High-potential Isomeric Ruthenium(III) Complexes of 2-(Phenylazo)pyridine†

Goutam Kumar Lahiri, Samaresh Bhattacharya, Sreebrata Goswami, and Animesh Chakravorty*
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India

Three geometrical isomers, (**5**)—(**7**), of $[RuL_2Cl_2]ClO_4{\cdot}H_2O$ [L = 2-(phenylazo)pyridine] have been isolated *via* stereoretentive oxidation of the corresponding ruthenium(II) isomers with concentrated nitric acid. The low-spin (t_2^5, $S = \frac{1}{2}$) complexes display rhombic e.s.r. spectra in frozen solution (77 K). The axial (Δ) and rhombic (V) distortion parameters (in the order Δ, V) are (in cm^{-1}): 5 230, −3 520 (**5**); −5 150, 3 970 (**6**); and −4 900, 4 610 (**7**). The sign changes correspond to energy inversion of split t_2 components. The magnitude of V increases with decreasing symmetry as expected, (**5**) < (**6**) < (**7**). Two predicted optical transitions within the Kramers doublets are experimentally observed or indicated in the near-i.r. region [(**5**), 7 000, <4 500; (**6**), 6 900, 5 000; and (**7**), 6 900, 5 100 cm^{-1}]. The $[RuL_2Cl_2]^+$–$[RuL_2Cl_2]$ couple is reversible in acetonitrile and has E_{298}° values 0.92, 1.07, and 1.16 V *vs.* s.c.e. in the cases of (**5**), (**6**), and (**7**) respectively. These potentials correlate linearly with the energy of the highest t_2 component. The complexes bring about the oxidative coupling of *N,N*-dimethylaniline, the oxidation of tris(1,2-naphthoquinone 1-oximato)nickel(II) to the corresponding nickel(III) complex, and the oxidation of free 1,2-naphthoquinone 1-oxime (Hnqo) to the corresponding iminoxy radical. In the cyclic voltammetric oxidation of $[RuL_2Cl_2]$ in the presence of Hnqo the observed current is in excess of the sum of currents due to the components taken separately. This has been analysed in terms of an electrocatalytic model. The excess current as well as the turnover number vary linearly with the ratio of the concentration of Hnqo to that of $[RuL_2Cl_2]$.

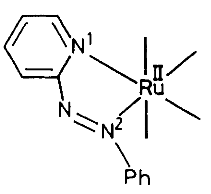
The high affinity of bivalent ruthenium for the azoimine function –N=N–C=N– is well documented.[1–7] In the particular case of 2-(phenylazo)pyridine (L), this is reflected in the thermodynamic stability of the [RuL] chelate ring (**1**) and in the generally high formal potentials of couples of the type defined

$$[Ru^{III}L] + e \rightleftharpoons [Ru^{II}L] \qquad (1)$$

by equation (1).[1–6] For example, E_{298}° of the $[RuL_3]^{3+}$–$(RuL_3]^{2+}$ couple is 2.10 V[4d] *vs.* saturated calomel electrode (s.c.e.), *cf.* $[Ru(bipy)_3]^{3+}$–$[Ru(bipy)_3]^{2+}$, 1.30 V[8] (bipy = 2,2′-bipyridine). Thus $[Ru^{III}L]$ species are of interest as potent one-electron oxidants. For the same reason, however, these have been synthetically inaccessible and isolation of none has been reported so far. This gap in the ruthenium chemistry of L is bridged in the present work which deals with the preparation, properties, and reactions of a group of isomeric $[Ru^{III}L]$ complexes.

Results and Discussion

Synthesis.—The direct reaction of ruthenium(III) salts with L in solution failed to afford tractable $[Ru^{III}L]$ species; the metal underwent reduction and complexes of bivalent ruthenium resulted. Oxidation of preformed $[Ru^{II}L]$ complexes by strong oxidants was then explored. The usual starting material for synthesis of various $[Ru^{II}L]$ complexes is $[RuL_2Cl_2]$.[1–6] We examined this as a substrate for oxidation. For preparative oxidation of ruthenium(II) to ruthenium(III) Cl_2, Br_2, and Ce^{IV} are commonly used as oxidants.[9] However, none of these was effective in affording any characterisable ruthenium(III) derivative of $[RuL_2Cl_2]$. Concentrated HNO_3 was, however, found to oxidise $[RuL_2Cl_2]$ smoothly at room temperature and from the reaction mixture $[RuL_2Cl_2]^+$ could be isolated in high yields as the perchlorate monohydrate. Nitric acid is rarely used for synthesis of ruthenium(III) chelates from ruthenium(II) congeners.[10]



(**1**)

Table 1. Analytical, conductivity, and spectral data[a]

Compound	Elemental analysis (%)[b] C	H	N	Λ_M/Ω^{-1} cm^2 mol^{-1}	U.v.–visible spectral data, $\lambda_{max.}$/nm (ε/dm^3 mol^{-1} cm^{-1})
(**5**)	40.30 (40.25)	3.10 (3.05)	13.00 (12.80)	145	555 (3 500), 400 (1 600), 310 (13 000)
(**6**)	40.20 (40.25)	3.05 (3.05)	12.90 (12.80)	140	825 (sh) (160), 575 (sh) (3 900), 525 (4 700), 370 (20 900)
(**7**)	40.35 (40.25)	3.10 (3.05)	12.80 (12.80)	145	555 (sh) (4 200), 510 (4 700), 360 (19 600)

[a] Molar conductivity and spectral data in MeCN at 298 K. [b] Calculated values are in parentheses.

The $[RuL_2Cl_2]$ precursor occurs in three isomeric forms: green *trans-trans-trans* [ttt, (**2**)], blue *cis-trans-cis* [ctc, (**3**)], and blue *cis-cis-cis* [ccc, (**4**)].[1,2,4a] Upon oxidation with HNO_3 each isomer afforded a characteristic $[RuL_2Cl_2]ClO_4{\cdot}H_2O$ salt that

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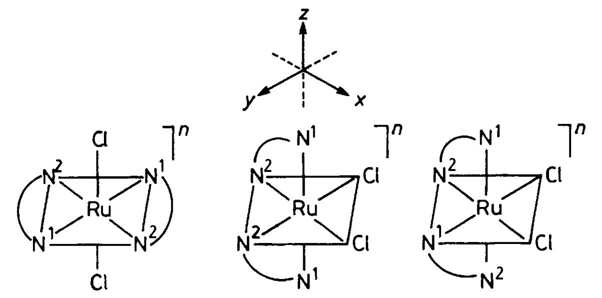
† *Non-S.I. unit employed:* G = 10^{-4} T.



n = 0 **(2)** **(3)** **(4)**

n = +1 **(5)** **(6)** **(7)**

Table 2. Magnetic moments,[a] e.s.r. g values,[b] and electrochemical data[c]

Compound	$\mu_{eff.}$	g_1	g_2	g_3	Ru^{III}–Ru^{II} couple $E_{298}{}^0$/V	Ru^{III}–Ru^{II} couple ΔE_p/mV
(5)	1.95	2.636	2.268	1.833	0.92	60
(6)	1.93	2.520	2.253	1.865	1.07	70
(7)	1.96	2.445	2.261	1.890	1.16	70

[a] In the solid state at 298 K. [b] Measurements were made in an acetonitrile–toluene (1:1) glass at 77 K. [c] Conditions: solvent, acetonitrile; supporting electrolyte, $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}); working electrode, platinum; reference electrode, s.c.e.; solute concentration, $\approx 10^{-3}$ mol dm^{-3}. Cyclic voltammetric data: $E_{298}{}^0 = 0.5 (E_{p_a} + E_{p_c})$, where E_{p_a} and E_{p_c} are the anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{p_a} - E_{p_c}$; scan rate, 50 mV s^{-1}.

differed from the other two. Chemical as well as electrochemical reduction (see below) of each salt in solution quantitatively reconverted it into the parent $[RuL_2Cl_2]$ isomer. Thus the redox interconversion of each $[RuL_2Cl_2]^+$–$[RuL_2Cl_2]$ pair occurs without geometrical changes. The three $[RuL_2Cl_2]ClO_4 \cdot H_2O$ salts differ in the geometric structure of the cation: **(5)**, **(6)**, and **(7)** which arise from oxidations of **(2)**, **(3)**, and **(4)** respectively. To our knowledge this is the first report of the isolation of three isomers of the $[Ru^{III}Cl_2]$ fragment bis chelated by an unsymmetrical bidentate ligand.

The visual colours of the $[RuL_2Cl_2]^+$ isomers are very similar: the solid perchlorates are dark coloured and their 1:1 electrolytic solutions (Table 1) are deep red. In each case a strong absorption occurs near 550 nm but the structure, intensity, and exact energy of the band differ from isomer to isomer (Figure 1, Table 1). The band is a single feature for the ttt isomer but is structured for the ctc and ccc isomers; the ctc structure lies at lower energy.

Electronic Structure: E.S.R. and Near-I.R. Spectra.—The magnetic moments (Table 2) of the complexes correspond to low-spin d^5 configurations (idealised $t_{2g}{}^5$; $S = \frac{1}{2}$). None of the isomers possesses rotational symmetry greater than two-fold. Their e.s.r. spectra (Table 2, Figure 2) in frozen acetonitrile–toluene (77 K) are accordingly rhombic,

The spectra have been examined in terms of the crystal field g-tensor theory[11] of low-spin d^5 complexes. Among the parameters that can be derived from this theory are: splitting due to axial distortions (Δ) which transforms the t_2 shell into $e + b$ (tetragonal distortion); splitting due to rhombic distortion (V) which splits e further into non-degenerate components; the energies (ΔE_1 and ΔE_2) of the two optical transitions among the three Kramers doublets originating from the application of Δ, V, and λ (spin-orbit coupling constant) on t_2; the orbital reduction factor (k). The goodness of the analysis can be assessed by independent observation of the transitions ΔE_1 and ΔE_2 in optical spectra.

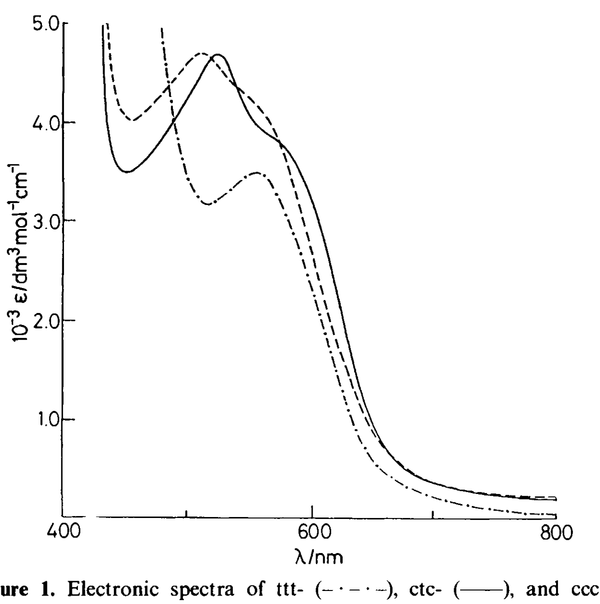


Figure 1. Electronic spectra of ttt- (–·–·–), ctc- (——), and ccc-$[RuL_2Cl_2]ClO_4 \cdot H_2O$ (— — —)

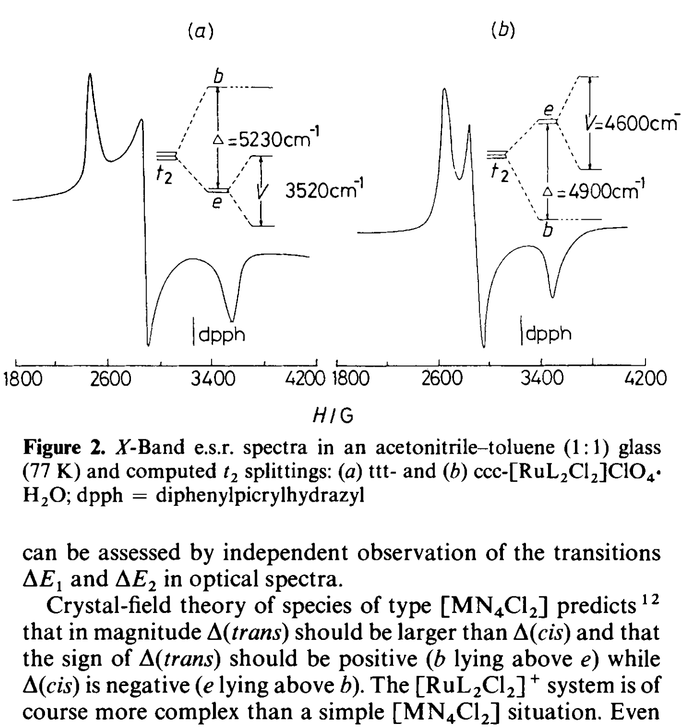


Figure 2. X-Band e.s.r. spectra in an acetonitrile–toluene (1:1) glass (77 K) and computed t_2 splittings: (*a*) ttt- and (*b*) ccc-$[RuL_2Cl_2]ClO_4 \cdot H_2O$; dpph = diphenylpicrylhydrazyl

Crystal-field theory of species of type $[MN_4Cl_2]$ predicts[12] that in magnitude Δ(*trans*) should be larger than Δ(*cis*) and that the sign of Δ(*trans*) should be positive (b lying above e) while Δ(*cis*) is negative (e lying above b). The $[RuL_2Cl_2]^+$ system is of course more complex than a simple $[MN_4Cl_2]$ situation. Even then the crystal-field requirement of the sign and magnitude of Δ is satisfied by the g assignment shown [axis system as in **(5)**—**(7)**] in Table 3. The splittings in the ttt and ccc isomers (ctc is similar to ccc) are depicted in Figure 2. The magnitude of rhombic splitting increases with decreasing symmetry as expected: **(5)** < **(6)** < **(7)**. The value of λ for complexed ruthenium(III) is set at 1 000 cm^{-1}.[13]

The ΔE_1 and ΔE_2 transitions have been observed in the near-i.r. region in acetonitrile solution (Figure 3). In the ttt complex a low-intensity transition occurs at 7 000 cm^{-1} (ΔE_2) and there is clear sign of another band below 4 500 cm^{-1}. In the case of the ctc isomer a peak is observed at $\approx$5 000 cm^{-1} (ΔE_1) with a shoulder at $\approx$7 000 cm^{-1} (ΔE_2). The spectrum of the ccc isomer is closely similar to that of the ctc isomer. In view of approximations of the theory, the agreement between calculated and observed transition energies (Table 3) is quite satisfactory.

The observed k values are slightly higher than 1. This can be

Table 3. Assignments of e.s.r. g values, distortion parameters, near-i.r. transitions, and energy of the highest t_2 component[a]

							$\Delta E_1/\lambda$		$\Delta E_2/\lambda$		
Compound	g_x	g_y	g_z	k	Δ/λ	V/λ	Calc.	Obs.[b]	Calc.	Obs.[b]	E_{ro}(cm^{-1})
(**5**)	−2.636	−2.268	1.833	1.131	5.234	−3.515	3.612	*c*	7.203	7.0	3 490
(**6**)	1.865	−2.253	−2.520	1.051	−5.146	3.967	4.076	5.0	7.337	6.9	3 700
(**7**)	1.890	−2.261	−2.445	1.042	−4.896	4.609	4.685	5.1	7.411	6.9	3 940

[a] Symbols have the same meaning as in the text. [b] Set equal to ν/λ where ν is the observed near-i.r. frequency in cm^{-1} and λ = 1 000 cm^{-1}. [c] Band maximum lies below 4 500 cm^{-1}.

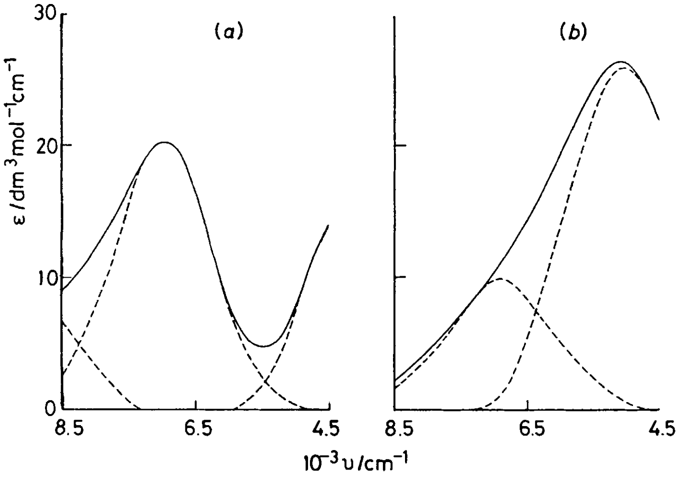


Figure 3. Near-i.r. spectra of (*a*) ttt- and (*b*) ctc-[RuL_2Cl_2]$ClO_4 \cdot H_2O$ in acetonitrile. The broken curves represent Gaussian components

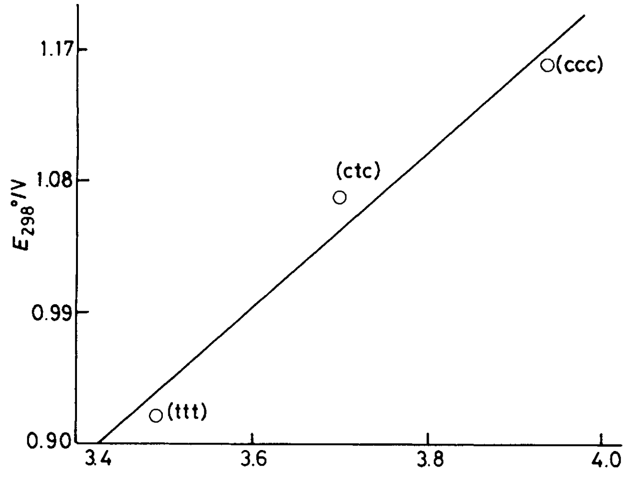


Figure 4. Plot of $E_{298}{}^0$ *versus* E_{ro}, energy of the highest t_2 component

due to admixture of excited states ($t_2{}^4e$) with the ground $t_2{}^5$ configuration. This effect has not been explicitly considered in the model used. The k values can be approximately corrected[14] for this by multiplying with the factor ($1 + 12B/E_{av.}$) where B is the Racah parameter and $E_{av.}$ is an average excitation energy. Using $B \approx 600$ cm^{-1} and $E_{av.} \approx 30\,000$ cm^{-1}, the corrected k values are: ttt, 0.91; ctc, 0.85; and ccc, 0.84.

Redox Behaviour: Reduction Potentials and Their Correlation with Distortion Parameters.—Each isomer of [RuL_2Cl_2]$^+$ displays a reversible one-electron cyclic voltammogram near 1 V (all potentials in this paper are referenced to s.c.e.) in acetonitrile solution at a platinum electrode. Under identical conditions, this voltammogram (initial scan cathodic) is superposable on that of the corresponding isomer of [RuL_2Cl_2] (initial scan anodic) showing that the redox process (2) is

$$[RuL_2Cl_2]^+ \rightleftharpoons [RuL_2Cl_2] \qquad (2)$$

stereoretentive. Upon exhaustive constant-potential reduction of complex (**5**) at 0.6 V the coulomb count corresponded to one electron; the reduced solution is green in colour and its absorption spectrum matches quantitatively with that of (**2**). Similarly coulometric reduction of (**6**) and (**7**) quantitatively affords blue (**3**) and (**4**) respectively.

The formal potentials of couple (2) follow the order ttt < ctc < ccc (Table 2). This can be rationalised in terms of the distortion parameters Δ and V considered in the last section. In the reduction of [RuL_2Cl_2]$^+$ to [RuL_2Cl_2] the electron is added to the highest t_2 component which is half-filled (Figure 2). The formal potentials are therefore expected to increase as the energy (E_{ro}) of this redox orbital increases. The approximate energies of this orbital are given by equations (3) and (4) where

$$E_{ro}(\text{ttt}) = 2\Delta/3 \qquad (3)$$

$$E_{ro}(\text{ctc,ccc}) = \Delta/3 + V/2 \qquad (4)$$

only the magnitudes of Δ and V are to be inserted. The calculated E_{ro} values are in Table 3. These follow the order ttt < ctc < ccc. Indeed a plot of $E_{298}{}^0$ *vs.* E_{ro} is satisfactorily linear (Figure 4).

The high reduction potentials of the [RuL_2Cl_2]$^+$ isomers and their stereochemical and substitutional inertness make them good one-electron oxidants. Three examples are cited below illustrating (*i*) oxidative coupling, (*ii*) oxidation of nickel from the bivalent to the trivalent state, and (*iii*) iminoxy radical formation.

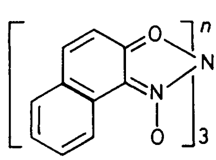
Oxidative Coupling.—The [RuL_2Cl_2]$^+$ isomers are quantitatively reduced to the corresponding [RuL_2Cl_2] isomers by *N,N*-dimethylaniline (dma) in acetonitrile. The resultant solution displays the characteristic cyclic voltammogram[15] ($E_{298}{}^0$ 0.4 V) of *N,N,N′,N′*-tetramethylbenzidine (tmb) evidently formed by oxidative coupling, equation (5). In a

$$2\text{dma} + 2[RuL_2Cl_2]^+ \longrightarrow \text{tmb} + 2[RuL_2Cl_2] + 2H^+ \qquad (5)$$

solution prepared by mixing (**3**) ($\approx 10^{-3}$ mol dm^{-3}) with dma ($\approx 2 \times 10^{-2}$ mol dm^{-3}) the cyclic voltammetric current height of the tmb response corresponded to 50% utilisation of the oxidation equivalents for the coupling reaction. The rest are evidently lost in side reactions.[16]

Formation of Trivalent Nickel.—Tris(1,2-napthoquinone 1-oximato)nickel(II) (**8**), is stoicheiometrically and quantitatively oxidised to the corresponding nickel(III) chelate (**9**), by any of the isomers of [RuL_2Cl_2]$^+$, equation (6). This provides

$$(\mathbf{8}) + [Ru^{III}L_2Cl_2]^+ \longrightarrow (\mathbf{9}) + [Ru^{II}L_2Cl_2] \qquad (6)$$



$n = -1$ (**8**)
$n = 0$ (**9**)

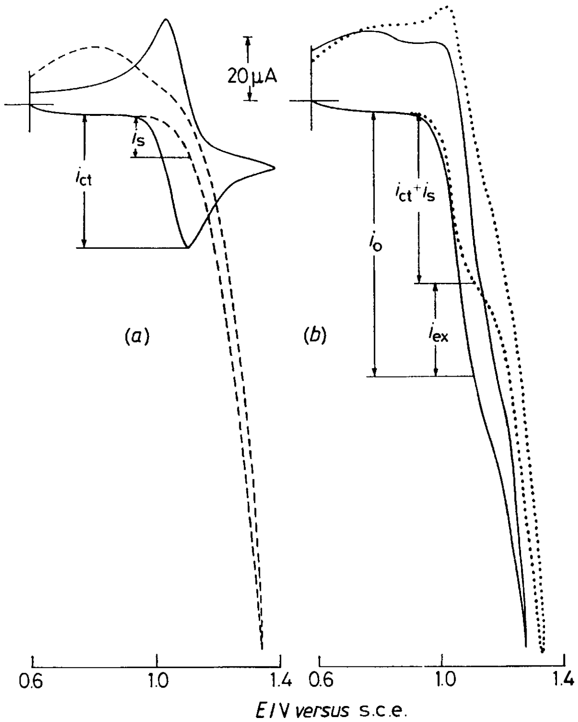
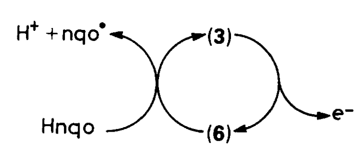


Figure 5. Cyclic voltammograms (298 K) in acetonitrile at a platinum electrode of (*a*) (1.04×10^{-3} mol dm^{-3}) ctc-[RuL_2Cl_2] (——) and (16.79×10^{-3} mol dm^{-3}) Hnqo (— — —), (*b*) a mixture of the two taken at the same concentrations (——). The dotted line (· · · ·) represents the sum of the two voltammograms in (*a*)



Scheme.

a chemical route for the synthesis of (**9**) which had earlier been obtained only electrochemically.[17]

Interestingly, free 1,2-naphthoquinone 1-oxime (Hnqo) is also oxidised by the [RuL_2Cl_2]$^+$ isomers and in this case a radical is formed. Significant results obtained with the ctc isomer are noted below.

Generation of an Iminoxy Radical: An Electrocatalytic Effect.—Addition of complex (**6**) to Hnqo in acetonitrile instantly produces the characteristic blue colour of (**3**) and the solution displays a strong e.s.r. triplet (g = 2.006, A_N = 27 G) characteristic of the iminoxy radical nqo•.[18] Spectrophotometric titration using the intensity of the band of complex (**3**) at 580 nm established that the reaction has a 1:1 stoicheiometry, equation (7).

$$(\mathbf{6}) + \text{Hnqo} \longrightarrow (\mathbf{3}) + \text{nqo}^{\bullet} + \text{H}^+ \qquad (7)$$

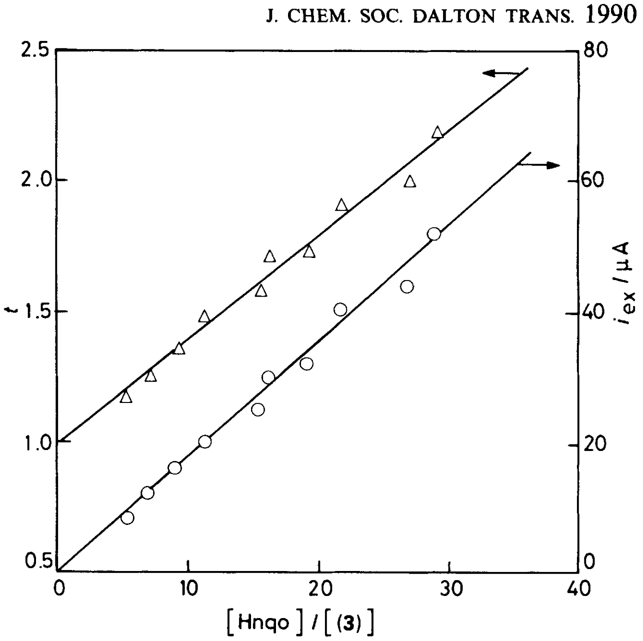


Figure 6. Plot of excess current (i_{ex}) and turnover number (t) *versus* the ratio of concentrations of Hnqo and ctc-[RuL_2Cl_2]

An electrocatalytic version of this reaction has been observed cyclic voltammetrically (scan rate, 50 mV s^{-1}) in acetonitrile solutions containing both Hnqo and complex (**3**). In the voltammogram of Hnqo alone no well defined oxidation peak is observed but above 1.1 V the anodic current increases, first slowly and then rapidly. The voltammogram of (**3**) alone has the anodic peak potential at 1.12 V. In voltammograms of mixtures the anodic currents are substantially larger than the sum of those of the two individual components (Figure 5). This is rationalised in the Scheme. The anodic oxidation of complexes (**3**) to (**6**) is followed rapidly by the reaction (7) and the regenerated (**3**) is reoxidised before it can diffuse away from the electrode surface. Here the role of (**3**) is that of a catalyst. Evidently this effect should become more pronounced as the concentration of Hnqo increases. Results are shown in Figure 6. The concentration of (**3**) was kept close to 1.0×10^{-3} mol dm^{-3} and progressively larger amounts of Hnqo were added. The concentration ratio [Hnqo]/[(**3**)] was varied within the range 5—30:1 in this manner.

We define the excess current (i_{ex}) which is a measure of the catalytic effect by equation (8). Here i_o is the observed current in

$$i_{ex} = i_o - i_{ct} - i_s \qquad (8)$$

the mixture, i_{ct} is the current due to the catalyst only [*i.e.* solution of (**3**) alone at the same concentration as in the mixture], and i_s is the current due to the substrate Hnqo alone (same concentration as in the mixture). Current data were compared at 1.12 V which happens to be the anodic peak potential of complex (**3**). A plot of i_{ex} *vs.* the ratio of the concentrations of (**3**) and Hnqo is satisfactorily linear (Figure 6). The total turnover (t) defined by equation (9) lies in the range

$$t = (i_{ex} + i_{ct})/i_{ct} \qquad (9)$$

1.2—2.2 for the data points of Figure 6. It is linear function of the ratio [Hnqo]/[(**3**)] (Figure 6) since i_{ct} has been kept more or less constant corresponding to 1×10^{-3} mol dm^{-3} (**3**). The catalytic effect is quite significant even on the cyclic voltammetric time-scale. Further studies on oxidations by [RuL_2Cl_2]$^+$ isomers are in progress.

Experimental

Starting Materials.—The three isomers of $[Ru^{II}L_2Cl_2]$ [L = 2-(phenylazo)pyridine] were prepared using reported procedures.[1,2] The $Na[Ni(nqo)_3]$ was prepared according to the literature method.[19] Purification of solvents and preparation of tetraethylammonium perchlorate for electrochemical work was done as before.[13] Dinitrogen gas was purified by successively bubbling it through alkaline dithionite and concentrated sulphuric acid. All other chemicals and solvents were reagent-grade commercial materials.

Physical Measurements.—U.v.–visible–near-i.r. spectra were recorded by using a Hitachi 330 spectrophotometer. Gaussian analysis of near-i.r. bands was performed as before.[20,21a] Infrared (4 000—300 cm^{-1}) spectra were taken on a Perkin-Elmer 783 spectrophotometer. The magnetic susceptibility was measured on a PAR 155 vibrating-sample magnetometer fitted with a Walker Scientific L75FBAL magnet. Electrochemical, e.s.r., and microanalytical measurements were done as before.[13]

Treatment of E.S.R. Data.—We have used the d^5 approach of Hill[14] and some of the details have been outlined in our recent publications.[13,21] It is reiterated that when g_1, g_2, and g_3 are presented in slots of g_x, g_y, and g_z having fixed signs a set of six solutions arise that are physically equivalent and are characterised by the same k, ΔE_1, and ΔE_2 values, and the same splitting pattern. The permutation merely changes the names of axes and hence of orbitals. Our specific choice (Table 3) has been made such that the sign and magnitude of Δ follow a certain trend (see text). The sign of V can be changed by simply interchanging g_x and g_y and is therefore not of any particular importance in the present work. Lastly we note that a second solution entirely different from the one chosen also exists but this corresponds to very small distortions and ΔE_1 and ΔE_2 values ($\approx$ 1 500 cm^{-1}). The near-i.r. results clearly eliminate this solution as unacceptable.

Preparation of Complexes.—The three isomers of $[RuL_2Cl_2]ClO_4\cdot H_2O$ were synthesized using a general procedure. Yields varied in the range of 80—85%. Details for one complex are given below.

trans-trans-trans-*Dichlorobis*[2-(*phenylazo*)*pyridine*]-*ruthenium*(III) *perchlorate monohydrate*, ttt-$[RuL_2Cl_2]ClO_4\cdot H_2O$. Concentrated nitric acid (5 cm^3) was added to finely powdered ttt-$[RuL_2Cl_2]$ (200 mg, 0.46 mmol) at *ca.* 298 K. The solid compound dissolved to produce a deep red solution with evolution of nitrous fumes. The solution was cooled to 273 K and a saturated aqueous solution of sodium perchlorate (25 cm^3) was added. Dark crystals deposited which were collected by filtration, washed with dilute nitric acid, and finally with a few drops of cold water. These were dried *in vacuo* over P_4O_{10} (yield *ca.* 80%).

Acknowledgements

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