2$ (**5**) | 278 | 3.75 | | | |
| | 288 | 2.43 | | | |
| | 303 | 2.89 | −13.3(0.7) | −4.1 | −31(3) |
| [Ru(picoph)(2-MeIm)Cl]Cl$_2$ (**6**) | 278 | 3.27 | | | |
| | 288 | 2.98 | | | |
| | 303 | 2.52 | −11.6(0.5) | −3.4 | −27(2) |
| [Ru(picen)Cl$_2$]Cl (**7**) | 278 | 2.47 | | | |
| | 288 | 2.33 | | | |
| | 303 | 2.08 | −6.1(0.4) | −2.8 | −10(1) |
| [Ru(picen)(Im)Cl]Cl$_2$ (**8**) | 278 | 3.33 | | | |
| | 288 | 3.08 | | | |
| | 303 | 2.68 | −10.1(0.4) | −3.6 | −21(1) |
| [Ru(picen)(2-MeIm)Cl]Cl$_2$ (**9**) | 278 | 2.67 | | | |
| | 288 | 2.44 | | | |
| | 303 | 2.09 | −9.0(0.2) | −2.9 | −20(1) |
| [Ru(saldien)Cl] (**10**) | 278 | 3.38 | | | |
| | 288 | 3.03 | | | |
| | 303 | 2.69 | −10.5(1.0) | −3.2 | −23(3) |
| [Ru(picdien)Cl]Cl$_2$ (**11**) | 278 | 2.86 | | | |
| | 288 | 2.64 | | | |
| | 303 | 2.27 | −9.1(0.5) | −3.1 | −20(2) |

$^a$ $K_{O_2}$ is in units of M$^{-1}$.
$^b$ $\Delta H^\circ$ was calculated from van't Hoff plots; $\Delta G^\circ$ was calculated from the equation $\Delta G^\circ = -RT \ln K_{O_2}$, estimated error = ±0.5; $\Delta S^\circ$ was calculated from the equation $T\Delta S^\circ = \Delta H^\circ - \Delta G^\circ$.
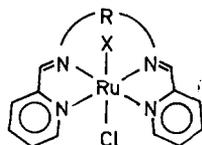
by using a Specord M80 spectrophotometer. Electrochemical measurements were made with a Princeton Applied Research (PAR) instrument.[25] EPR spectra were recorded on a Bruker ESP-300 X-band spectrometer using 100 kHz field modulation. The g values were determined by calibrating with DPPH powder ($g = 2.0036$).

## RESULTS AND DISCUSSION

All the complexes were characterized by elemental analysis, molar conductivity, IR, UV–vis, magnetic susceptibility and EPR studies as described earlier.[27] These studies have revealed that the coordination around ruthenium in all the complexes is distorted octahedral. The Schiff base salen coordinates through $N_2O_2$ donor atoms, while picen and picoph coordinate through $N_4$ donor atoms. However, saldien and picdien coordinate as pentadentate ligands bonding through $N_3O_2$ and $N_5$ donor sites, respectively. The tetradentate Schiff bases occupy the equatorial plane of the ruthenium octahedron; Cl$^-$, Im and 2-MeIm occupy the axial positions (structure I).
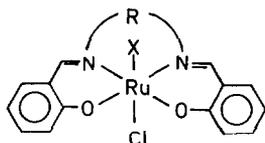
| Complex | R | X |
|---|---|---|
| 1,2,3 Salen | $-(CH_2)_2-$ | Cl$^-$, Im, 2-MeIm |
| 11 Saldien | $-(C_2H_4)NH(C_2H_4)-$ | N of R |

| Complex | R | X |
|---|---|---|
| 4,5,6 Picoph | $-(C_6H_4)-$ | Cl$^-$, Im, 2-MeIm |
| 7,8,9 Picen | $-(CH_2)_2-$ | Cl$^-$, Im, 2-MeIm |
| 12 Picdien | $-(C_2H_4)NH(C_2H_4)-$ | N of R |

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### Oxygenation studies

The oxygenation constants ($\log K_{O_2}$) determined by a manometric technique (Table 1) indicate the formation of 1 : 1 Ru$^{III}$ dioxygen adducts. The Schiff bases show pronounced effects on the $\log K_{O_2}$ values which vary in the order Ru(picoph) > Ru(salen) > Ru(picen). The greater conjugation brought about by picoph seems to induce a greater extent of negative charge on the metal ion and thereby increases the thermodynamic stability of the dioxygen complexes. A similar observation was also made for the complexes prepared from naphthaldehyde and various amines.

The variation in the axial ligands also affects the stability of the dioxygen complexes. The thermodynamic stability of the dioxygen complexes at the three temperatures decreases with axial bases in the order Im > 2-MeIm > Cl$^-$. Except for 2-MeIm the trend is in accordance with a decrease in the lability of the axial ligand. 2-MeIm is more basic than Im and hence its dioxygen adduct is expected to be more stable than the Im complex. However, the lower stability observed for 2-MeIm complexes could be due to the steric effect of the methyl groups.

The thermodynamic stabilities for the dioxygen complexes with pentadentate Schiff base ligands are in the order saldien > picdien. These complexes are relatively less stable than the Im coordinated complexes of salen and picen which have the same overall donor atoms, $N_3O_2$ and $N_5$, respectively. This reflects on the fact that Im is a better $\sigma$-donor as an axial ligand than the secondary NH group in chelated dien ligands.

Thermodynamic parameters (Table 1) indicate that the formation of Ru$^{III}$ dioxygen adducts is highly favoured by exothermic enthalpies associated with negative entropies. It is of interest to compare the effect of the o-phenylenediamine group in complexes 4–6 with the ethylenediamine group in complexes 1–3 and 7–9. The enthalpies are more exothermic by about 2–3 kcal mol$^{-1}$ in complexes 4–6 as compared to 1–3 and 7–9, indicating the stabilization of the M—O$_2$ bond by the presence of an extra aromatic ring. The large stability due to the presence of the o-phenylenediamine group observed here is in accordance with our earlier observations with bis(naphthaldehyde)imine complexes.[26] The manometric measurements therefore reveal that complexes 1–11 interact with molecular oxygen and yield 1 : 1 Ru$^{III}$–dioxygen adducts.

### Characterization of Ru$^{III}$ Schiff base dioxygen complexes

*Electrochemical studies under nitrogen.* Electrochemical measurements on complexes 1–11 in DMF, containing tetrabutylammonium perchlorate (TBAP), under nitrogen at a glassy carbon electrode (GEC) showed three one-electron redox couples in the potential range 0.8 to $-1.2$ V vs saturated calomel electrode (SCE). A representative cyclic voltammogram for complex 3 is depicted in Fig. 1. The couple appearing at positive potentials
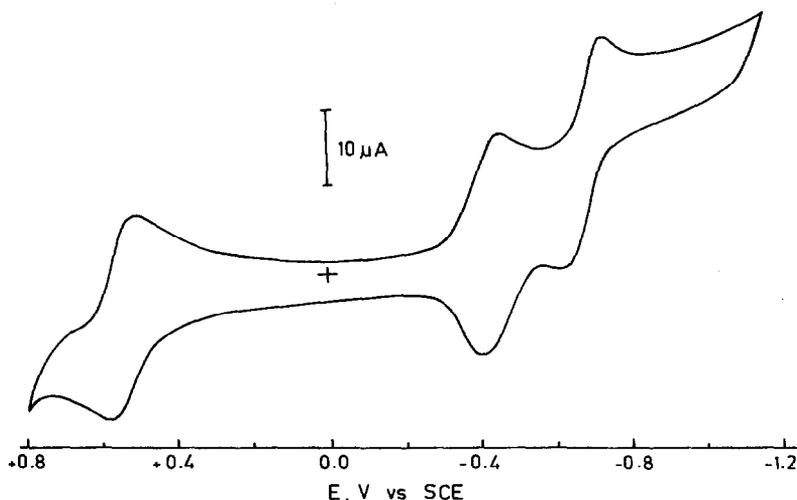
Fig. 1. Cyclic voltammogram of [Ru(salen)(2-MeIm)Cl] (3; 1 mM) in 0.1 M [Bu$_4$N][ClO$_4$]/DMF. Scan rate = 100 mV s$^{-1}$.

(0.4–0.55 V) is assigned to the metal centred redox couple Ru$^V$/Ru$^{IV}$, while the other two appearing in the region −0.2 to −1.01 V are assigned to the Ru$^{IV}$/Ru$^{III}$ and Ru$^{III}$/Ru$^{II}$ couples, respectively. Most of the Ru$^{III}$ complexes also showed an irreversible ligand-based anodic oxidation wave in the range +0.9 to +1.1 V when the anodic scans were futher extended.

The d.c. and differential pulse polarograms of these complexes in DMF under nitrogen showed two anodic waves and a cathodic wave. The anodic wave observed in the range +0.2 to −0.15 V against Ag/AgCl was attributed to the interaction

of chloride ions with the electrode. The cathodic wave in the range −0.43 to −0.70 V against Ag/AgCl was assigned to the Ru$^{III}$/Ru$^{II}$ reduction couple. The d.c. and differential pulse polarograms for complex 8 are shown in Figs 2a and b, respectively. The $E_{1/2}$ values corresponding to Ru$^{III}$/Ru$^{II}$ at DME are summarized in Table 2. It is obvious

Table 2. Polarographic data for Ru$^{III}$ Schiff base complexes (1 mM) in DMF under nitrogen and oxygen atmospheres [$E_{1/2}$ (V) vs Ag/AgCl]; $t$ = 298 K, $\mu$ = 0.1 M tetrabutylammonium perchlorate

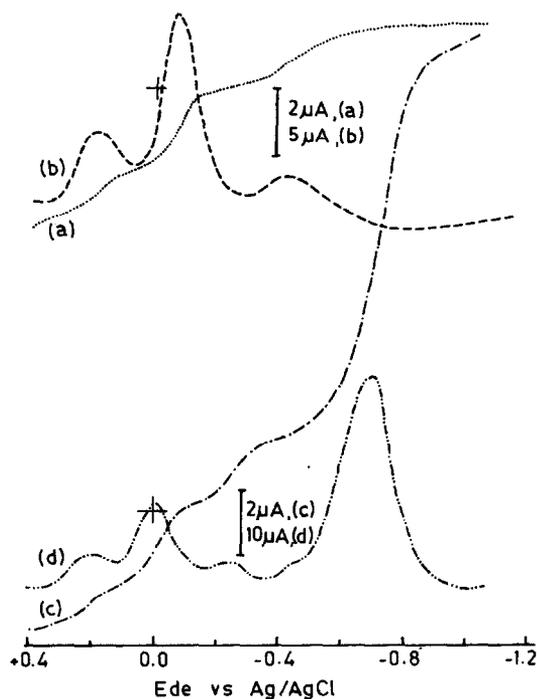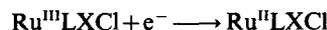| | Under nitrogen | Under oxygen | |
|---|---|---|---|
| Complex | Ru$^{III}$/Ru$^{II}$ $E_{1/2}$ (V) | Ru$^{IV}$/Ru$^{III}$ $E_{1/2}$ (V) | Ru$^{III}$/Ru$^{II}$ $E_{1/2}$ (V) |
| 1 | −0.450 | −0.220 | −0.403 |
| 2 | −0.513 | −0.255 | −0.500 |
| 3 | −0.482 | −0.234 | −0.435 |
| 4 | −0.544 | −0.206 | −0.450 |
| 5 | −0.686 | −0.269 | −0.555 |
| 6 | −0.576 | −0.241 | −0.520 |
| 7 | −0.427 | −0.210 | −0.426 |
| 8 | −0.515 | −0.235 | −0.500 |
| 9 | −0.466 | −0.216 | −0.450 |
| 10 | −0.466 | −0.248 | −0.443 |
| 11 | −0.435 | −0.236 | −0.430 |



Fig. 2. Direct-current polarograms under nitrogen (a) and under oxygen (c) and differential pulse polarograms under nitrogen (b) and under oxygen (d) of [Ru(picen)(Im)Cl]Cl$_2$ (8; 1 mM) in DMF at 298 K.
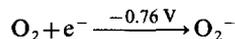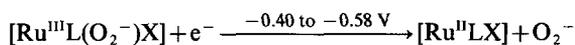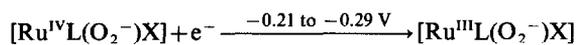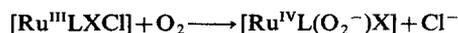
from the polarographic data for the Ru$^{III}$/Ru$^{II}$ couple that the Schiff bases and axial ligands have pronounced effects on the $E_{1/2}$ values. The potentials shift towards the more negative side with Schiff bases in the order picoph > salen > saldien > picen > picdien. Also, the $E_{1/2}$ values shifted towards negative potentials as the basicity of the axial ligand was increased. All the Im-substituted complexes showed more negative $E_{1/2}$ values than 2-MeIm- and Cl$^-$-substituted complexes. The $E_{1/2}$ values (Table 2) at DME are relatively more positive than those at GCE. The anodic oxidation step expected for Ru$^{III}$/Ru$^{IV}$ did not appear at DME, probably because it is suppressed or overlapped by the anodic currents due to chloride ions.

*Electrochemical studies under oxygen.* Through a millimolar solution of complexes 1–11 in DMF, molecular oxygen was passed for a period of 1 h, and d.c. and DPP responses at 298 K were recorded under an oxygen atmosphere. Apart from the two anodic waves for the Cl$^-$ ion and the cathodic wave for the Ru$^{III}$/Ru$^{II}$ couple, two additional reductive waves appeared (Fig. 2c,d), one in the range $-0.210$ to $-0.293$ V assigned to the Ru$^{IV}$/Ru$^{III}$ couple and the other near $-0.762$ V against Ag/AgCl assigned to the reduction of dissolved molecular oxygen to superoxide anion.[28] The potential data for the oxygenated solutions are listed in Table 2. Interaction of molecular oxygen with ruthenium results in a positive shift of the $E_{1/2}$ values. On flushing nitrogen through the oxygenated solutions both the additional waves disappeared and only the Ru$^{III}$/Ru$^{II}$ couple was seen in the range as observed

Under nitrogen

$$Ru^{III}LXCl + e^- \longrightarrow Ru^{II}LXCl$$

Under oxygen

$$[Ru^{III}LXCl] + O_2 \longrightarrow [Ru^{IV}L(O_2{}^-)X] + Cl^-$$

$$[Ru^{IV}L(O_2{}^-)X] + e^- \xrightarrow{-0.21 \text{ to } -0.29 \text{ V}} [Ru^{III}L(O_2{}^-)X]$$

$$[Ru^{III}L(O_2{}^-)X] + e^- \xrightarrow{-0.40 \text{ to } -0.58 \text{ V}} [Ru^{II}LX] + O_2{}^-$$

$$O_2 + e^- \xrightarrow{-0.76 \text{ V}} O_2{}^-$$

L = Schiff base
X = Cl$^-$, Im and 2-MeIm

Scheme 1.

under nitrogen. However, the additional waves reappeared by passing oxygen again through the deoxygenated solutions. The oxygenation/ deoxygenation cycle that could be repeated several times indicates reversible binding of molecular oxygen to Ru$^{III}$ Schiff base complexes. The Ru$^{IV}$/Ru$^{III}$ couple (Table 2) showed a similar trend with respect to Schiff bases and axial ligands as was observed for the Ru$^{III}$/Ru$^{II}$ couple. The electrochemical reactions of the complexes before and after oxygenation are depicted in Scheme 1.

*Spectral studies.* The UV–vis spectra of all the Ru$^{III}$ complexes before and after oxygenation were recorded in DMF at 298 K. No remarkable change was observed in the spectra as a consequence of oxygenation except for a modest increase in absorb-

Table 3. EPR $g$ tensor componnts for Ru$^{III}$ Schiff base complexes as frozen solutions at 77 K

| Complex | Solvent[a] | Species[b] | $g_1{}^c$ | $g_2{}^c$ | $g_3{}^c$ |
|---|---|---|---|---|---|
| K[Ru(salen)Cl$_2$] | DMF | A | 2.452 | 2.261 | 1.795 |
| | | B | 2.357 | 2.357 | 1.862 |
| [Ru(salen)(Im)Cl] | DMF | A | 2.428 | 2.244 | 1.796 |
| | | B | 2.355 | 2.355 | 1.862 |
| [Ru(salen)(2-MeIm)Cl] | DMF | A | 2.432 | 2.228 | 1.783 |
| | | B | 2.356 | 2.356 | 1.862 |
| [Ru(picoph)Cl$_2$]Cl | DMF | | 2.382 | 2.382 | 1.820 |
| [Ru(picoph)(Im)Cl]Cl$_2$ | DMF | | 2.416 | 2.416 | 1.777 |
| [Ru(picoph)(2-MeIm)Cl]Cl$_2$ | DMF | | 2.425 | 2.425 | 1.782 |
| [Ru(picen)Cl$_2$]Cl | DMF | | 2.273 | 2.273 | 1.855 |
| [Ru(picen)(Im)Cl]Cl$_2$ | DMF | | 2.261 | 2.261 | 1.876 |
| [Ru(picen)(2-MeIm)Cl]Cl$_2$ | DMF | | 2.269 | 2.269 | 1.881 |
| [Ru(picdien)Cl] | DMF | | 2.268 | 2.268 | 1.914 |

[a] DMF = $N,N$-dimethylformamide.
[b] A = monosolvated complex; B = disolvated complex.
[c] Estimated error = $\pm 0.002$.

ance. Similar observations were made earlier for Ru[III] complexes[26] prepared from naphthaldehyde and amines and some Co[II] Schiff base complexes.[24] The IR spectra of Ru[III] dioxygen complexes show a new peak in the narrow range 1040–1050 cm$^{-1}$, apart from the ligational peaks. The new peak is assigned to the $v$(O—O) stretching mode and falls in the range of values reported for transition metal superoxo complexes.

The EPR spectra of complexes 1–3 in DMF at 77 K indicate that the Ru—Cl bond in solution decomposes and forms monosolvated (A) and disolvated (B) species. Species A is characterized by a rhombic $g$ tensor while B is characterized by an axial $g$ tensor (Table 3). The $g$ values are different from those of their powder samples.[27] However, EPR spectra for the rest of the complexes are characterized by an axial $g$ tensor (Table 3).

When molecular oxygen (1 atm.) was passed through THF solutions of complexes 4 and 5 for about 5 min at 233 K, a dramatic change in the EPR spectra was observed. The resonances due to Ru[III] complexes disappeared and instead there appeared a spectrum characterized by a rhombic $g$ tensor having small $g$ anisotropy [$g_1 = 2.095(1)$, $g_2 = 2.083(1)$ and $g_3 = 2.067(1)$ for 4 and $g_1 = 2.050(1)$, $g_2 = 2.011(1)$ and $g_3 = 1.988(1)$ for 5]. Earlier a similar observation was also noted in the EPR spectra of Ru[III] complexes prepared from naphthaldehyde[26] or salicylaldehyde[29] and $o$-phenylenediamine. The $g$ values and the other spectral and electrochemical studies characterize the Ru[III] dioxygen adducts as Ru[IV] superoxo complexes. The superoxo complexes are unstable at ambient temperatures. The EPR resonance positions suggest that the unpaired electron in Ru[IV] superoxo complexes occupies an MO having a predominant oxygen $\pi^*$ character while it occupies a $d_{xy}$ orbital in the unoxygenated complex. The rhombic nature of the $g$ tensor further indicates that oxygen has an end-on coordination in the superoxo complexes.

## CONCLUSIONS

Syntheses of several Ru[III] complexes containing Schiff bases and axial ligands having varying $\sigma$-donor capacities are reported. The complexes interact with molecular oxygen in DMF solutions and form Ru[IV] Schiff base superoxo complexes. The superoxo complexes are characterized by electrochemical and spectral studies, and thermodynamic quantities associated with them were computed. The log $K_{O_2}$ values for the present complexes are smaller than those for complexes prepared earlier from naphthaldehyde and amines,[26] indicating that the present complexes form less

stable Ru[IV] superoxo complexes and thereby could act as versatile homogeneous catalysts in oxygen atom transfer reactions.

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