Pergamon

0277-5387(95)00306-1

Polyhedron Vol. 15, No. 7, pp. 1191–1196, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277-5387/96 \$15.00+0.00

ISOMERIC RUTHENIUM(III) COMPLEXES OF N-PHENYL-2-PYRIDINE CARBOXALDIMINE. SYNTHESIS, CHARACTERIZATION AND ELECTRON-TRANSFER PROPERTIES

SREEBRATA GOSWAMI†

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science,
Calcutta 700 032, India

and

SUBRATA CHOUDHURY

Department of Chemistry, North-Eastern Hill University, Shillong 793 003, India

(*Received* 16 *May* 1995; *accepted* 23 *June* 1995)

Abstract—Three geometric isomers of $[RuCl_2L_2](ClO_4)$ (L = N-phenyl-2-pyridine carboxaldimine) have been isolated by stereoretentive oxidation of the corresponding isomeric ruthenium(II) complexes using $Cl_2(g)$ as an oxidant, followed by the addition of aqueous sodium perchlorate. These complexes are paramagnetic (low-spin d^5, $S = 1/2$) and display rhombic EPR spectra at 77 K. The electronic transition energies have been computed, using the observed g values, which agree well with the experimentally observed transitions in the IR region of the optical spectra. In addition to the ligand field transitions, all the complexes also show multiple charge-transfer transitions in the visible region. Each of the complexes display a reversible reductive response due to an Ru^{III}/Ru^{II} couple in the range 0.3–0.5 V *versus* SCE at a platinum electrode. Chemical reductions of these trivalent complexes by hydrazine revert almost quantitatively to the parent bivalent ruthenium complexes. In acetonitrile, $RuCl_2L_2^+$ complexes act as mild oxidants.

Structure and reactivity studies on ruthenium complexes containing N-phenyl-2-pyridine carboxaldimine (L, **1**) have received recent attention.[1–5] The ligand L has low lying π^* orbital and can enter[6] in $d\pi$–$p\pi$ interactions effectively in the complexes of electron-rich metal ions. This effect is generally reflected in charge-transfer spectra and redox potential data of the complexes of L.

Recently, we reported our work [3] on complexes of ruthenium(II) with L, where three geometric isomers of $RuCl_2L_2$ were isolated and characterized. The redox stabilities of all $RuCl_2L_2$ isomers are evidenced by the moderate positive formal potentials of the ruthenium(III)–ruthenium(II) couples. This report describes chemical oxidation of the above complexes, isolation and characterization of the trivalent congeners. The reversibility and relatively easy accessible potentials for the ruthenium(III)–ruthenium(II) couples in isomeric $RuCl_2L_2$ led us to explore the possibility of synthesizing the corresponding trivalent compounds in the pure state. It may be noted in the present context that the examples of isolable isomeric trivalent ruthenium complexes[7,8] are scarce. In this oxidation state metal–ligand π-interactions become insignificant and the geometry preference of these complexes are totally controlled by steric interactions. Here we also explore the possibilities of using the above trivalent compounds as mild oxidants, especially in non-aqueous solvents.

---

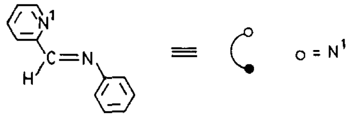
† Author to whom correspondence should be addressed.

RESULTS AND DISCUSSION

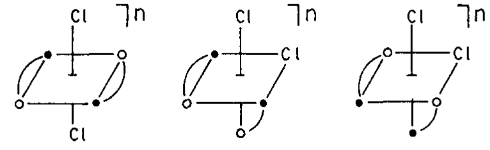
Synthesis and geometry

We have reported[3] that in the direct reaction of ruthenium(III) chloride with L in solution the metal ion undergoes reduction with concomitant partial chloride substitution to yield bivalent ruthenium complexes, $RuCl_2L_2$. In order to obtain an access to the trivalent complexes, preformed $Ru^{II}Cl_2L_2$ was, therefore, chosen for chemical oxidation. Accordingly, an acetonitrile solution of $RuCl_2L_2$ was exposed to $Cl_2(g)$ followed by addition of aqueous $NaClO_4$ led to the synthesis of $[RuCl_2L_2](ClO_4)$. The role of aqueous $NaClO_4$ was to bring about precipitation of the product as a perchlorate salt.

The starting complex, $RuCl_2L_2$, thus far has been obtained[3,9] in three isomeric forms: green *trans–trans–trans* (*ttt*, **2**), bluish-green *cis–cis–trans* (*cct*, **3**) and blue *cis–trans–cis* (*ctc*, **4**). On oxidation, each afforded a characteristic $[RuCl_2L_2](ClO_4)$ salt. Interestingly, chemical as well as electrochemical reductions of each of the trivalent complexes (**5**–**7**) quantitatively regenerates the parent $RuCl_2L_2$. Thus, the redox reaction involved in the above interconversion



L, 1



n = 0 2 3 4
n = +1 5 6 7

$$(Ru^{II}Cl_2L_2 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} Ru^{III}Cl_2L_2{}^+)$$

is reversible and stereoretentive. Stereoretention of the above reaction allows isolation of isomeric $RuCl_2L_2{}^+$ in the three geometries. The examples of such isomeric trivalent ruthenium complexes are scanty in the literature.[7,8] We note here that isomer preference in the trivalent state is primarily sterically controlled. As a result, in many cases, oxidations of isomeric bivalent complexes lead to isomerization[10] to yield only the *trans* isomer of least steric hindrance.

Characterization

Yellowish-brown salts of $[RuCl_2L_2](ClO_4)$ were obtained in almost quantitative yields. These are all microcrystalline products, highly soluble in redox inert polar organic solvent such as acetonitrile, but insoluble in non-polar solvents. These were formulated by elemental (C, H, N) analyses and these behave as 1 : 1 electrolytes in acetonitrile (Table 1).

IR spectral data of the complexes were collected as KBr discs in the range 4000–250 cm^{-1}. Only a few characteristic frequencies are considered here. All complexes showed bands near 1100 and 620 cm^{-1} assignable to $\nu_{ClO_4^-}$. $\nu_{C=N}$ were observed[11] in the range 1620–1590 cm^{-1}. Interestingly, the *ttt* isomer (**5**) showed a strong absorption at 325 cm^{-1} due to $\nu_{Ru—Cl}$. In contrast, each of the other two *cis* isomers (**6** and **7**) displayed a doublet absorption between the 330–300 cm^{-1} frequency range. The singlet nature of $\nu_{Ru—Cl}$ in **5** does confirm[3] a linear grouping of the $RuCl_2$ moiety, whereas a doublet $\nu_{Ru—Cl}$ is characteristic for a *cis*-$RuCl_2$ unit. Furthermore, we note here that $\nu_{Ru—Cl}$ frequencies in the trivalent complexes (**5**–**7**) are systematically higher than those in bivalent complexes (**2**–**4**). This is surely due to stronger Ru—Cl bonds in $[RuCl_2L_2]ClO_4$ salts. Solution electronic spectra of **5**–**7** were recorded in the range 2000–300 nm. The spectral pattern for all three complexes is similar except for slight variation in the absorption energies. The spectral data are collected in Table 2 and a representatives spectrum of the *ttt* isomer is displayed in Fig. 1. The spectrum of **5**–**7** each consists of multiple intense absorptions in the visible region due to the allowed transitions[7] involving metal and ligand orbitals and a low energy weak absorption in the range 1625–1450 nm. This low energy transition is due to *d*–*d* transitions originating from splitting of the t_2 orbitals due to the low symmetry and spin-orbit coupling. Interestingly, the energy of the ligand field band is in good agreement with the calculated transition energies using the observed *g*-values from the respective EPR spectrum (see below).

The magnetic moments (Table 3) of the complexes correspond to low-spin d^5 configurations (idealized $t_{2g}{}^5$, $S = 1/2$). None of the isomers possess rotational symmetry greater than two-fold. Their EPR spectra in frozen acetonitrile–toluene (77 K) are accordingly rhombic (Fig. 2). The theory of EPR spectra of distorted octahedral low-spin d^5 complexes is well documented[12,13] in the literature. Only the essential features of relevance to this work are stated here. The molecular symmetry of the complexes is reflected in their rhombic EPR spectra. The extent of distortions from idealized O_h sym-

Table 1. Analytical, conductivity and IR data

Compound	Elemental analysis (%)[a] C	H	N	Λ_M[b] (Ω^{-1} cm^2 mol^{-1})	IR (cm^{-1}) $\nu_{C=N}$	ν_{Ru-Cl}
5	44.9 (45.3)	3.0 (3.1)	8.9 (8.8)	135	1602	320
6	45.2 (45.3)	3.2 (3.1)	9.0 (8.8)	140	1605	325, 310
7	45.1 (45.3)	3.1 (3.1)	8.9 (8.8)	140	1605	320, 300

[a] Calculated values are in parentheses.

[b] In MeCN at 298 K with a solute concentration of *ca* 10^{-3} M.

metry has been ascertained in terms of axial (Δ) and rhombic (V) components. Under the combined influence of this low symmetry and spin-orbit coupling, the three t_2(Ru) levels become well separated and hence two electronic transitions (transition energies ΔE_1, and ΔE_2; $\Delta E_2 > \Delta E_1$) are possible within these three levels. These transition energies have been computed using the observed g values. The ΔE_2 transition in each of the complexes has indeed been observed in the range 6800–6155 cm^{-1} (Table 2), while ΔE_1 transitions could not be observed due to solvent cut off.

Redox properties

The electron-transfer properties of the isomeric salt $[RuCl_2L_2](ClO_4)$ were studied cyclic voltammetrically in acetonitrile at a platinum electrode using tetrabutyl ammonium bromide as supporting electrolyte. Potential data are collected in Table 3 and segmented voltammograms are displayed in Fig. 3. All potentials are referenced to saturated calomel electrode (SCE). The complexes showed ligand-based multiple reductive responses, which are identical to the responses occurring[1,3] in the corresponding bivalent complexes. We do not consider these any further. Each isomer of $[RuCl_2L_2]^+$ displays a reversible, reductive, one-electron cyclic voltammogram in the potential range 0.3–0.7 V. Under identical conditions, this voltammogram (initial scan cathodic) is superimposable on that of the corresponding isomer of $RuCl_2L_2$ (initial scan anodic). This clearly indicates that the redox process under consideration is reversible and stereoretentive. Exhaustive constant potential electrolyses of isomeric **5**–**7** were performed at 0.0 V. The coulomb count in each case corresponds to one-electron and the absorption spectrum of solution

Table 2. Electrochemical and electronic spectral data

Compound	Electronic spectra[a] λ_{max}(nm)(ε, M^{-1} cm^{-1})	$\mathrm{Ru^{III}}$–$\mathrm{Ru^{II}}$ couple[b] E°_{298}(V)	ΔE_p (mV)	n[c]
5	1460(43), 500,[d] 470(2665)	0.31	70	0.98
6	1500(40), 500,[d] 457(2760), 390,[d] 340(8170)	0.33	65	1.01
7	1625(45), 490,[d] 450(2880), 325(8500)	0.47	70	1.01

[a] In MeCN at 298 K.

[b] Conditions: solvent, MeCN; supporting electrolyte, $[NBu^t_4][ClO_4]$ (10^{-1}M); working electrode, platinum; reference electrode, SCE; solute concentration, *ca* 10^{-3}M. Cyclic voltammetric data: $E^{\circ}_{298} = 0.5(E_{pa}+E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{pa} - E_{pc}$; scan rate, 50 mV s^{-1}.

[c] $n = Q'/Q$; where Q is the calculated coulomb count for the transfer of one electron and Q' is the observed coulomb count after exhaustive electrolysis; oxidation in each case was performed at 0.10 V versus SCE in CH_3CN (0.1 M $[NBu^+_4][ClO_4]$.

[d] Shoulder.

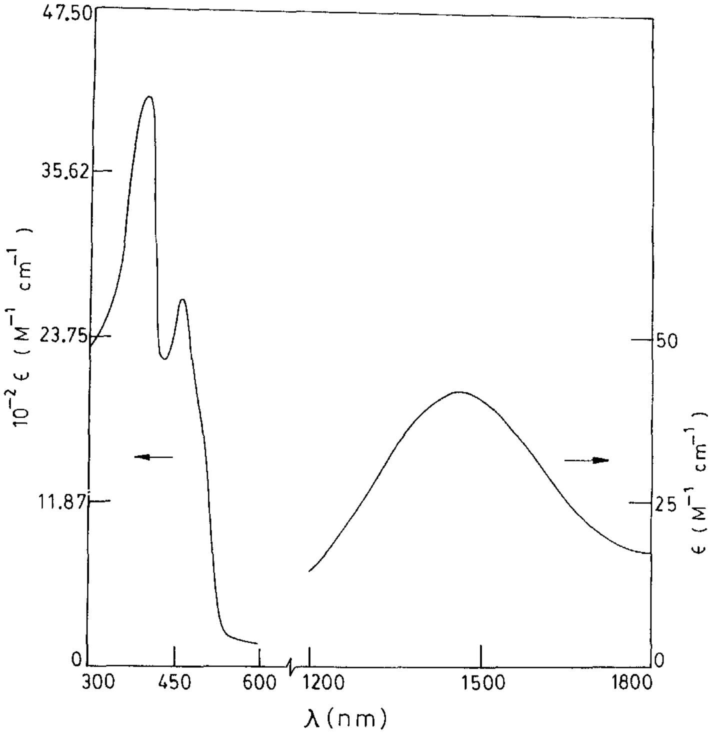


Fig. 1. Electronic spectrum of *ttt*-[$RuCl_2L_2$]ClO_4 in acetonitrile.

of electrogenerated bivalent complex matches quantitatively with the corresponding isomer of $RuCl_2L_2$. The formal potentials of the ruthenium(III)/ruthenium(II) couple follow the order: *ttt* < *cct* < *ctc*. Thus, the trivalent complex in *ctc* geometry (**7**) is the strongest oxidizing agent in this series. This may be rationalized[8] in terms of the strongest $d\pi$–$p\pi$ interactions in the corresponding bivalent complex (**4**).

The stabilities of the trivalent complexes, $RuCl_2L_2^+$, together with the reduction potentials suggest that they might act as moderate one-electron oxidants. Accordingly, two redox reactions were performed which indeed showed that the trivalent complexes successfully participate in the redox reactions.

Addition of a few drops of hydrazine hydrate to the brown solution of isomeric **5**–**7** in acetonitrile causes an instantaneous colour change to the corresponding colour of **2**–**4**. This reaction was followed spectrophotometrically, which showed almost quantitative reduction of the trivalent complex. No attempt has, however, been made to detect the oxidation product of hydrazine. In another experiment equimolar solutions of $Fe^{II}(C_5H_5)_2$ and $Ru^{III}Cl_2L_2^+$ in acetonitrile were mixed together and the resultant solution was examined cyclic voltammetrically. Immediately there was a colour change. In addition to the reversible oxidative wave of $Ru^{II}Cl_2L_2$, a reductive response at 0.18 V confirmed the generation of $Fe^{III}(C_5H_5)_2^+$ evidently due to electron transfer in solution.

Table 3. Magnetic moments, EPR *g* values and derived energy parameters

		g values[b]			Derived energy parameters (cm^{-1})	
Compound	μ_{eff}[a](B.M.)	g_1	g_2	g_3	ΔE_1	ΔE_2
5	1.82	2.8018	2.2491	1.7309	2783	6332
6	1.89	2.8009	2.2350	1.7436	2813	6690
7	1.85	2.8120	2.2632	1.7220	2776	6138

[a] In the solid state at 298 K.
[b] In acetonitrile–toluene (1–1) glass at 77 K.

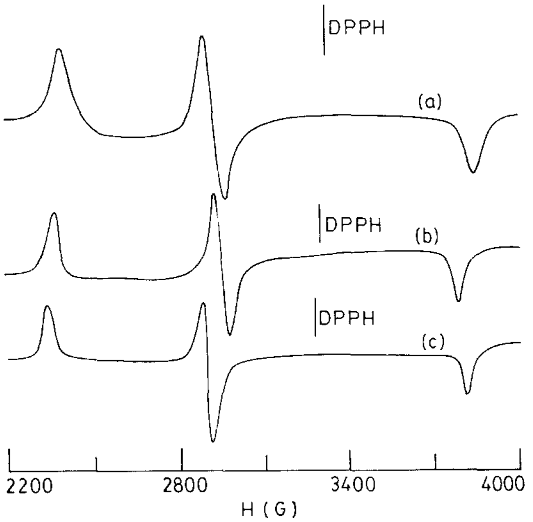


Fig. 2. X-Band EPR spectra in an acetonitrile–toluene (1–1) glass (77 K) of (a) *ttt*- (b) *cct*- and (c) *ctc*-$[RuCl_2L_2]ClO_4$.

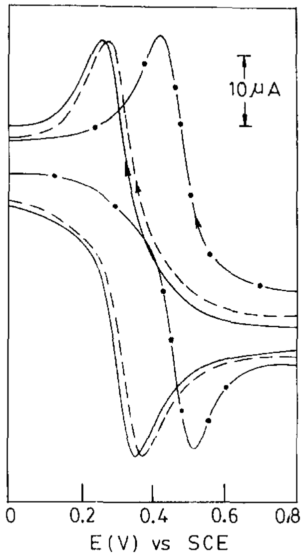


Fig. 3. Segmented cyclic voltammograms of: (i) *ttt*- (——), (ii) *cct*- (---) and (iii) *ctc*-$[RuCl_2L_2]ClO_4$ (— · — · —) at 50 mV s^{-1} scan rate.

EXPERIMENTAL

Materials

The three isomers of $[RuCl_2L_2]$(L = N-phenyl-2-pyridine carboxaldimine) were prepared using reported[2,8] methods. Purification of solvents and preparation of tetrabutylammonium perchlorate for electrochemical work were carried out as before.[1] Dinitrogen gas was purified by successively bubbling it through an alkaline aqueous solution of sodium dithionite and concentrated sulphuric acid. All other chemicals and solvents were reagent-grade commercial materials.

Physical measurements

Microanalyses (C, H, N) were performed using a Perkin–Elmer 240C elemental analyser. IR spectra were obtained on a Perkin–Elmer IR-983 spectrophotometer with samples prepared as KBr pellets. Solution electronic spectra were recorded on a Hitachi 330 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer. X-band EPR spectra were recorded on a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at 77 K (Liquid nitrogen) and the spectra were calibrated with DPPH ($g = 2.0037$). Solution electrical conductivity was measured using a Elico CM 82T conductivity bridge with a solute concentration of *ca* 10^{-3} M. Electrochemical measurements were made using a PAR model 370-4 electrochemistry system as before.[10] A saturated calomel reference electrode (SCE) was used as a reference electrode. All electrochemical data were collected at 298 K and uncorrected for junction potentials.

Preparation of the complexes

The three isomers of $[RuCl_2L_2](ClO_4)$ were synthesised using a general procedure. Yields varied in the range 80–90%. Details for the preparation of one of the isomers are given below.

trans-trans-trans-Dichlorobis[2-(*phenylpyridine*) *carboxaldimine*]*ruthenium*(III) *perchlorate*, *ttt*-$[RuCl_2L_2](ClO_4)$. To a green solution of freshly prepared *ttt*-$RuCl_2L_2$ (100 mg of powdered sample in 25 cm^3 of CH_3CN) was bubbled Cl_2 (g) until the solution colour changed to light yellow. The solution was then filtered to remove any insoluble material. A saturated aqueous solution of sodium perchlorate (2 cm^3) was then added and the mixture was left in the refrigerator for *ca* 30 min. A crystalline yellowish-brown precipitate thus formed and was filtered and washed with ice-cold water, and dried *in vacuo* over P_4O_{10}. Yield 80%.

Acknowledgements—The authors thank Professor Animesh Chakravorty (IACS, Calcutta), Dr Samaresh Bhattacharya (JU, Calcutta) and Dr Alok K. Deb (NEHU, Shillong) for their help.

REFERENCES

1. S. Choudhury, A. K. Deb and S. Goswami, *J. Chem. Soc., Dalton Trans.* 1994, 1305.

2. M. Menon, S. Choudhury, A. Pramanik, A. K. Deb, S. K. Chandra, N. Bag, S. Goswami and A. Chakravorty, *J. Chem. Soc., Chem. Commun.* 1994, 57.
3. S. Choudhury, M. Kakoti, A. K. Deb and S. Goswami, *Polyhedron* 1992, **11**, 3183.
4. P. Belser and A. Von Zelewsky, *Helv. Chim. Acta* 1980, **63**, 1675.
5. E. V. Dose and L. J. Wilson, *Inorg. Chem.* 1978, **17**, 2600.
6. J. Reinhold, R. Benedix, P. Birner and H. Hennig, *Inorg. Chim. Acta* 1979, **33**, 209.
7. G. K. Lahiri, S. Bhattacharya, S. Goswami and A. Chakravorty, *J. Chem. Soc., Dalton Trans.* 1990, 561.
8. M. Menon, A. Pramanik, S. Chattopadhyay, N. Bag and A. Chakravorty, *Inorg. Chem.* 1995, **34**, 1361.
9. S. Choudhury and S. Goswami, manuscript under preparation.
10. A. Pramanik, N. Bag, D. Ray, G. K. Lahiri and A. Chakravorty, *Inorg. Chem.* 1991, **30**, 410; N. Bag, G. K. Lahiri and A. Chakravorty, *J. Chem. Soc., Dalton Trans.* 1990, 1557; A. Pramanik, N. Bag and A. Chakravorty, *J. Chem. Soc., Dalton Trans.* 1993, 237.
11. S. Choudhury, A. K. Deb and S. Goswami, *Polyhedron* 1994, **13**, 1068.
12. B. Bleany and M. C. M. O'Brien, *Proc. Phys. Soc. London, Sect. B*, 1956, **69**, 1216; J. S. Griffith, *The Theory of Transition Metal Ions*, p. 364. Cambridge University Press, London (1961); P. H. Rieger, *Coord. Chem. Rev.* 1994, **135/136**, 203.
13. S. Bhattacharya and A. Chakravorty, *Proc. Indian Acad. Sci.* (*Chem. Sci.*) 1985, **95**, 159; G. K. Lahiri, S. Bhattacharya, M. Mukherjee, A. K. Mukherjee, and A. Chakravorty, *Inorg. Chem.* 1987, **26**, 3359.