the ligand-field manifold upon complexation of a second Rh(III) metal center. The shift to lower energy of the charge-transfer manifold extends the threshold irradiation wavelength used to generate H_2 from 405 and 436 nm. Apparently, internal conversion to the photoactive state is competitive with nonradiative decay to the ground state in these complexes, but emission is not a competitive process.

The heterobimetallic complexes $(bpy)_2RuLRhH_2(PPh_3)_2^{3+}$ display competitive emission and photochemistry, but in a unique manner. The photochemistry is the photoelimination from a Rh(III)-based excited state with threshold excitation energies that are the same as those for the dirhodium system. However, as pointed out in an earlier section, the emission is characteristic of a ruthenium-based MLCT. In Figure 2, the absorption, excitation, and emission spectra are overlayed on the same diagram. Once again, the excitation profile approaches the base line at higher energies, indicating that upper excited states can bypass the emissive state during interconversion/intersystem crossing back to the ground state. The photochemical quantum yields also illustrated in Figure 2 indicate that the lowest MLCT state is not capable of populating the photoactive state (see Figure 4c). While the lowest MLCT state is presumed to be a M → L MLCT state where M has substantial Ru(II) character on the basis of the emission spectrum and lifetime, the similarity in potential for Ru(II) and Rh(III) oxidations would suggest that the d orbitals are close in energy and thus capable of mixing (Figure 4c). There may be a substantial mixing in the MLCT states which when irradiated lead to interconversion to the LF state on Rh(III) responsible for photochemistry. If there is substantial Ru(II) character in the transitions in this region, the process involved is an intramolecular, energy-transfer process between two metal centers in the molecule.

Further work is ongoing to extend the threshold irradiation wavelength into the visible region of the spectrum and to attempt

to determine the actual mechanism and states involved in the photochemistry and photophysics.

Conclusion

The monometallic dihydride complexes $RhH_2(PPh_3)_2L^+$ undergo photochemistry and photophysics from two different excited states. Photophysics occurs from an MLCT excited state generated by promoting a π-symmetry electron from Rh(III) into a π^* orbital on L. The photochemistry occurs from an LF state and is relatively independent of the nature of L.

When L is bpm, dpp, or dpq, a second $RhH_2(PPh_3)_2$ fragment can be bound to L to form a homonuclear, bimetallic complex, $[RhH_2(PPh_3)_2]_2L^{2+}$. The same type of LF photochemistry is observed for this bimetallic complexes as was observed for the monometallic species. However, room-temperature emission is not observed in this system due to the presence of a low-lying MLCT state, which efficiently deactivates the molecule back to the ground state.

Coupling the Rh(III) dihydride to a highly absorbing Ru(bpy)$_2$ fragment through bpm, dpp, or dpq results in the homonuclear, bimetallic complexes $(bpy)_2RuLRhH_2(PPh_3)_2^{3+}$. These complexes display photophysics characteristic of MLCT excited states associated with the Ru center and photochemistry characteristic of the LF state on the Rh center. The partitioning of the incident energy into processes that occur at different metal centers in these systems suggests that some intramolecular energy transfer is occurring in these systems. The wavelength dependence of the photochemistry also enables the approximation of the energy of the LF state responsible for photochemical H_2 production in these systems.

Synthesis, Characterization, and EPR Studies of Stable Ruthenium(III) Schiff Base Chloro and Carbonyl Complexes

M. M. Taqui Khan,* D. Srinivas, R. I. Kureshy, and N. H. Khan

Stable ruthenium(III) carbonyl chelates of Schiff bases with axial ligands chloro, imidazole, and 2-methylimidazole are synthesized by interacting the methanolic solutions of their correspondng Ru(III) chloro complexes with carbon monoxide. The Schiff bases used are bis(salicylaldehyde) ethylenediimine (salen), bis(salicylaldehyde) o-phenylenediimine (saloph), bis(salicylaldehyde) diethylenetriimine (saldien), bis(picolinaldehyde) ethylenediimine (picen), bis(picolinaldehyde) o-phenylenediimine (picoph), and bis(picolinaldehyde) diethylenetriimine (picdien). These complexes are characterized by elemental analysis and IR, UV–visible, differential-pulse polarography, conductivity, magnetic susceptibility, and EPR techniques. The oxidation state of the metal ion in these complexes is confirmed to be +3 by electrochemical, magnetic susceptibility, and EPR measurements. The complexes belong to a low-spin Ru(III) 4d^5 configuration. EPR studies indicate that the unpaired electron in the carbonyl complexes occupies the d$_{xy}$ orbital. The distortion from the octahedral symmetry and delocalization parameters vary with the axial ligands, as well as with temperature. MO coefficients of T$_2$ orbitals in these complexes were estimated. A comparison of EPR results on chloro and carbonyl complexes is made. In the case of salen and saloph complexes, replacement of the axial ligand Cl$^-$ by CO changes the energy level ordering. Differential-pulse polarographic study of the carbonyls reveals that the redox potential of Ru(III)/Ru(II) couple becomes more negative with increasing basicity of the axial ligand.

Introduction

Carbonyl complexes of transition-metal ions, especially those of ruthenium, are important in homogeneous catalysis of carbonylation and oxo reactions.[1-3] Much of the understanding about
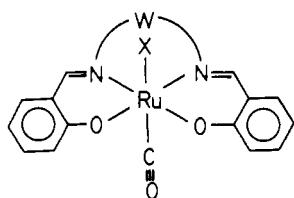
carbonyl complexes comes from the study of metal complexes in lower oxidation states[4] mainly due to the stabilization of these oxidation states by CO. Information on the higher valent carbonyls of ruthenium in aqueous solution is, however, restricted because of the hydrolytic tendencies of the metal ion in aqueous solution.[5,6]

(1) Süss-Fink, G.; Schmidt, G. F. *J. Mol. Catal.* **1987,** *42,* 361. Squarez, T.; Fontal, B. *Ibid.* **1985,** *32,* 191. Jenner, G.; Bitsi, G.; Schleiffer, E. *Ibid.* **1987,** *39,* 233.

(2) Taqui Khan, M. M.; Halligudi, S. B.; Abdi, S. H. R. *J. Mol. Catal.* **1988,** *44,* 179; Taqui Khan, M. M.; Halligudi, S. B.; Abdi, S. H. R. *Ibid.* **1988,** *45,* 215.

(3) Taqui Khan, M. M.; Halligudi, S. B.; Shukla, S. *Angew. Chem., Int. Ed. Engl.* in press.

(4) Schröder, M.; Stephenson, T. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 4, Chapter 45, p 277.

(5) Taqui Khan, M. M.; Ramachandraiah, G.; Shukla, R. S. *Inorg. Chem.* **1988,** *27,* 3274.

Reactions of $RuCl_3 \cdot xH_2O$ with CO in acidic medium were reported to give[7] the octahedral species $[RuCl_5(CO)]^{2-}$, for which EPR and MO studies were reported.[8] Kinetics of formation of carbonyl complexes by the interaction of ruthenium(II) chloride and HCOOH and their conversion to other species were investigated.[9] The enthalpy of the formation of the Ru(II) carbonyl species $[Ru(NH_3)_5(CO)]^{2+}$ was evaluated.[10] Coordination of CO to ruthenium(III) in γ-Al_2O_3[11] and Y-type zeolite[12] was reported to give octahedral and tetrahedral ruthenium carbonyl species, respectively, with a strong Ru–CO bond.

In view of the growing interest in oxygenation and carbonylation of Ru(III) complexes[13-15] for new catalysts, we report in the present communication the synthesis and characterization of some stable Ru(III) Schiff base chloro and carbonyl complexes of the composition $[Ru^{III}LX(Cl)]^{n+}$ and $[Ru^{III}LX(CO)]^{n+}$ where L is a Schiff base, bis(salicylaldehyde) ethylenediimine (salen), bis-(salicylaldehyde) o-phenylenediimine (saloph), bis(salicylaldehyde) diethylenetriimine (saldien), bis(picolinaldehyde) ethylenediimine (picen), bis(picolinaldehyde) o-phenylenediimine (picoph), or bis(picolinaldehyde) diethylenetriimine (picdien); X = Cl⁻, imidazole (Im), or 2-methylimidazole (2-MeIm); and n = 0, 1, 2, or 3 (structures **1–14**). Although there is a wealth of information

	Complex	W	X
1, 2, 3	Salen	-(CH$_2$)$_2$-	Cl⁻, Im, 2-MeIm
4, 5, 6	Saloph	-(C$_6$H$_4$)-	Cl⁻, Im, 2-MeIm
7	Saldien	-(C$_2$H$_4$)NH(C$_2$H$_4$)-	N of W

I
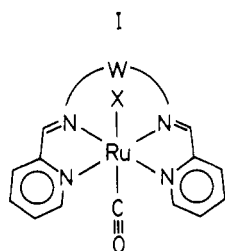
	Complex	W	X
8, 9, 10	Picen	-(CH$_2$)$_2$-	Cl⁻, Im, 2-MeIm
11, 12, 13	Picoph	-(C$_6$H$_4$)-	Cl⁻, Im, 2-MeIm
14	Picdien	-(C$_2$H$_4$)NH(C$_2$H$_4$)-	N of W

II

available on transition-metal complexes of Schiff bases,[16] it is

largely confined to the first-row metals, notably iron, cobalt, and nickel.[17,18] Very little has been reported for the Schiff base complexes of ruthenium.[19,20] We have reported in earlier communications the synthesis of the parent chloro complexes of Ru(III) with various Schiff bases used in this investigation.[21,22]

The Schiff base carbonyl complexes were characterized by elemental analysis, IR, UV–visible, differential-pulse polarography (DPP), conductivity, magnetic susceptibility, and EPR techniques. The complexes possess a low-spin $4d^5$ configuration. Distortion from the octahedral geometry and covalency parameters with a change in the nature of the Schiff base axial ligand and temperature were studied. MO coefficients of the T_2 orbitals were estimated. The EPR results for the parent chloro complexes are presented here and compared with the results for their carbonyl analogues. In the case of salen and saloph complexes, the ordering of the energy levels is changed in the chloro and carbonyl complexes.

Experimental Section

A. Materials. The materials $RuCl_3 \cdot 3H_2O$ (Johnson and Mathey), imidazole, and 2-methylimidazole (Fluka) were of AR grade and were used as such. Salicylaldehyde, pyridine-2-carboxaldehyde, ethylenediamine, and diethylenetriamine (Fluka) were distilled prior to use. o-Phenylenediamine (Alfa) was recrystallized twice from benzene. All the solvents were of AR grade and purified further by the usual laboratory procedures.[23]

The complex $K_2RuCl_5 \cdot H_2O$[24] and Schiff bases salen,[25] saloph,[26] saldien,[25] picen,[27] picoph,[28] and picdien[29] were prepared according to the literature procedures. All the synthetic manipulations such as filtrations and distillations were conducted under N_2/Ar atmosphere. Completion of the reaction and homogeneity of the complexes were checked on silica gel coated glass thin-layer chromatographic plates.

B. Synthesis. The complexes (bis(salicylaldehyde) ethylenediiminato)chlorocarbonylruthenium(III), [Ru(salen)(Cl)(CO)] (**1a**), (bis(salicylaldehyde) ethylene diiminato)(imidazole)carbonylruthenium-(III) chloride, [Ru(salen)(Im)(CO)]Cl (**2a**), (bis(salicylaldehyde) ethylenediiminato)(2-methylimidazole)carbonylruthenium(III) chloride, [Ru(salen)(2-MeIm)(CO)]Cl (**3a**), (bis(salicylaldehyde) o-phenylenediiminato)chlorocarbonylruthenium(III), [Ru(saloph)(Cl)(CO)] (**4a**), (bis(salicylaldehyde) o-phenylenediiminato)(imidazole)carbonyl-ruthenium(III) chloride, [Ru(saloph)(Im)(CO)]Cl (**5a**), (bis(salicyl-aldehyde) o-phenylenediiminato)(2-methylimidazole)carbonyl-ruthenium(III) chloride, [Ru(saloph)(2-MeIm)(CO)]Cl (**6a**) (bis(sali-cylaldehyde) diethylenetriiminato)carbonylruthenium(III) chloride, [Ru(saldien)(CO)]Cl (**7a**), (bis(picolinaldehyde) ethylenediimine)-chlorocarbonylruthenium(III) dichloride, [Ru(picen)(Cl)(CO)]Cl$_2$ (**8a**), (bis(picolinaldehyde) ethylenediimine)(imidazole)carbonylruthenium(III) trichloride, [Ru(picen)(Im)(CO)]Cl$_3$ (**9a**), (bis(picolinaldehyde) ethy-lenediimine)(2-methylimidazole)carbonylruthenium(III) trichloride, [Ru(picen)(2-MeIm)(CO)]Cl$_3$ (**10a**), (bis(picolinaldehyde) o-phenylenediimine)chlorocarbonylruthenium(III) dichloride, [Ru(pi-

(6) Taqui Khan, M. M.; Amjad Hussain; Venkatasubramanian, K.; Ramachandraiah, G.; Oomen, V. *J. Mol. Catal.* **1988**, *44*, 117.
(7) Halpern, J.; James, B. R.; Kemp, A. L. W. *J. Am. Chem. Soc.* **1966**, *88*, 5142.
(8) Sakaki, S.; Yanase, Y.; Hagiwara, N.; Takeshita, T.; Naganuma, H.; Ohyoshi, A.; Ohkubo, K. *J. Phys. Chem.* **1982**, *86*, 1038.
(9) Halpern, J.; Kemp, A. L. W. *J. Am. Chem. Soc.* **1966**, *88*, 5147.
(10) Wishart, J. F.; Taube, H.; Breslauer, K. J.; Isied, S. S. *Inorg. Chem.* **1984**, *23*, 2997.
(11) Cattania, M. G.; Gervasini, A.; Morazzoni, F.; Scotti, R.; Strumolo, D. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3619.
(12) Gustafson, B. L.; Lin, M.-J.; Lunsford, J. H. *J. Phys. Chem.* **1980**, *84*, 3211.
(13) Taqui Khan, M. M.; Sreelatha, Ch.; Mirza, S. A.; Ramachandraiah, G.; Abdi, S. H. R. *Inorg. Chim. Acta* **1988**, *154*, 103.
(14) Taqui Khan, M. M.; Prakash Rao, A.; Mirza, S. A.; Bhatt, S. D. *Inorg. Chem.*, submitted for publication.
(15) Taqui Khan, M. M.; Khan, N. H.; Kureshy, R. I.; Boricha, A. B. *Inorg. Chim. Acta*, in press.
(16) Hobday, M. D.; Smith, T. D. *Coord. Chem. Rev.* **1973**, *9*, 311. Calligaris, M. *Ibid.* **1972**, *7*, 385.

(17) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.
(18) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137.
(19) Thornback, J. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 110.
(20) Doine, H.; Stephens, F. F.; Cannon, R. D. *Inorg. Chim. Acta* **1984**, *82*, 149. Doine, H.; Stephens, F. F.; Cannon, R. D. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1327.
(21) (a) Taqui Khan, M. M.; Mirza, S. A.; Sreelatha, Ch.; Abdi, S. H. R.; Shaikh, Z. A. *Proceedings of an International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidations*; Tsukuba, Japan, July 12–16, 1987; Elsevier Publications: Amsterdam, 1987; Vol 33, p 211. (b) Taqui Khan, M. M.; Mirza, S. A.; Prakash Rao, A.; Sreelatha, Ch. *J. Mol. Catal.* **1988**, *44*, 107.
(22) Taqui Khan, M. M.; Mirza, S. A.; Shaikh, Z. A.; Sreelatha, Ch.; Paul, P.; Srinivas, D.; Abdi, S. H. R.; Bhatt, S. D.; Ramachandraiah, G. *Inorg. Chem.*, submitted for publication.
(23) Uemori, Y.; Kyuno, E. *Inorg. Chim. Acta.* **1987**, *138*, 9.
(24) Mercer, E. E.; Buckley, R. R. *Inorg. Chem.* **1965**, *4*, 1692.
(25) Coleman, W. M.; Boggess, R. K.; Hughes, J. W.; Taylor, L. T. *Inorg. Chem.* **1981**, *20*, 700.
(26) Marvel, C. S.; Aspey, S. A.; Dudley, E. A. *J. Am. Chem. Soc.* **1956**, *78*, 4905.
(27) Busch, D. H.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1956**, *78*, 1137.
(28) Battaglia, L. P.; Ferrari, M. B.; Corrdi, A. B.; Fava, G. G.; Pelizzi, C.; Vidoni Tani, M. E. *J. Chem. soc., Dalton Trans.* **1976**, 2197.
(29) Itoh, Y. *Chem. Abstr.* **1983**, *98*, 136728Z.

coph)(Cl)(CO)]Cl₂ (11a) (bis(picolinaldehyde) o-phenylenediimine)(imidazole)carbonylruthenium(III) trichloride, [Ru(picoph)(Im)(CO)]Cl₃, (12a), (bis(picolinaldehyde) o-phenylenediimine)(2-methylimidazole)-carbonylruthenium(III) trichloride, [Ru(picoph)(2-MeIm)(CO)]Cl₃ (13a), and (bis(picolinaldehyde) diethylenetriimine)carbonylruthenium-(III) trichloride, [Ru(picdien)(CO)]Cl₃ 14a were prepared from their respective parent chloro compounds viz. K[Ru(salen)Cl₂] (1b) for 1a, [Ru(salen)(Im)(Cl)] (2b) for 2a, [Ru(salen)(2-MeIm)(Cl)] (3b) for 3a, K[Ru(saloph)Cl₂] (4b) for 4a, [Ru(saloph)(Im)(Cl)] (5b) for 5a, [Ru-(saloph)(2-MeIm)(Cl)] (6b) for 6a, [Ru(saldien)Cl] (7b) for 7a, [Ru-(picen)Cl₂]Cl (8b) for 8a [Ru(picen)(Im)(Cl)]Cl₂ (9b) for 9a, [Ru(picen)(2-MeIm)(Cl)]Cl₂ (10b) for 10a, [Ru(picoph)Cl₂]Cl (11b) for 11a, [Ru(picoph)(Im)(Cl)]Cl₂ (12b) for 12a, [Ru(picoph)(2-MeIm)Cl]Cl₂ (13b) for 13a, and [Ru(picdien)Cl]Cl₂ (14b) for 14a. Synthesis and characterization of the parent complexes were reported elsewhere.[21b,22]

Carbon monoxide gas was bubbled through methanolic solutions of the parent compounds (approximately 0.2 mmol) for 8–10 h under constant stirring. Except for complexes 1a and 4a, the rest of the carbonyl complexes obtained were concentrated over a rotary evaporator. Dark brown solids were precipitated by the addition of diethyl ether to the concentrated solutions. The complexes were recrystallized from dry diethyl ether and ethyl acetate.

In the case of complexes 1a and 4a, KCl was filtered off and the filtrates were concentrated and precipitated in the same manner as described above. Salen complexes were precipitated as dark green solids while the rest of the complexes were precipitated as dark brown solids. The yields of these complexes are in the range 55–65%. The complexes are highly soluble in DMF.

C. Physical Measurements. Microanalysis of the compounds was done by using a CHN Carlo Erba 1106 elemental analyzer. Solution electrical conductivity was measured at room temperature (298 K) by a Digisun Electronics conductivity bridge with solute concentrations of 1 mM. The IR spectra were recorded at 298 K on a Shimadzu IR-435 spectrometer. Measurements were made on samples as KBr pellets (1% w/w).

Electronic spectra were recorded in DMF solutions on a Shimadzu UV-Visible spectrometer (Model UV-160). Matched 2-mm quartz cuvettes were used in all the experiments. Differential pulse polarographic data were recorded by a Princeton Applied Research (PAR) electrochemistry system (Model 174) equipped with a precision X-Y recorder, and the conditions maintained were the same as those discussed earlier.[22] Magnetic measurements were carried out at 298 K with a PAR (Model 155) vibrating sample magnetometer in combination with a Walker/Magnion L-75 electromagnet; Hg[Co(NCS)₄] was used as a standard.

EPR investigations were carried out with a Bruker ESP-300 X-band spectrometer using a 100-kHz field modulation. Magnetic field was calibrated by using a ER 035M NMR gaussmeter. DPPH was used as a field marker (g = 2.0036). EPR experiments were conducted on powder samples at 298 and at 77 K. Low-temperature measurements were performed by using a quartz Dewar.

The EPR studies were also conducted in DMF solutions at 298 and 77 K. The lines in solution were narrower than those in the solid state but could not give much information about ruthenium hyperfine coupling. The absence of hyperfine features of Ru(III) species in solution was also observed by other investigators.[30] Spectra of these complexes in solution indicated the presence of two species obtained by the dissociation of carbonyl complex in DMF solution. There is thus an equilibrium between the carbonyl and the solvated complex species in solution.

D. g Tensor Theory. The g tensor theory for low-spin d⁵ systems was developed decades ago and discussed by several workers.[31–35] In our calculations, we have followed the approach developed by Hill.[35]

The unpaired electron of a low-spin d⁵ octahedral complex occupies one of the T_{2g} orbitals, which split under the effects of noncubic ligand fields and spin–orbit coupling (λ). In the case of axial distortion, Δ (tetragonal or trigonal), these orbitals split such that the singlet A or B (depending on the type of distortion) lies above the degenerate level when Δ is positive and A or B lies below the level E when Δ is negative. In

other words, the unpaired electron occupies the d_{xy} orbital when the distortion is positive. A low-symmetry (rhombic) distortion, V, removes the degeneracy of E levels. For a positive value of V, the orbital d_{yz} lies above the d_{xz} orbital.

The combined effect of low-symmetry field and spin–orbit coupling interaction,[36] splits the T_{2g} level into three well-separated Kramers' doublets, one in the ground state and the other two in the excited states. In the most general case, the ground-state doublet in which resonance is observed may be written as[30]

$$\psi = a|1\rangle + b|\bar{\xi}\rangle + c|-1\rangle$$

$$\psi^* = a|\overline{-1}\rangle + b|\xi\rangle + c|\bar{1}\rangle \qquad (1)$$

where the MO coefficients a, b, and c are real; $|1\rangle = -(d_{xz} + id_{yz})/\sqrt{2}$, $|-1\rangle = (d_{xz} - id_{yz})/\sqrt{2}$, and $|\xi\rangle = id_{xy}$; the bars on top of the spin states represent β-spin. The components of g obtained as eigenvalues of $\mu_B\bar{B}(2\bar{S} + k\bar{L})$ when operated on the ground-state wave function are

$$g_x = -2[2ac + b^2 + \sqrt{2}kb(a + c)]$$

$$g_y = -2[-2ac + b^2 + \sqrt{2}kb(a - c)] \qquad (2)$$

$$g_z = -2[a^2 - b^2 + c^2 + k(a^2 - c^2)]$$

where $\bar{B}$ is the static field; μ_B is the Bohr magneton, and k is the orbital reduction factor. The MO coefficients are related by the normalization condition:

$$a^2 + b^2 + c^2 = 1 \qquad (3)$$

A computer program was written on an HP-1000 calculator to calculate the parameters a, b, c, and k from eqs 2 and 3 by using a least-squares procedure. For systems with axial symmetry, the value of c becomes zero. In the case of complexes, the value of k should be less than 1.0. However, systems with pseudooctahedral configuration were reported with k values in the range 0.4–1.2.[30] This was rationalized by considering the admixture of t_2^5 state with the excited t_2^4e and $t_2^3e^2$ states. However, in carbonyl complexes the crystal field splitting is expected to be very large, and hence the value of k does not exceed 1.0.

The distortion parameters and average excitation energy to excited Kramers' doublets (in units of λ) are given as

$$\frac{V}{\lambda} = \frac{\sqrt{2}c(a\sqrt{2} + b)}{c^2 - a^2}$$

$$\frac{\Delta}{\lambda} = \frac{1}{2} + \frac{b^2 - a^2}{\sqrt{2}ab} + \left(\frac{c}{2a}\right)\left(\frac{V}{\lambda}\right) \qquad (4)$$

$$\frac{\Delta E}{\lambda} = \frac{A}{B\sqrt{2}} + \Delta$$

The transition energies (ΔE_1 and ΔE_2) to the excited Kramers' doublets are obtained as $\Delta E + V/2$ and $\Delta E - V/2$, respectively.

EPR spectra of powder samples afford the magnitude of g_1, g_2, and g_3, but do not provide any information about their relationship with the tensor axes and their signs. There are 48 possible combinations depending on the labeling (x, y, z) and signs chosen for the experimental g values.[8,37–40] The parameters, a, b, c, k, Δ/λ, V/λ, and $\Delta E_i/\lambda$ were calculated for all the combinations. A reasonable set of values were selected by considering the following conditions: (a) Although by definition k takes values 0.75 < k < 1.0, solutions with 0.75 < k < 2.0 were however examined in this work, taking into account the admixture of the ground state with the excited states.[30] (2) The tetragonal distortion Δ, is considered to be larger than the rhombic distortion, V. As a consequence of this, two solutions, (1) $g_z < g_x$ and g_y and g_x, g_y, and g_z are all

(30) Hudson, A.; Kennedy, M. J. *J. Chem. Soc. A* **1969**, 1116. Raynor, J. B.; Jeliazkowa, B. G. *J. Chem. Soc., Dalton Trans.* **1982**, 1185. Bhattacharya, S.; Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1985**, *24*, 3224. Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1982**, 615.
(31) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance in Transition Ions*; Clarendon Press: Oxford, England, 1970.
(32) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: London, 1961; p 364.
(33) Bleaney, B.; O'Brien, M. C. M. *Proc. Phys. Soc. London* **1956**, *B69*, 1216.
(34) Thornley, J. H. M. *J. Phys. C* **1968**, *1*, 1024.
(35) Hill, N. J. *J. Chem. Soc., Faraday Trans.* **1972**, 427.

(36) The spin–orbit coupling constant of Ru(III) ion is 1150 cm⁻¹. In complexes it is assumed to be 1000 cm⁻¹: Earnshaw, A.; Figgis, B. N.; Lewis, J.; Nyholm, R. S. *Nature (London)* **1957**, *170*, 1121. Figgis, B. N.; Lewis, J.; Nyholm, R. S.; Peacock, R. D. *Discuss. Faraday Soc.* **1958**, *26*, 103. Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1614.
(37) Medhi, O. K.; Agarwala, U. *Inorg. Chem.* **1980**, *19*, 1381.
(38) Stebler, A.; Ammeter, J. H.; Fürholz, U.; Ludi, A. *Inorg. Chem.* **1984**, *23*, 2764.
(39) Mahapatra, A. K.; Datta, S.; Goswami, S.; Mukherjee, M.; Mukherjee, A. K.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 1715.
(40) Manoharan, P. T.; Mehrotra, P. K.; Taqui Khan, M. M.; Andal, R. K. *Inorg. Chem.* **1973**, *12*, 2753.

Table I. Elemental Analysis, Conductivity, and $E_{1/2}$ for Ru(III)/Ru(II) Reduction Couple Data for Ru(III) Schiff Base Carbonyl Complexes

complex		elemental anal., %								molar conductivity[b]	
		calcd				found					
no.	formula	C	H	N	Cl	C	H	N	Cl	Λ_M	$E_{1/2}$[c]
1a	[Ru(salen)(Cl)(CO)][a]	47.39	3.27	6.50	8.23	47.29	3.24	6.42	8.19	42	−0.57
2a	[Ru(salen)(Im)(CO)]Cl	48.10	3.63	11.22	7.11	48.02	3.60	11.17	7.05	75	−0.58
3a	[Ru(salen)(2-MeIm)(CO)]Cl	49.26	3.93	10.92	6.92	49.21	3.90	10.79	6.86	70	−0.57
4a	[Ru(saloph)(Cl)(CO)][a]	52.66	2.94	5.84	14.82	52.58	2.90	5.80	14.76	48	−0.58
5a	[Ru(saloph)(Im)(CO)]Cl	52.70	3.31	10.24	6.49	52.65	3.27	10.20	6.42	80	−0.61
6a	[Ru(saloph)(2-MeIm)(CO)]Cl	53.53	3.59	9.98	6.32	53.46	3.56	9.89	6.28	78	−0.57
7a	[Ru(saldien)(CO)]Cl	48.15	4.04	8.86	7.49	48.10	4.00	8.81	7.41	68	−0.53
8a	[Ru(picen)(Cl)(CO)]Cl₂	38.02	2.97	11.82	22.47	37.96	2.93	11.76	22.41	135	−0.55
9a	[Ru(picen)(Im)(CO)]Cl₃	42.07	3.53	10.90	20.72	42.01	2.50	10.83	20.65	205	−0.56
10a	[Ru(picen)(2-MeIm)(CO)]Cl₃	41.04	3.62	15.11	19.15	41.01	3.60	15.09	19.12	201	−0.55
11a	[Ru(picoph)(Cl)(CO)]Cl₂	41.40	2.70	10.73	20.41	41.37	2.68	10.70	20.36	137	−0.56
12a	[Ru(picoph)(Im)(CO)]Cl₃	44.78	3.07	14.24	18.05	44.74	3.05	14.23	18.02	208	−0.55
13a	[Ru(picoph)(2-MeIm)(CO)]Cl₃	45.69	3.33	13.91	17.63	45.65	3.30	13.88	17.60	206	−0.57
14a	[Ru(picdien)(CO)]Cl₃	39.46	3.70	13.54	20.60	39.42	3.65	13.48	20.52	202	−0.48

[a] Non-electrolyte. [b] Molar conductivity at 298 K given in units of Ω^{-1} cm² M^{-1}; solvent is DMF. [c] Given in units of V; dropping mercury electrode is the working electrode. Solvent is DMF. Supporting electrolyte is tetrabutyl ammonium perchlorate (0.001 M); the standard electrode is Ag/AgCl.

Table II. IR Stretching Frequencies and UV–visible Data for Ru(III) Schiff Base Carbonyl Complexes at 298 K

complex		ν(C=N), cm^{-1}	ν(C≡O), cm^{-1}	electronic spectral data[a] λ_{max}, nm (ϵ, M^{-1} cm^{-1})
no.	formula			
1a	[Ru(salen)(Cl)(CO)]	1580	1985	607 (785), 349 (4465), 240 (12 495), 268 (7220), 390 (3200)[b]
2a	[Ru(salen)(Im)(CO)]Cl	1590	1990	638 (1290), 346 (7845), 370 (6540), 278 (12 495)[b]
3a	[Ru(salen)(2-MeIm)(CO)]Cl	1585	2000	640 (8600), 348 (74 100), 372 (6790),[b] 278 (12 500)
4a	[Ru(saloph)(Cl)(CO)]	1590	1990	551 (13 700),[b] 452 (23 900), 273 (56 900), 375 (8320)[b]
5a	[Ru(saloph)(Im)(CO)]Cl	1580	2010	552 (5750),[b] 395 (37 800), 279 (58 275)
6a	[Ru(saloph)(2-MeIm)(CO)]Cl	1600	2000	556 (935), 319 (3950), 420 (1755),[b] 256 (12 500)
7a	[Ru(saldien)(CO)]Cl	1610	2005	329 (28 600), 251 (12 500), 370 (3520)[b]
8a	[Ru(picen)(Cl)(CO)]Cl₂	1590	2000	500 (19 200), 349 (2755), 256 (12 500)
9a	[Ru(picen)(Im)(CO)]Cl₃	1595	1990	499 (29 400), 362 (37 200), 258 (12 500)
10a	[Ru(picen)(2-MeIm)(CO)]Cl₃	1595	1995	499 (29 350), 362 (36 992), 258 (12 550)
11a	[Ru(picoph)(Cl)(CO)]Cl₂	1590	2000	452 (7350), 357 (1780), 520 (5960)[b]
12a	[Ru(picoph)(Im)(CO)]Cl₃	1600	2005	471 (8800), 326 (24 990)
13a	[Ru(picoph)(2-MeIm)(CO)]Cl₃	1600	2005	471 (12 150), 349 (24 990)
14a	[Ru(picdien)(CO)]Cl₃	1600	1995	513 (25 857), 349 (4155), 328 (39 800), 253 (12 500)

[a] Solvent is DMF. [b] Shoulder to the main peak.

positive and (2) $g_z > g_x$ and g_y and g_z is negative, were found to be physically meaningful. The two solutions differ widely in the values of distortion parameters as well as of ΔE_1 and ΔE_2. Distortion and ΔE_i are much higher in solution 1.

It is therefore understood from the above treatment that EPR studies on powder or frozen glass solutions, with nonaxial **g** tensors, do not yield a singular, unambiguous result, instead yielding two solutions, 1 and 2. This unambiguity can be overcome only by performing experiments on single crystals. In cases where it is extremely difficult to grow single crystals suitable for EPR studies, as in the present situation, the correct assignment can, however, be deduced by an equally good alternative method of comparing the electronic spectral data (for the d–d transitions from the ground Kramers' doublet to the excited states) obtained experimentally with the theoretically predicted (ΔE_i) values for solutions 1 and 2. A comparison of this (vide infra) tentatively indicated that complexes **4b**, **5b**, and **6b** adopt solution 2 (with d_{xz}/d_{yz} as the ground state) while the rest of the complexes adopt solution 1 (with d_{xy} as the ground state). Electronic spectral data thereby complements the EPR of powder samples, resulting in a single set of **g** values. The MO coefficients, distortion parameters, and excitation energies for the correct assignment, for all the complexes, are listed in Table IV.

Results and Discussion

The analytical and molar conductivity data of all the carbonyl complexes are listed in Table I. Molar conductivities of DMF solutions, containing these complexes in millimolar concentrations, indicate that complexes **1a** and **4a** are non-electrolytes while the rest of the complexes are electrolytes.

The magnetic moments (μ_{eff} values) of these complexes fall in the range 1.97–2.08 μ_B, corresponding to a single unpaired electron in a low-spin 4d^5 configuration.

IR spectral data of these complexes in the solid state indicate the presence of a coordinated carbonyl group. Representative IR spectra of a parent and carbonyl complexes of saloph are shown
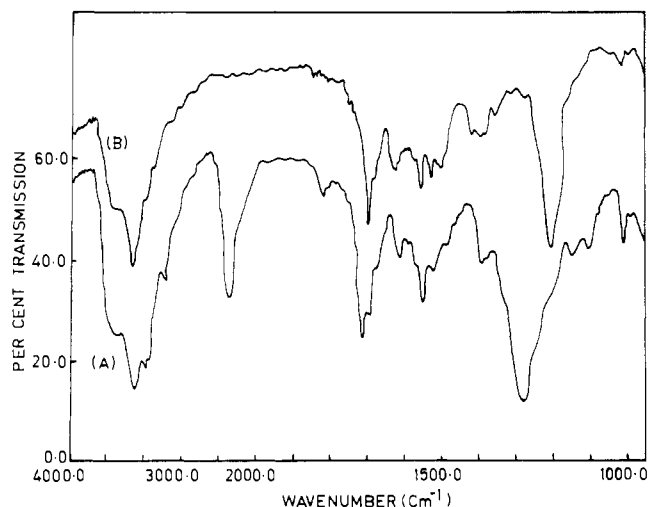

Figure 1. IR spectra of (A) [Ru(saloph)(2-MeIm)(CO)]Cl and (B) [Ru(saloph)(2-MeIm)(Cl)] as KBr pellets at 298 K.

in Figure 1. The spectra consist of an intense band in the region 1590–1610 cm^{-1} assigned to $\nu_{C=N}$ of the azomethine group (H—C=N) coordinated to the metal ion. For uncoordinated Schiff bases, this band occurs at somewhat higher wavenumbers. A strong band absent in the parent compound spectrum appears in the spectrum of the carbonyl complexes in the narrow range 1985–2010 cm^{-1}. This is assigned to the C≡O stretching mode of the coordinated carbonyl group. This band for free carbon monoxide is observed at 2155 cm^{-1}. The band position is consistent with those reported earlier.[19,41] The bands corresponding to the

Table III. g Values for Ru(III) Schiff Base Chloro and Carbonyl Complexes[a]

		298 K				77 K			
no.	formula	g_1	g_2	g_3	g_{av}[b]	g_1	g_2	g_3	g_{av}[b]
1b	K[Ru(salen)Cl$_2$][c]		2.105		2.105		2.125		2.125
1a	[Ru(salen)(Cl)(CO)]	2.332	2.113	1.900	2.115	2.340	2.112	1.897	2.116
2b	[Ru(salen)(Im)(Cl)][c]		2.105		2.105		2.125		2.125
2a	[Ru(salen)(Im)(CO)]Cl	2.248	2.000	1.913	2.054	2.359	2.100	1.889	2.116
3b	[Ru(salen)(2-MeIm)(Cl)][c]		2.120		2.120		2.145		2.145
3a	[Ru(salen)(2-MeIm)(CO)]Cl	2.299	2.144	1.909	2.094	2.312	2.160	1.866	2.112
4b	K[Ru(saloph)Cl$_2$]	2.314	2.147	1.974	2.145	2.416	2.188	1.936	2.180
4a	[Ru(saloph)(Cl)(CO)]	2.251	2.114	1.936	2.100	2.243	2.112	1.929	2.090
5b	[Ru(saloph)(Im)(Cl)]	2.420	2.179	1.927	2.175	2.433	2.209	1.952	2.198
5a	[Ru(saloph)(Im)(CO)]Cl	2.254	2.130	1.968	2.117	2.224	2.114	1.966	2.107
6b	[Ru(saloph)(2-MeIm)(Cl)]	2.363	2.179	1.987	2.176	2.393	2.190	1.995	2.194
6a	[Ru(saloph)(2-MeIm)(CO)]Cl	2.339	2.139	1.938	2.139	2.295	2.121	1.977	2.131
7b	[Ru(saldien)(Cl)]	2.264	2.264	1.916	2.148	2.270	2.270	1.910	2.150
7a	[Ru(saldien)(CO)]Cl	2.347	2.120	1.906	2.124	2.419	2.169	1.943	2.177
8b	[Ru(picen)Cl$_2$]Cl	2.269	2.269	1.878	2.139	2.273	2.273	1.855	2.133
8a	[Ru(picen)(Cl)(CO)]Cl$_2$	2.350	2.350	1.887	2.252	2.315	2.315	1.825	2.205
9b	[Ru(picen)(Im)(Cl)]Cl$_2$	2.254	2.254	1.863	2.124	2.261	2.261	1.876	2.133
9a	[Ru(picen)(Im)(CO)]Cl$_3$	2.469	2.306	1.801	2.192	2.488	2.324	1.797	2.203
10b	[Ru(picen)(2-MeIm)(Cl)]Cl$_2$	2.269	2.269	1.889	2.142	2.269	2.269	1.881	2.140
10a	[Ru(picen)(2-MeIm)(CO)]Cl$_3$	2.465	2.269	1.881	2.205	2.465	2.281	1.866	2.204
11b	[Ru(picoph)Cl$_2$]Cl	2.411	2.411	1.794	2.205	2.412	2.412	1.796	2.206
11a	[Ru(picoph)(Cl)(CO)]Cl$_2$	2.410	2.410	1.796	2.205	2.399	2.399	1.791	2.196
12b	[Ru(picoph)(Im)(Cl)]Cl$_2$	2.401	2.401	1.796	2.199	2.416	2.416	1.777	2.203
12a	[Ru(picoph)(Im)(CO)]Cl$_3$	2.409	2.409	1.792	2.033	2.416	2.416	1.759	2.197
13b	[Ru(picoph)(2-MeIm)(Cl)]Cl$_2$	2.397	2.397	1.792	2.195	2.425	2.425	1.782	2.211
13a	[Ru(picoph)(2-MeIm)(CO)]Cl$_3$	2.383	2.383	1.798	2.188	2.382	2.382	1.782	2.182
14b	[Ru(picdien)(Cl)]Cl$_2$	2.306	2.306	1.863	2.158	2.300	2.300	1.855	2.152
14a	[Ru(picdien)(CO)]Cl$_3$	2.421	2.301	1.868	2.143	2.442	2.292	1.845	2.236

[a] Estimated error in g values is ± 0.008. [b] $g_{av} = (g_1 + g_2 + g_3)/3$. [c] Only an average spectrum is observed.
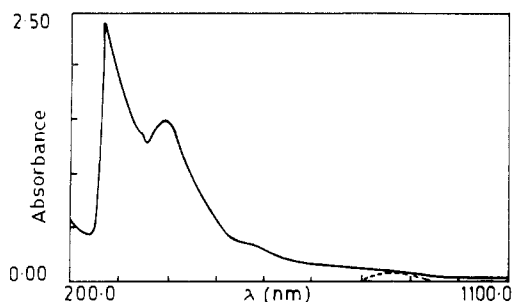

Figure 2. UV–visible spectrum of [Ru(saloph)(Im)(CO)]Cl in DMF at 298 K. The dotted feature indicates the weak ligand field transition.

stretching modes of M–Cl and M–N occur almost in the same region, 325–360 cm^{-1}, in complexes **1a** and **4a**. Band positions for $\nu_{C=N}$ and $\nu_{C=O}$ are reported in Table II.

A representative electronic spectrum of [Ru(saloph)(Im)-(CO)]Cl in DMF is depicted in Figure 2. In the UV region, an intense band near 260 nm, which is also present in the free ligand is assigned to $\pi-\pi^*$ transitions from the benzene ring and the double bond of the azomethine group. The band at 350 nm is due to n–π^* transitions of nonbonding electrons present on the nitrogen of azomethine group in the Schiff base. In the complexes this band undergoes a hypsochromic shift due to coordination of the Schiff base ligand to metal ion. The moderately intense bands in the range 490–640 nm could be assigned to LMCT and the d–d transitions of the metal ion. The absorption data are summarized in Table II.

Differential-pulse polarography (DPP) studies of the ruthenium Schiff base carbonyl complexes under dropping mercury electrode indicate that ruthenium is in the +3 oxidation state. Only a single Ru(III)/Ru(II) reduction couple was observed. The $E_{1/2}$ values for all these complexes are reported in Table I. In case of [Ru^{III}(saloph)XCl] complexes the Ru(III)/Ru(II) redox couple was observed at larger negative values (-0.686, -0.701, and -0.655 V for X = Cl, Im, and 2-MeIm).[13] The low $E_{1/2}$ values in carbonyl

complexes could be due to greater delocalization of electron density to the axial CO ligand than to Cl$^-$ in the parent chloro complexes. EPR results further support this observation. Though 2-MeIm is more basic than Im the $E_{1/2}$ values for Im complexes are larger than for 2-MeIm complexes. This may be because of the steric effects of 2-MeIm in the axial position.

EPR Studies. A. Chloro Complexes. EPR spectra of salen chloro complexes **1b–3b** consist of a single isotropic resonance with unresolved hyperfine structure due to ruthenium.[42] Cooling the sample to 77 K narrowed the lines, and a slight change in the g parameter with no g anisotropy could be observed. Isotropic lines are usually observed by the following phenomena: (1) intermolecular spin exchange, which can broaden the lines; (2) occupancy of the unpaired electron in a degenerate orbital.

As in the rest of the chloro complexes, especially saloph complexes, well-resolved g features were observed even at 298 K; in the case of the salen complexes, the spin exchange may not be the main reason for isotropy. In this case the effective electronic environment may be such that the unpaired electron is in a low-spin state with a degenerate d_{xz}, d_{yz} ground state. Such systems that have degenerate or nearly degenerate ground states are prone to Jahn–Teller instability.[43] If the instability is dynamic, one observes only an averaged g value (g_{av}). It is therefore, tentatively proposed that the salen complexes of Ru(III) exhibit a dynamic Jahn–Teller effect.

The spectra of saloph complexes **4b–6b** at 298 and 77 K were characterized by three well-separated lines. The g_{av} values, as in the case of other Ru(III) Schiff base complexes, vary with the temperature and with the axial ligand. The nature of the spectra is consistent with nondegenerate t_{2g} orbitals. Saldien (**7b**), picen (**8b–10b**), picoph (**11b–13b**), and picdien (**14b**) complexes gave spectra characterized by an axial g tensor. EPR g parameters for all the chloro complexes are given in Table III along with the results for their carbonyl complexes. It is obvious from Table III that the components of g tensor and symmetry are sensitive to the equatorial Schiff base ligands and axial ligands. The g_{av} values

(41) Taqui Khan, M. M.; Nazeeruddin, Md. K. *Inorg. Chim. Acta.* **1988**, *147*, 33.

(42) Ruthenium has two magnetic nuclei ^{99}Ru and ^{101}Ru with natural abundances of 12.89 and 16.98% and nuclear moments of 0.63 and 0.69 nm, respectively. Both isotopes have a nuclear spin of $^5/_2$.

(43) Jahn, H. A.; Teller, E. *Proc. R. Soc. London* **1937**, *A101*, 220.

Table IV. g Values,[a] MO Coefficients, Delocalization Parameters, Distortion Parameters, and Excitation Energies of Ruthenium(III) Schiff Base Chloro and Carbonyl Complexes at 77 K

no.	formula	g_x	g_y	g_z	a	b	c	k	Δ/λ	V/λ	$\Delta E_1/\lambda$	$\Delta E_2/\lambda$
1b	K[Ru(salen)Cl₂][b]		2.125					1.094				
1a	[Ru(salen)(Cl)(CO)]	2.340	2.112	1.897	0.134	0.990	0.045	0.708	6.411	-4.722	4.167	8.942
2b	[Ru(salen)(Im)(Cl)][b]		2.125					1.094				
2a	[Ru(salen)(Im)(CO)]Cl	2.359	2.100	1.889	0.139	0.989	0.051	0.704	6.395	-5.171	3.938	9.150
3b	[Ru(salen)(2-MeIm)(Cl)][b]		2.145					1.109				
3a	[Ru(salen)(2-MeIm)(CO)]Cl	2.312	2.160	1.886	0.157	0.987	0.031	0.654	5.040	-2.224	4.024	6.398
4b	K[Ru(saloph)Cl₂]	2.188	1.936	-2.416	0.837	0.544	0.025	1.139	-0.130	-0.086	1.455	1.555
4a	[Ru(saloph)(Cl)(CO)]	2.243	2.112	1.929	0.114	0.993	0.029	0.641	7.071	-3.897	5.201	9.185
5b	[Ru(saloph)(Im)(Cl)]	2.209	1.952	-2.433	0.838	0.544	0.025	1.152	-0.129	-0.087	1.455	1.555
5a	[Ru(saloph)(Im)(CO)]Cl	2.224	2.114	1.966	0.076	0.997	0.021	0.845	10.495	-5.938	7.596	13.575
6b	[Ru(saloph)(2-MeIm)(Cl)]	2.190	1.995	-2.393	0.835	0.549	0.019	1.147	-0.110	-0.067	1.462	1.545
6a	[Ru(saloph)(2-MeIm)(CO)]Cl	2.295	2.121	1.977	0.058	0.998	0.022	1.117	14.838	-11.676	9.049	20.749
7b	[Ru(saldien)(Cl)]	2.270	2.270	1.910	0.126	0.992	0.000	0.856	5.999	0.000	5.678	6.589
7a	[Ru(saldien)(CO)]Cl	2.419	2.169	1.943	0.093	0.995	0.033	1.100	9.277	-7.069	5.823	12.929
8b	[Ru(picen)Cl₂]Cl	2.273	2.273	1.855	0.163	0.987	0.000	0.716	4.653	0.000	4.387	5.270
8a	[Ru(picen)(Cl)(CO)]Cl₂	2.315	2.315	1.825	0.178	0.984	0.000	0.764	4.283	0.000	4.039	4.911
9b	[Ru(picen)(Im)(Cl)]Cl₂	2.261	2.261	1.876	0.151	0.989	0.000	0.727	5.028	0.000	4.744	5.636
9a	[Ru(picen)(Im)(CO)]Cl₃	2.488	2.324	1.797	0.186	0.982	0.025	0.923	4.192	-1.289	3.624	5.161
10b	[Ru(picen)(2-MeIm)(Cl)]Cl₂	2.269	2.269	1.881	0.147	0.989	0.000	0.760	5.159	0.000	4.869	5.764
10a	[Ru(picen)(2-MeIm)(CO)]Cl₃	2.465	2.281	1.866	0.148	0.990	0.027	1.000	5.298	-2.144	4.305	6.610
11b	[Ru(picoph)Cl₂]Cl	2.412	2.412	1.796	0.189	0.982	0.000	0.929	4.088	0.000	3.857	4.723
11a	[Ru(picoph)(Cl)(CO)]Cl₂	2.399	2.399	1.791	0.190	0.982	0.000	0.893	4.016	0.000	3.790	4.653
12b	[Ru(picoph)(Im)(Cl)]Cl₂	2.416	2.416	1.777	0.196	0.981	0.000	0.907	3.899	0.000	3.682	4.541
12a	[Ru(picoph)(Im)(CO)]Cl₃	2.416	2.416	1.759	0.205	0.979	0.000	0.883	3.738	0.000	3.533	4.385
13b	[Ru(picoph)(2-MeIm)(Cl)]Cl₂	2.425	2.425	1.782	0.193	0.981	0.000	0.933	3.961	0.000	3.738	4.599
13a	[Ru(picoph)(2-MeIm)(CO)]Cl₃	2.382	2.382	1.782	0.196	0.980	0.000	0.845	3.901	0.000	3.684	4.543
14b	[Ru(picdien)(Cl)]Cl₂	2.300	2.300	1.855	0.161	0.987	0.000	0.781	4.707	0.000	4.438	5.322
14a	[Ru(picdien)(CO)]Cl₃	2.442	2.292	1.845	0.162	0.987	0.023	0.930	4.796	-1.546	4.090	4.857

[a] Estimated error in g_1, g_2, and g_3 is ±0.008. [b] Isotropic spectrum is observed, and k is calculated by using the expression $g_{av} = {}^2/_3(2k + 1)$.

for complexes with the o-phenylene group are larger than those for complexes with ethylene group (saloph > salen and picoph > picen), and g_{av} values for picolinaldehyde Schiff base complexes are larger than their corresponding salicylaldehyde Schiff base complexes. The nature of the spectrum in general is isotropic, axial or rhombic (Figure 3).

The MO results, listed in Table IV, of the chloro complexes **4b–14b** indicate that in the case of saloph complexes the distortion parameter is negative and small while in the rest of the chloro complexes it is positive and large. These calculations were not done for salen complexes as they gave only g_{av} values. Thus the ground state for salen and saloph complexes is d_{xz}/d_{yz} while for the rest of the complexes the unpaired electron occupies the d_{xy} orbital. For saloph complexes the value of a is larger than b and c and for saldien, picen, picoph, and picdien chloro complexes b is larger than a and c. The UV–visible and IR spectral results were used as complementary data to support these MO results. An IR band observed around 1500 cm^{-1} in saloph complexes agrees well with the calculated values of ΔE_1 (1455 cm^{-1}) and ΔE_2 (1550 cm^{-1}). This IR band could not be unequivocally assigned to electronic transition alone as vibrational transitions may also occur in this region. From the MO results, it is generalized that systems with more than two nitrogens such as N_4 and N_5 have a d_{xy} ground state while N_2O_2 systems have d_{xz}/d_{yz} ground state.

The delocalization parameter varies in a linear way with the basicity order of the axial ligand. Complexes with the axial ligands such as Im and 2-MeIm impart enough basicity on the metal ion to favor carbon monoxide and dioxygen adducts formation than the mere acidic dichloro complexes.[22] Also, the saloph and picoph complexes, with an o-phenylene bridging group, have a higher covalency parameter than for salen and picen, suggesting more affinity for CO.

B. Carbonyl Complexes. EPR spectra of complexes **1a–14a** as powder samples were recorded at 298 and 77 K. The spectra are in general characterized by a rhombic **g** tensor with narrow lines at 77 K. However, hyperfine coupling due to ruthenium[42] could not be resolved in powder samples even at lower temperatures. EPR studies of these complexes in DMF solutions at 77 K also did not yield any information regarding hyperfine coupling.
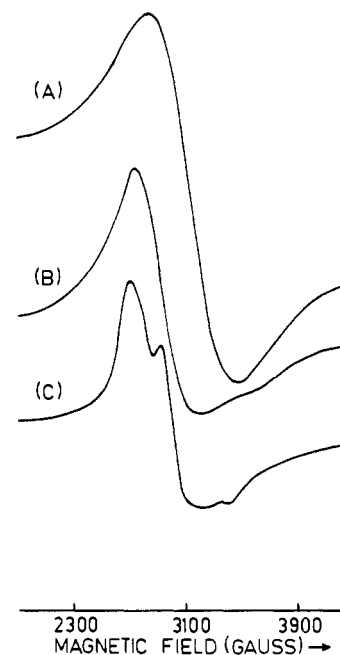

Figure 3. EPR spectra (X-band) of (A) K[Ru(salen)Cl₂], (B) [Ru(picen)Cl₂]Cl, and (C) K[Ru(saloph)Cl₂] as powder samples at 77 K.

It, however, indicated the presence of two species in solution obtained by the dissociation of carbonyl complex in DMF solution. Figure 4 depicts the EPR spectra of complex **4a** as powder sample and as frozen DMF solution. Extensive study is not made on solutions as they did not reveal additional information and the remaining part of the investigation is concerned with the powder samples only. The components of the g tensor are listed in Table III.

It is understood from EPR results that the complexes belong to a low-spin 4d^5 configuration and the symmetry at ruthenium is as low as C_s. This is in agreement with the proposed structures **1–14**. The g values at 77 K are slightly different from those at
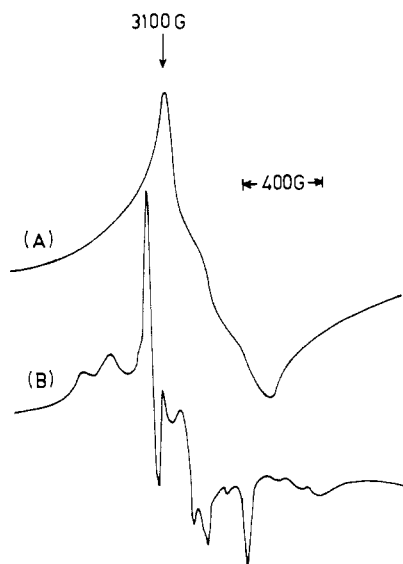
Figure 4. X-Band EPR spectra of the powder sample of [Ru(saloph)-(Cl)(CO)] at 298 K (A) and its frozen solution in DMF at 77 K (B).

Figure 5. Energy level ordering of d orbitals for Ru(III) carbonyl and chloro complexes of salen and saloph.

298 K, indicating that the geometry of the ruthenium octahedron changes with temperature. Also, the axial ligands have a significant effect on the g components. The g tensor theory given in the experimental section was used to calculate the MO coefficients of the ground state Kramers' doublet, distortion, and delocalization parameters. These parameters for all the carbonyl complexes are listed in Table IV.

The axial distortion parameter in units of λ is positive for all the carbonyl complexes and the value of b is larger than a and c, indicating that the d_{xy} orbital lies above d_{xz}, d_{yz} orbitals with the electronic configuration $(d_{xz,yz})^4(d_{xy})^1$. The covalency parameter, ranging from 0.700 to 1.000, and the smaller values for a and c suggest that the excited states are well separated from the ground state, and the mixing of the lowest Kramers' doublet with the excited states is negligible. The optical transitions from the ground-state doublet to the two excited Kramers' doublets (ΔE_1 and ΔE_2) occur in the near-IR region (Table IV). In the case of the [Ru(saloph)(2-MeIm)(CO)]Cl complex, these transitions are expected around 5500 and 11 000 cm^{-1} (Table IV); λ is assumed to be 1000 cm^{-1}. The electronic spectrum of this complex (Figure 2) indeed shows a weak band near 11 364 cm^{-1} corresponding to ΔE_2.

In the case of the picoph complexes, however, the symmetry is higher than that for the rest of the complexes. The spectra are consistent with an axial g tensor ($g_\parallel < g_\perp$). The axial distortion and delocalization parameters vary with the nature of the axial ligand (X). However, no relationship between the basicity of the axial base (X) and delocalization parameter (k) could be made.

The crystal field splitting parameter is expected to be very large in carbonyl complexes. Considering $g_\perp = 2.0 - 2\lambda/\Delta_1$ (2.22 in the present case), the value of Δ_1 was calculated to be 10000 cm^{-1}. This value is in good agreement with the MO results ($\Delta \sim$ 9000–11 500 cm^{-1}). The EPR data on Ru(III) carbonyl complexes is in general scarce. It is interesting to note that the electronic ground state is also d_{xy} in the complex $(NH_4)_2RuCl_5(CO)$[8] and the CO complexes of Ru/γ-Al$_2$O$_3$[11] and Ru(III) in a Y-type zeolite.[12]

A comparison of the EPR and MO results on chloro and carbonyl Schiff base complexes indicate that the replacement of Cl$^-$ by CO in the axial position of the Ru(III) octahedron resulted in a d_{xy} orbital ground state irrespective of the nature of the Schiff base ligand. A qualitative representation of the energy level ordering for both chloro and carbonyl complexes of salen and saloph is shown in Figure 5. It is noted that a change in the substituent on Schiff base ligand or axial ligand can change the electronic ground state and its symmetry. The extent of distortion (Δ) and excitation energies (ΔE_i) are more for saloph carbonyl complexes than for saloph chloro complexes. The orbital delo-
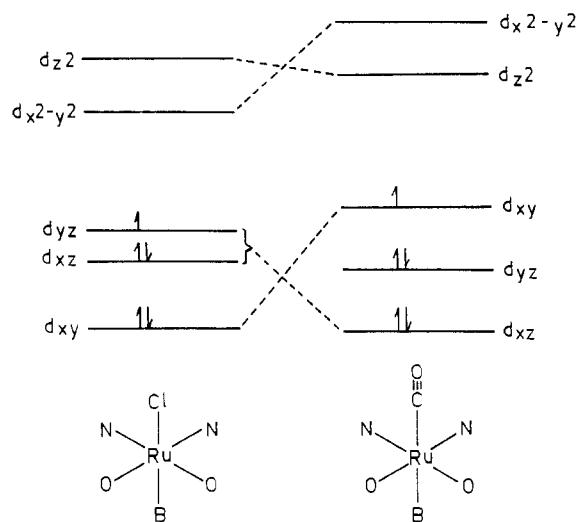
calization factor for chloro complexes is in general larger than that for their carbonyl complexes, suggesting a larger amount of electron density at ruthenium in chloro complexes than in carbonyl complexes. Because of the dπ–pπ back-bonding interaction of ruthenium(III) with the carbonyl group the Ru–CO bond is more covalent than the Ru–Cl bond.

The EPR studies of the chloro complexes of Ru(III) have supported the facile displacement of the axial Cl$^-$ group in the parent Schiff base complexes by a solvent or CO. The lability of chloro group is very important for catalysis of these complexes in carbonylation reactions.[44] The fact that the axial Cl$^-$ in parent Schiff base complexes is readily displaced by CO is probably a consequence of the difference in the nature of the ligand bonding, Cl$^-$ is a π-donor whereas CO is a π-acceptor. Consequently, when d_{xz} and d_{yz} orbitals (assuming the z axis is directly toward Cl$^-$ or CO) are occupied, the pπ orbitals of Cl$^-$ are unable to donate to ruthenium where as CO can accept dπ density into its low-lying π^* orbital, indicating that the Ru–CO bond is more covalent than Ru–Cl. This is clearly brought out by the low value of the orbital reduction factor for carbonyl complexes compared with that for chloro complexes. These complexes have a relatively weaker Ru–CO bond, or in other words, a lower amount of spin density available on ruthenium to back-donate to CO, compared to Ru-(II)–carbonyl complexes and therefore are very reactive in nucleophilic reactions of CO.

The higher covalency parameters for saloph and picoph chloro complexes indicate their high affinity for CO as compared to other complexes. This has been confirmed experimentally by the maximum reactivity of [Ru^{III}(saloph)(CO)Cl] in the reductive carbonylation of nitro compounds to form isocyanides[44] and also in the catalysis of hydroformylation reactions.[45]

Conclusions

In this paper, we have reported the synthesis of a large number of Ru(III) Schiff base carbonyls with three axial bases. All these complexes were characterized by several physicochemical methods. The presence of a coordinated carbonyl group was unequivocally determined by IR spectroscopy. Axial and equatorial ligands have significant effect on the EPR g values. Molecular orbital coefficients of the T$_2$ orbitals in the ground-state Kramers' doublet, the transition energies to the excited Kramers' doublets, and the distortion parameters were calculated. The saloph and picoph chloro complexes show higher affinity for CO in solution than the rest of the parent chloro complexes. A comparison in the EPR parameters is made between carbonyl and chloro complexes.

(44) Taqui Khan, M. M.; Halligudi, S. B.; Shukla, S.; Shaikh, Z. A. *J. Mol. Catal.* **1990**, *57*, 301, 307.
(45) Taqui Khan, M. M.; Sumita Rao, N. To be submitted for publication.