

RUTHENIUM(III) SCHIFF BASE CHLORO AND CARBONYL COMPLEXES: SYNTHESIS, CHARACTERIZATION AND EPR STUDIES

M. M. TAQUI KHAN,* D. SRINIVAS, R. I. KURESHY and N. H. KHAN

Discipline of Coordination Chemistry and Homogeneous Catalysis,
Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India

(Received 18 March 1991; accepted 9 July 1991)

Abstract—The synthesis and characterization of stable ruthenium(III) Schiff base chloro and carbonyl complexes with the axial ligands chloro (Cl), imidazole (Im) and 2-methylimidazole (2-MeIm) are reported. The Schiff bases were synthesized by the interaction of naphthaldehyde with amines such as *o*-phenylenediamine, ethylenediamine, propylenediamine and diethylenetriamine. The geometry around ruthenium in these complexes is pseudooctahedral. The complexes are low-spin $4d^5$ ($S = 1/2$) and display characteristic EPR spectra in the powder samples and in frozen solutions at 298 and 77 K. The EPR data and EHMO calculations on model complexes indicate that the d_{xy} orbital lies above d_{xz} and d_{yz} orbitals.

Studies on carbonyl complexes of ruthenium are confined so far to the low-valent oxidation state of ruthenium with only a few reports available on Ru^{III} carbonyl complexes.^{1,2} Several ruthenium complexes are known as homogeneous catalysts in carbonylation, hydroformylation and oxo reactions.^{3–7} With the intention of synthesizing high valent stable ruthenium complexes and to study their catalytic activity, we initiated work on some Ru^{III} Schiff base chloro and carbonyl complexes derived from aldehydes, namely salicylaldehyde and picolinaldehyde and several amines.^{8,9} Some of these complexes were found to be good homogeneous catalysts in the reductive carbonylation of nitrobenzene to phenylurethane by a phosgene-free route¹⁰ and in the oxidation reaction of cyclohexene to its epoxide.¹¹

In continuation of our earlier work,^{8–11} we now report the synthesis and characterization of a new class of Ru^{III} Schiff base chloro (**1a–10a**) and carbonyl (**1b–10b**) complexes of the type $[\text{RuLX}(\text{Cl})]^m$ and $[\text{RuLX}(\text{CO})]^n$, respectively, where L = Schiff base, namely bis(naphthaldehyde)-*o*-phenylenediamine (naphoph), bis(naphthaldehyde)ethylenediamine (naphen), bis(naphthaldehyde)propylenediamine (naphprop) and bis(naphthaldehyde)di-

ethylenetriamine (naphdien); $m = -1$ and $n = 0$ for $\text{X} = \text{Cl}^-$; $m = 0$ and $n = 1$ for $\text{X} = \text{Im}$ and 2-MeIm (Structure 1). The geometry around ruthenium in these complexes is distorted octahedral with naphoph, naphen and naphprop coordinating as tetradentate ligands and naphdien as a pentadentate ligand.

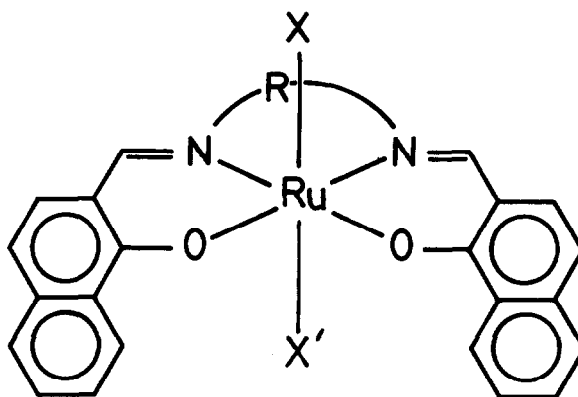
The complexes were characterized by analytical data and spectroscopic (UV-visible, IR and EPR), magnetic susceptibility and differential pulse polarographic (DPP) techniques. The EPR spectroscopy is used as a probe to study the molecular distortions caused by the substituents on the Schiff bases and on axial ligands (X) and the catalytic activity of the complexes. Extended Hückel Molecular Orbital (EHMO) calculations were performed on model chloro and carbonyl complexes to estimate the electronic ground state wave function and MO energy level scheme.

EXPERIMENTAL

Preparation of the complexes

Ruthenium(III) Schiff base chloro complexes, $\text{K}[\text{Ru}(\text{naphoph})\text{Cl}_2]$ (**1a**), $[\text{Ru}(\text{naphoph})(\text{Im})\text{Cl}]$ (**2a**), $[\text{Ru}(\text{naphoph})(2\text{-MeIm})\text{Cl}]$ (**3a**), $\text{K}[\text{Ru}(\text{naphen})\text{Cl}_2]$ (**4a**), $[\text{Ru}(\text{naphen})(\text{Im})\text{Cl}]$ (**5a**), $[\text{Ru}(\text{na-}$

* Author to whom correspondence should be addressed.



Complex No.	X'	X	R
1a, 2a, 3a	Cl	Cl, Im, 2-MeIm	-(C ₆ H ₄)-
1b, 2b, 3b	CO		
4a, 5a, 6a	Cl	Cl, Im, 2-MeIm	-(CH ₂) ₂ -
4b, 5b, 6b	CO		
7a, 8a, 9a	Cl	Cl, Im, 2-MeIm	-(CH(CH ₃)CH ₂)-
7b, 8b, 9b	CO		
10a	Cl	N of R	-(C ₂ H ₄)NH(C ₂ H ₄)-
10b	CO		

Structure 1

phen)(2-MeIm)Cl] (6a), K[Ru(naphprop)Cl₂] (7a), [Ru(naphprop)(Im)Cl] (8a), [Ru(naphprop)(2-MeIm)Cl] (9a) and [Ru(naphdien)Cl] (10a) were prepared according to the reported procedure.¹²

The carbonyl complexes, [Ru(naphoph)(Cl)(CO)] (1b), [Ru(naphoph)(Im)(CO)]Cl (2b), [Ru(naphoph)(2-MeIm)(CO)]Cl (3b), [Ru(naphen)(Cl)(CO)] (4b), [Ru(naphen)(Im)(CO)]Cl (5b), [Ru(naphen)(2-MeIm)(CO)]Cl (6b), [Ru(naphprop)(Cl)(CO)] (7b), [Ru(naphprop)(Im)(CO)]Cl (8b), [Ru(naphprop)(2-MeIm)(CO)]Cl (9b) and [Ru(naphdien)(CO)]Cl (10b) were synthesized from their respective parent chloro complexes 1a–10a.

Carbon monoxide was bubbled through the methanolic solutions of the parent complexes (2 mM) for about 10 h under constant stirring. Except complexes 1b, 4b and 7b, for the rest of the carbonyl complexes the above reaction mixture was con-

centrated and precipitated by the addition of dry diethyl ether. The complexes were recrystallized from dry diethyl ether and ethyl acetate. The carbonyl complexes thus obtained were dried *in vacuo* over CaCl₂.

In the cases of complexes 1b, 4b and 7b, KCl was filtered off, the filtrates were concentrated and the complexes were precipitated and recrystallized in the same way as discussed above. Naphoph complexes 1b–3b were dark brown while the rest of the carbonyl complexes were dark green in colour (yield: 60–70%). All the chemicals and solvents used were of AR grade and purified further prior to use.

Physical measurements

Microanalyses (C, H, N) of the complexes were done by a Carlo Erba 1106 elemental analyser. Solution electrical conductivity was measured at

298 K by using a Digisun Electronics Conductivity bridge. IR spectra were obtained at 298 K on a Nicolet 200 SXV FT-IR instrument as Nujol mulls/KBr pellets. Electronic spectra were recorded in DMF solutions on a Shimadzu Model UV-160 spectrophotometer. DPP data were recorded at 298 K on a Princeton Applied Research Model 174 electrochemical system.

Magnetic moment of the solid complexes were measured by a PAR model 155 vibrating sample magnetometer. The complex $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a calibrant and the experimental magnetic moments were corrected for diamagnetism. EPR spectra were recorded on a Bruker X-band spectrometer using 100 kHz field modulation. The organic free radical DPPH was used as a field marker ($g = 2.0036$). Experiments were conducted in powder samples as well as in solutions at 298 and 77 K.

Molecular orbital calculations

MO calculations were performed by using the EHMO method described by Hoffmann.¹³ The off-diagonal elements were calculated by a weighted Wolfberg–Helmholz formula,¹⁴ with the Hückel constant of 1.65. The input parameters such as Coulomb integrals and orbital exponents for Ru, Cl, O, N and H were taken from ref. 15.

In the present Schiff base complexes such as complex **1a** one has to deal with a basis set containing 173 AOs to evaluate the MOs and their energies. As the program cannot handle such large molecules, calculations were performed on model chloro and carbonyl complexes in which the bridging group between N and O (Structure 1) was replaced by $=\text{CH}-\text{CH}=\text{CH}-$ and that between N atoms was replaced by a NH group. As the crystal structures of the complexes are not known average Ru^{III}-ligand distances were assumed (Ru—Cl = 2.36, Ru—O = 2.03, Ru—N = 2.11, N—H = 1.0, C—H = 1.09 Å, N—Ru—O = 96° and N₁—Ru—N₂ = 84°). The Schiff base ligand was assumed to be in the *xy* plane and the *z*-axis coincides with the Cl—Ru—X axis. The Ru—C≡O bond was assumed linear with Ru—C = 1.84 Å and C≡O = 1.13 Å.

RESULTS AND DISCUSSION

The analytical data for the solid Ru^{III} Schiff base carbonyl complexes **1b–10b** are listed in Table 1. The freshly prepared DMF solutions of complexes **2b**, **3b**, **5b**, **6b**, **8b** and **9b** (1 mM) are 1:1 electrolytes while the rest of the carbonyl complexes are non-electrolytes.

In the IR spectra of the complexes a band at

1625–1635 cm⁻¹ due to the azomethine group of the ligands undergoes shift to lower frequency (1590–1610 cm⁻¹) after complexation indicating the coordination of imine nitrogen to ruthenium.^{16,17} The $\nu(\text{Ru}-\text{Cl})$ band is more intense than $\nu(\text{Ru}-\text{N})$ band and occurs around 320 cm⁻¹ in all the complexes. Imidazole and 2-methylimidazole complexes show additional bands near 620 and 1000 cm⁻¹ for the coordinated Im and 2-MeIm groups, respectively. The IR spectra of solid carbonyl complexes are characterized by an intense $\nu(\text{C}\equiv\text{O})$ band in the range 1940–1980 cm⁻¹ (Table 1) which was completely absent in the parent chloro complexes.¹² This band for free CO occurs at 2155 cm⁻¹. The shift in $\nu(\text{C}\equiv\text{O})$ on coordination is consistent with those reported earlier.⁹

The electronic absorption spectra for complexes **1b–10b** are almost similar to those for the parent chloro complexes **1a–10a** except for some changes in peak intensities and positions.¹² Intense bands around 270, 305 and 345 nm in the UV region (Table 1) are assigned to the $\pi-\pi^*$ and $n-\pi^*$ transitions of the Schiff base ligand. The latter band undergoes a hypsochromic shift in all the complexes due to coordination of the Schiff base ligand to ruthenium. Three resolved and moderately intense CT bands appear in the range 420–760 nm. Some of the *d-d* bands are masked by the CT bands in this region.

The DPP of complexes **1b–10b** under dropping mercury electrode consists of a single Ru^{III}/Ru^{II} reduction couple. The equatorial and axial ligands have a significant effect on the $E_{1/2}$ values (Table 1). The $-E_{1/2}$ values for complexes **1b–10b** vary with the Schiff bases in the order naphoph > naphprop > naphen > naphdien and with the axial ligands in the order Im > 2-MeIm > Cl⁻. A similar trend in $E_{1/2}$ values with the axial ligands was also observed with the other Ru^{III} Schiff base complexes reported earlier.⁹ Though 2-MeIm is more basic than Im, large negative $E_{1/2}$ values for Im complexes compared to that for 2-MeIm complexes could be due to the intermolecular H-bonding in the former case than in the latter.

The magnetic moment (μ_{eff}) for all the chloro and carbonyl complexes as powder samples at 298 K falls in the range 1.97–2.08 μ_{B} corresponding to a single unpaired electron.

The EPR spectra for complexes **1a–10a** and **1b–10b**, as powders at 298 K consist of three partially resolved *g* features characteristic of the +3 oxidation state for ruthenium with the unpaired electron in one of the *t*₂ orbitals and a low-symmetry crystal field around ruthenium. The EPR lines at 298 K are broad probably due to short spin–lattice relaxation time and intermolecular spin exchange

Table 1. Elemental analysis, IR data, $E_{1/2}$ values for the Ru^{III}/Ru^{II} reduction couple and UV-visible spectral data for Ru^{III} Schiff base carbonyl complexes

Complex no.	Elemental analysis ^a (%)			$\nu(\text{C}\equiv\text{O})^b$ (cm ⁻¹)	$E_{1/2}^c$ Ru ^{III} / Ru ^{II}	Electronic spectral data ^d λ_{max} (nm) (ϵ , M ⁻¹ cm ⁻¹)
	C	H	N			
1b	60.0 (60.1)	3.0 (3.1)	4.3 (4.8)	1970	-0.54	760(1490), 559(3505), 471(4935), 345(8550) ^e 317(1900), 269(11,790)
2b	62.1 (62.9)	3.1 (3.5)	9.0 (9.2)	1980	-0.59	715(2920), 555(3498), 469(5080), 346(7848), 310(6740), 268(7220)
3b	63.2 (63.3)	3.3 (3.9)	8.3 (8.9)	1980	-0.56	735(2970), 545(3445), ^e 348(74,100), 309(4800), 278(12,500)
4b	56.3 (56.6)	3.1 (3.4)	5.2 (5.3)	1965	-0.48	620(1670), 550(13,700), ^e 453(23,900), 375(8320), 273(56,900)
5b	59.1 (59.8)	3.1 (3.8)	9.3 (10.0)	1970	-0.56	690(2420), 550(935), 420(1755), ^e 319(3950), 259(12,500)
6b	60.1 (60.4)	4.0 (4.0)	9.1 (9.7)	1945	-0.54	624(4100), 553(19,200), 394(2755), ^e 315(6710), 270(13,500)
7b	57.1 (57.4)	3.2 (3.5)	5.0 (5.1)	1950	-0.54	670(2020), 550(18,550), 450(5003), 420(14,405), 339(8523), 290(53,200)
8b	60.2 (60.5)	3.4 (3.8)	9.1 (9.7)	1970	-0.62	624(4130), 555(936), 420(14,160), ^e 319(3950), 279(58,275)
9b	63.1 (63.3)	3.4 (3.9)	8.0 (8.9)	1975	-0.59	660(1900), 550(29,900), 425(20,710), ^e 362(37,200), 259(12,502)
10b	60.0 (60.4)	4.0 (4.1)	7.3 (7.8)	1980	-0.53	653(1800), 554(29,350), 410(2510), ^e 340(8250), 305(1250)

^a Found (Calc).^b In KBr pellets at 298 K.^c Dropping mercury electrode is the working electrode; solvent is DMF, supporting electrode is tetrabutyl ammonium perchlorate (0.1 M), the standard electrode is Ag/AgCl.^d Solvent is DMF.^e Shoulder.

interaction. Cooling the samples to 77 K narrowed the lines. No hyperfine coupling due to ruthenium could be observed. The absence of ruthenium hyperfine features was observed also by several investigators.^{18,19} The g -values at 77 K listed in Table 2 are slightly different from those at 298 K indicating the depopulation of paramagnetic excited J states which have become thermally inaccessible at low temperatures.

The EPR spectra of the carbonyl complexes as frozen DMF solutions are similar to those for their powder samples at 77 K. However, the spectra for the chloro complexes at 77 K vary considerably with the solvent indicating that Ru^{III} chloro complexes are unstable in solution while the carbonyl complexes are quite stable. The instability of the chloro complexes could be attributed to the lability of the Ru—Cl bond that dissociates in solution to form solvated species. As the chloro complexes are not stable in solution, we had restricted our study only to solid complexes in the latter part of the

section. Representative EPR spectra of the complexes are shown in Fig. 1.

The EPR data on powder samples, at 77 K, were analysed using the approach developed by Hill²⁰ and successfully applied to a number of low-spin d^5 systems by several investigators.^{9,18,19} The details of the calculation were discussed elsewhere.⁹ In the presence of low-symmetry (tetragonal, Δ and rhombic, V) distortions and spin-orbit coupling, the six T_2 orbitals of a low-spin d^5 configuration split into three Kramers' doublets. The ground state doublet is composed of t_2 functions, $|+1\rangle = -(d_{xz} + id_{yz})/\sqrt{2}$, $|\xi\rangle = id_{xy}$ and $|-1\rangle = (d_{xz} - id_{yz})/\sqrt{2}$, with admixture coefficients a , b and c , respectively.

For a particular g values set two solutions, (1) $g_z < g_x$ and g_y ; g_x , g_y and g_z are positive and (2) $g_z < g_x$ and g_y ; g_x and g_y are positive while g_z is negative, were found to be physically reasonable. The covalency parameter, k for solution 1 was less than 1.0 while it was greater than 1 for solution 2. The distortion parameters (Δ and V) and excitation

Table 2. *g* values,^a MO coefficients, delocalization parameter, distortion parameters and excitation energies of ruthenium(III) Schiff base chloro and carbonyl complexes at 77 K

Complex no.	<i>g_x</i>	<i>g_y</i>	<i>g_z</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>k</i>	Δ/λ	V/λ	$\Delta E_1/\lambda$	$\Delta E_2/\lambda$
1a	2.377	2.132	1.919	0.116	0.992	0.042	0.877	7.547	-5.886	4.707	10.634
1b	2.340	2.112	1.876	0.149	0.988	0.047	0.660	5.700	-3.954	3.849	7.871
2a	2.416	2.112	1.845	0.164	0.985	0.058	0.709	5.355	-4.196	3.409	7.655
2b	2.348	2.115	1.881	0.145	0.988	0.047	0.685	5.878	-4.167	3.919	8.148
3a	2.465	2.105	1.823	0.174	0.983	0.066	0.732	5.193	-4.402	3.161	7.602
3b	2.344	2.125	1.897	0.134	0.990	0.043	0.729	6.308	-4.366	4.237	8.666
4a	2.451	2.181	1.758	0.209	0.977	0.048	0.707	3.902	-2.112	3.007	5.251
4b	2.352	2.195	1.805	0.190	0.981	0.030	0.659	4.130	-1.520	3.472	5.200
5a	2.382	2.167	1.845	0.167	0.985	0.040	0.718	4.885	-2.665	3.675	6.454
5b	2.365	2.132	1.845	0.167	0.985	0.046	0.662	4.967	-3.094	3.556	6.740
6a	2.398	2.132	1.897	0.132	0.990	0.047	0.825	6.646	-5.159	4.184	9.389
6b	2.390	2.156	1.843	0.167	0.985	0.044	0.714	4.925	-2.918	3.597	6.614
7a ^b		2.096						1.072			
7b	2.373	2.105	1.860	0.157	0.986	0.054	0.670	5.529	-4.183	3.579	7.817
8a	2.365	2.086	1.855	0.161	0.985	0.058	0.634	5.521	-4.425	3.458	7.930
8b	2.357	2.132	1.855	0.162	0.986	0.045	0.667	5.135	-3.190	3.669	6.948
9a	2.415	2.066	1.887	0.136	0.989	0.066	0.752	7.408	-7.749	3.677	11.431
9b	2.373	2.149	1.863	0.156	0.987	0.043	0.720	5.301	-3.226	3.811	7.127
10a	2.425	2.160	1.866	0.152	0.987	0.046	0.810	5.577	-3.773	3.817	7.662
10b	2.390	2.100	1.924	0.111	0.993	0.050	0.884	8.620	-8.252	4.604	12.872

^a Estimated error in *g*₁, *g*₂, *g*₃ is ± 0.008 .

^b Isotropic spectrum was observed and *k* was calculated by using the expression $g_{av} = 2/3(2k + 1)$.

energies from the ground Kramers' doublet to excited doublets (ΔE_1 and ΔE_2) were larger for solution 1 than for solution 2. However, a molecular model for the complexes (Structure 1) and extended π -delocalization of the Schiff base ligand indicate that the covalency parameter must be less than 1 and distortions and excitation energies must be large. It is therefore concluded that solution 1 gives the correct ground state wave function. The MO admixture coefficients, covalency, distortion parameters and excitation energies corresponding to solution 1 for all the complexes are listed in Table 2. EHMO calculations on chloro and carbonyl complexes (vide infra) support these results.

It is clear from Table 2 that the tetragonal splitting, Δ , is larger than the rhombic splitting, V and further both these parameters are larger than the spin-orbit coupling constant (λ).^{*} The positive value for Δ/λ for all the complexes and the larger MO coefficient for d_{xy} orbital, *b*, than '*a*' and '*c*' indicate that in the absence of spin-orbit coupling

d_{xy} lies above ($d_{xz} + id_{yz}$) orbitals resulting in the ground state electronic configuration $d_{xz}^2 d_{yz}^2 d_{xy}^1$. The value for Δ is in general larger for carbonyl complexes than for chloro complexes. It is pertinent to note that Ru^{III} chloro complexes derived from salicylaldehyde have a d_{xz}/d_{yz} ground state while their carbonyl analogues have a d_{xy} ground state.⁹ However, in the present case the stabilization of d_{xz}/d_{yz} orbitals for both chloro and carbonyl complexes could be because of the additional π -interaction in the naphthaldehyde group.

The parameters *k*, Δ/λ and $\Delta E_i/\lambda$ (*i* = 1 and 2) change with the basicity of the axial ligands in the order 2-MeIm > Im > Cl⁻. The value of *k* is smaller for carbonyl complexes than for chloro complexes indicating that the Ru—CO bond is more covalent than Ru—Cl bond. This is because of the difference in the nature of binding of Cl⁻ and CO (Cl⁻ is a σ -donor whereas CO is a π -acceptor). As the $d\pi$ orbitals (assuming *z*-axis coincides with Ru—Cl or Ru—CO bond) are filled in these complexes they can donate electron density to the $p\pi$ orbitals of CO whereas the $p\pi$ orbitals of Cl⁻ cannot donate electron density to the metal $d\pi$ orbitals leading to a labile Ru—Cl bond. The value of *k*

* The spin-orbit coupling constant (λ) for the Ru^{III} ion is 1150 cm⁻¹. In complexes it is assumed to be 1000 cm⁻¹.

Table 3. Molecular orbital energy and wave function for model ruthenium(III) chloro and carbonyl complexes

MO ^a	Orbital energy (eV)	Wave function ^b
Ru^{III} Chloro Complex		
37	-11.140	$-0.93d_{xz}(\text{Ru}) + 0.11p_x(\text{C11} - \text{C12}) + 0.15d_{xz}(\text{C11} + \text{C12})$
38	-11.101	$-0.93d_{yz}(\text{Ru}) + 0.11p_y(\text{C11} - \text{C12}) + 0.15d_{yz}(\text{C11} + \text{C12}) + 0.10(\text{O1} - \text{O2})$
39	-11.030	$0.97d_{x^2-y^2}(\text{Ru}) + 0.10d_{xy}(\text{Ru}) + 0.12p_y(\text{O1} - \text{O2})$
40	-9.962	$-0.68d_{z^2}(\text{Ru}) - 0.19p_z(\text{C11} - \text{C12}) - 0.44d_{z^2}(\text{C11} + \text{C12}) - 0.10p_x(\text{N1} - \text{N2})$
41, 42	-9.490, -9.461	Ligand orbitals
43	-9.371	$-0.97d_{xy}(\text{Ru}) - 0.21p_x(\text{N1} - \text{N2}) - 0.20p_y(\text{N1} + \text{N2}) - 0.10p_x(\text{O1} - \text{O2}) + 0.17p_y(\text{O1} + \text{O2})$
Ru^{III} Carbonyl Complex		
38	-11.465	$0.82d_{xz}(\text{Ru}) + 0.09p_x(\text{Cl}) - 0.14d_{xz}(\text{Cl}) + 0.37p_x(\text{C}) - 0.25p_x(\text{O})$
39	-11.435	$0.81d_{yz}(\text{Ru}) + 0.09p_y(\text{Cl}) - 0.14d_{yz}(\text{Cl}) + 0.38p_y(\text{C}) - 0.25p_y(\text{O})$
40	-11.047	$-0.97d_{x^2-y^2}(\text{Ru}) - 0.10d_{xy}(\text{Ru}) - 0.12p_y(\text{O1} - \text{O2})$
41	-9.827	$0.41d_{z^2}(\text{Ru}) - 0.12p_z(\text{Cl}) + 0.84d_{z^2}(\text{Cl}) - 0.12s(\text{C}) + 0.09p_z(\text{C})$
42-47	-9.675, -9.461	Chlorine and ligand orbitals
48	-9.374	$0.95d_{xy}(\text{Ru}) + 0.17d_{xy}(\text{Cl}) - 0.11d_{yz}(\text{Cl}) - 0.21p_x(\text{N1} - \text{N2}) - 0.19p_y(\text{N1} + \text{N2})$

^a The HOMOs for chloro and carbonyl complexes are 39th and 40th MOs respectively. The symmetry at the site of ruthenium is as low as C_{2v} .

^b Atoms O1 and O2 belong to Schiff base; C and O belong to carbonyl group.

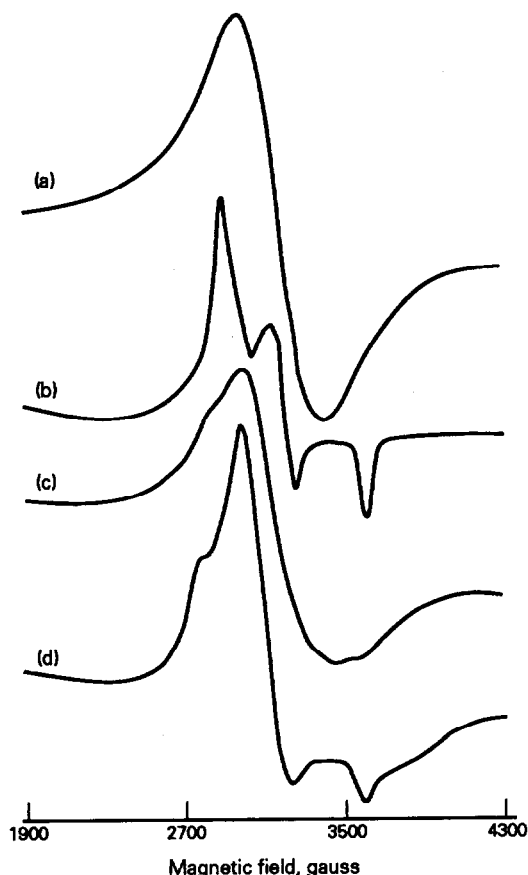


Fig. 1. X-band EPR spectra of $\text{K}[\text{Ru}(\text{naphprop})\text{Cl}_2]$ **7a** and $[\text{Ru}(\text{naphprop})(\text{Cl})(\text{CO})]$ **7b** complexes at 77 K. (a) **7a** as powder sample, (b) frozen acetone solution of **7a**, (c) **7b** as powder sample, and (d) frozen DMF solution of **7b**.

varies with the Schiff bases in the order salicylaldehyde > picolinaldehyde > naphthaldehyde. This suggests that the naphthaldehyde Schiff base complexes reported in this investigation are more stable than salicylaldehyde and picolinaldehyde complexes reported elsewhere.⁹ Because of the higher stability of the naphthaldehyde Schiff base complexes they are less active catalytically than salicylaldehyde and picolinaldehyde complexes.¹⁰

EHMO calculations

The HOMO in both chloro and carbonyl complexes is predominantly a $d_{x^2-y^2}$ orbital.* The wave functions for a few MOs above and below the HOMO along with their energies are listed in Table 3. It is obvious from Table 3 that replacement of Cl^- by CO has lowered the energy of d_{xz} and d_{yz} orbitals while that of $d_{x^2-y^2}$ is unaltered. The d_{z^2} and d_{xy} orbitals are more destabilized in the case of carbonyl complexes. Ruthenium d_{xz} and d_{yz} orbitals involve an antibonding interaction with $p\pi$ orbitals of Cl^- and CO. The $d\pi-p\pi$ interaction is more in the case of carbonyl complexes than in chloro complexes (the coefficients for $d\pi$ orbitals are smaller in the case of carbonyl complexes than in the chloro complexes) leading to more stabilized d_{xz} and d_{yz}

* The $d_{x^2-y^2}$ orbital in EHMO calculation is the same as the d_{xy} orbital discussed in the EPR provided the coordinate system used in EHMO calculation is rotated by 45° about z -axis.

orbitals in carbonyl complexes. It is therefore expected that the replacement of Cl⁻ by CO group increases the axial and crystal field splittings. EPR results on chloro and carbonyl complexes are consistent with this observation (the value for the axial distortion Δ is more for carbonyl complexes than for chloro complexes). A similar behaviour in the energy level ordering was observed for the chloro and carbonyl complexes of ferrous porphyrins.²¹

REFERENCES

1. M. Schröder and T. A. Stephenson, in *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson), Vol. 4, Chapter 45, p. 277. Pergamon Press, New York (1987).
2. A. J. Hewitt, J. H. Holloway, P. D. Peacock, J. B. Raynor and I. L. Willon, *J. Chem. Soc., Dalton Trans.* 1978, 579.
3. M. M. Taqui Khan and A. E. Martell, *Homogeneous Catalysis by Metal Complexes*, Vol. I and II. Academic Press, New York (1974).
4. G. N. Schrauzer (Ed.), *Transition Metals in Homogeneous Catalysis*. Marcel Dekker Inc., New York (1971).
5. A. E. Shilov (Ed.), *Fundamental Research in Homogeneous Catalysis*, Vol. I. Gordon and Breach, New York (1986).
6. G. Süss-Fink and G. F. Schmidt, *J. Mol. Catal.* 1987, **42**, 361; T. Squarez and B. Fontal, *ibid.* 1985, **32**, 191.
7. M. M. Taqui Khan, S. B. Halligudi and S. H. R. Abdi, *J. Mol. Catal.* 1988, **44**, 179; *ibid.* 1988, **45**, 215; M. M. Taqui Khan, S. A. Samad and M. R. H. Siddiqui, *J. Mol. Catal.* 1989, **53**, 23.
8. M. M. Taqui Khan, Ch. Sreelatha, S. A. Mirza, G. Ramachandraiah and S. H. R. Abdi, *Inorg. Chim. Acta* 1988, **154**, 103.
9. M. M. Taqui Khan, D. Srinivas, R. I. Kureshy and N. H. Khan, *Inorg. Chem.* 1990, **29**, 2320.
10. M. M. Taqui Khan, S. B. Halligudi, S. Shukla and Z. A. Shaikh, *J. Mol. Catal.* 1990, **57**, 301 and 307.
11. M. M. Taqui Khan, S. A. Mirza, A. Prakash Rao and Ch. Sreelatha, *J. Mol. Catal.* 1988, **44**, 107.
12. M. M. Taqui Khan, N. H. Khan, R. I. Kureshy and A. B. Boricha, *Inorg. Chim. Acta* 1990, **174**, 175.
13. R. Hoffmann, *J. Chem. Phys.* 1963, **39**, 1397; R. Hoffmann and W. N. Lipscomb, 1962, **37**, 177.
14. S. P. McGlynn, L. G. Vanquickenborne, M. Kinoshita and D. G. Carroll, *Introduction to Applied Quantum Chemistry*. Holt, Reinhart and Winston, New York (1972).
15. K. Tatsumi and R. Hoffmann, *J. Am. Chem. Soc.* 1981, **103**, 3328.
16. L. J. Boucher, *J. Inorg. Nucl. Chem.* 1974, **36**, 531; L. J. Boucher and M. O. Farrel, *ibid.* 1973, **35**, 3731.
17. F. M. Ashmawy, R. M. Issa, S. A. Amer, C. A. McAuliffe and R. V. Parish, *J. Chem. Soc., Dalton Trans.* 1986, 421.
18. A. Hudson and M. J. Kennedy, *J. Chem. Soc. A* 1969, 1116; J. B. Raynor and B. G. Jeliakowa, *J. Chem. Soc., Dalton Trans.* 1982, 1185.
19. A. R. Chakravarty and A. Chakravorty, *J. Chem. Soc., Dalton Trans.* 1982, 615; N. Bag, G. K. Lahiri, S. Bhattacharya, L. R. Felvello and A. Chakravorty, *Inorg. Chem.* 1988, **27**, 4396.
20. N. J. Hill, *J. Chem. Soc., Faraday Trans.* 1972, 427.
21. M. Zerner, M. Gouterman and H. Kobayashi, *Theoret. Chim. Acta* 1966, **6**, 363.