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A Ruthenium(IV)-Ruthenium(III) Dimer, Product of the Reaction of Aqua(ethylenediaminetetraacetato)ruthenium(III) with Chlorate Ions

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An oxo-bridged, mixed-valence complex of ruthenium(IV,III), $[(edta)Ru^{IV}ORu^{III}(edta)]^{3-}$, has been obtained from the oxidation of $[Ru^{III}(edta)(H_2O)]^-$ by chlorate ions. The formulation of the complex as a μ-oxo dimer of ruthenium(IV,III) is based on the results of a variety of experiments, including elemental analyses, magnetism, by spectrophotometry, and by electrochemical studies. These studies in acetate buffer solution show that the dimeric ion can be reduced at mercury electrode to $[(edta)Ru^{III}ORu^{III}(edta)]^{4-}$ and then is monomerized to the original $[Ru(edta)(H_2O)]^-$ in a fast reaction.

In the course of the studies of the chemical and electrochemical redox reactions of ruthenium(II)- and (III)-EDTA, it was found that the $[Ru(edta)(H_2O)]^-$ in an acetate buffer solution gave an intense green color on the addition of oxidizing agent such as sodium chlorate or hydrogen peroxide. Examination revealed that the coloration was due to the formation of a mixed-valence μ-oxo ruthenium(IV,III) dimeric complex.

Green or bluish green solutions of ruthenium complexes have become of much interest in recent years. Meyer *et al.*[1,2] have isolated several blue-green complexes of ruthenium, and identified them as μ-oxo dimers of ruthenium(III,III) or (IV,III). As early as 1966, Ezerskaya *et al.*[3,4] obtained a green complex from the reaction between Ru(III)-EDTA and hydrogen peroxide; this seems to be the same as the complex we obtained. They claimed that the complex might be μ-oxo and μ-peroxo double bridged dimer, however, no supporting evidence was presented.

Recently Uehiro *et al.*[5,6] also obtained the green complex from oxidation of Ru(III)-EDTA by Mn(III)-EDTA or platinum electrode, or from irradiation of light.

This paper reports the isolation of mixed-valence ruthenium(IV,III) dimer and the identification and electrochemical properties of the complex.

Experimental

Reagents. Aqua(hydrogenethylenediaminetetraacetato)-ruthenium(III) 4-water, $[Ru(Hedta)(H_2O)]\cdot 4H_2O$, was prepared according to the procedure described previously,[7] and characterized by elemental analysis, alkalimetric titration,[8] and UV-visible, and IR spectra.

Sodium chlorate was recrystallized from water and then dried under a vacuum. The assay was made by alkalimetric titration of the cation-exchanged solution of one-gram samples.

Deionized water distilled in an all-glass apparatus was used throughout the experiment. Nitrogen gas for deoxygenation was purified by passing it through an acid vanadium(II) sulfate solution and then water. The other chemicals were of guaranteed reagent grade and used without further purification.

Apparatus. UV-visible and IR spectra were measured with a Hitachi 624 Digital Spectrophotometer and a Hitachi EPI-G2 IR spectrophotometer.

Polarographic measurement, controlled potential coulometry, and cyclic voltammetry were carried out as described earlier.[9] The flow rate of the dropping mercury electrode (DME) was 1.77 mg s^{-1} under a mercury head of 50 cm. The drop time of the DME was mechanically controlled and the instantaneous currents at 3.50 s after the dislodgement were sampled by means of a dislodger-cutoff device.[10] All the potentials cited here are referred to the saturated calomel electrode (SCE). A Radiometer pH meter 25E was used for pH determination. All the electrochemical measurement was carried out at (25±0.1) °C under a nitrogen atmosphere.

Magnetic properties were measured by the Gouy method. The apparatus was calibrated with $Hg[Co(NCS)_4]$. The observed magnetic susceptibility was corrected for diamagnetism by means of Pascal's constants. The magneton number, magnetic moment $\boldsymbol{m}$ divided by Bohr magneton $\boldsymbol{m}_B$, was calculated by using the following expression:††

$$\boldsymbol{m}/\boldsymbol{m}_B = 798(T/\mathrm{K})^{1/2}(\chi V_m/\mathrm{m^3\ mol^{-1}})^{1/2},$$

where T is the thermodynamic temperature, χ is the corrected magnetic susceptibility, and V_m is the molar volume.

Isolation and Analysis of the Binuclear Complex. One-tenth gram of $[Ru(Hedta)(H_2O)]\cdot 4H_2O$ was dissolved in 50 cm^3 of sodium acetate–acetic acid solution (0.2 mol dm^{-3} each). A 20 cm^3 portion of 0.01 mol dm^{-3} $NaClO_3$ was added dropwise to the mixture. The color of the solution turned from pale yellow to deep green. The green solution was allowed to stand overnight in the dark. After the solution was concentrated to about one-fifth the initial volume by evaporation under a reduced pressure at 30 °C, its pH was adjusted to *ca.* 1 with hydrochloric acid. Ethanol was added to the resulting solution on cooling until fine, green crystals precipitated, which were collected by filtration. The crystals were washed several times with small volumes of ethanol, and then dried *in vacuo* at room temperature (yield 40 mg).

The ruthenium content of the green complex was determined spectrophotometrically according to the ruthenate method.[11] The amount of cation in the product was determined by the cation-exchange method. The elemental analysis of C, H, and N was carried out by means of a Yanagimoto MY2 CHN Corder.

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†† This expression is based on SI. What is often called inappropriately "molar susceptibility" corresponds to $\chi V_m/4\pi$.

Results and Discussion

D. c. Polarography and Stoichiometry of the Reaction between Aqua-edta-Ru(III) and ClO_3^-. A typical polarogram of the aqua-edta-Ru(III) complex, which shall be abbreviated as Ru(III)L,[†††] is shown in Fig. 1a. The step corresponds to the diffusion-controlled, Nernstian reduction of Ru(III)L to Ru(II)L.[12] When a small amount of sodium chlorate was added to the solution, the pale yellow solution turned green. At the same time, a new step (step A in Fig. 1b) began to appear at a more positive potential, while the original step remained essentially unchanged (step B in Fig. 1b). The limiting current of step A was diffusion-controlled unless a large excess (more than ten times) of chlorate ions was present, and the log-plot analysis indicated that step B was Nernstian (the reciprocal slope was −58 mV). The height of step A gradually increased with respect to time and finally reached a constant value after a few hours. The final step height depended on the amount of the chlorate ions added.

Amperometric and spectrophotometric titrations were carried out: acetate buffer solutions containing known amounts of Ru(III)L and sodium chlorate at various ratios were prepared and left to stand overnight. The polarograms and the UV-visible spectra were then recorded. As shown by the examples in Fig. 2, there was a clear end-point at $n(ClO_3^-)/n(\text{Ru(III)-L}) = 0.083$ or 1/12, where n is the amount of the specified substance. Beyond the end-point, the height of step A of the polarogram remained constant till a large excess of chlorate ions was added; the ratio of the heights of step A and step B was very close to 1:2.

These results are readily explained by assuming that a chlorate ion undergoes a six-electron reduction as in the case of the reaction with vanadium(II) ions,[13] oxidizing six Ru(III)L entities to the Ru(IV) state, and each Ru(IV) species combines with another Ru-

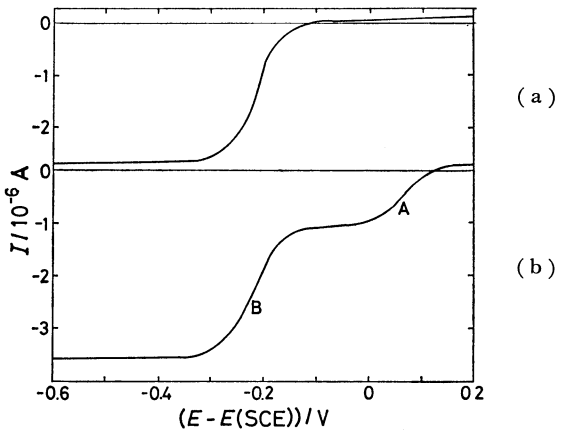

Fig. 1. D. c. polarograms of 1.0 mol m^{-3} [Ru(edta)-$(H_2O)]^-$ in 0.2 mol dm^{-3} sodium acetate-acetic acid buffer (pH=4.7) at 25 °C before (a) and after the addition of 0.1 mol m^{-3} $NaClO_3$ (b).

††† In the pH region under study, this complex actually exists mainly as $[Ru(edta)(H_2O)]^-$ ($pK_a = 2.65$).[7]

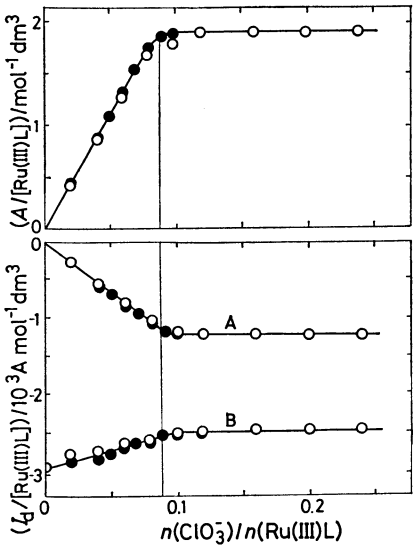

Fig. 2. Titration curves of $[Ru(edta)(H_2O)]^-$ with chlorate ions in 0.2 mol dm^{-3} sodium acetate-acetic acid buffer (pH=4.7) at 25 °C.
Upper: spectrophotometric at 630 nm. Lower: amperometric at −0.1 V (A) and −0.4 V (B). Concentration of $[Ru(Hedta)(H_2O)]\cdot 4H_2O$: -⊖-, 1.0 mol m^{-3}; -●-, 2.0 mol m^{-3}

(III)L to form a green mixed-valence dimeric species:

$$12\text{Ru(III)L} + ClO_3^- \longrightarrow 6\text{Ru(IV)-Ru(III)} + Cl^- + \cdots. \quad (1)$$

Here Ru(IV)–Ru(III) represents the green dimeric species; its chemical formula will be discussed later.

If the one-electron, Nernstian step A is the reduction of Ru(IV)–Ru(III), its immediate product should be an Ru(III)–Ru(III) dimer. But the fact that the half-wave potential of step B is the same as that of Ru(III)L indicates that the Ru(III)–Ru(III) dimer is unstable, so that it dissociates rapidly to give two Ru(III)L entities. In fact, a reversible reoxidation peak was observed on the cyclic voltammogram only at a high scan rate. The first-order rate constant of the dissociation reaction was about 1 s^{-1} at pH=4.7 at 25 °C; the details of the kinetics will be reported separately.

The Ru(III)L species thus produced would be reoxidized to Ru(IV)–Ru(III) in the presence of chlorate ions. However, this reaction is too slow to produce an appreciable polarographic catalytic current unless a large excess of chlorate ions is present. Controlled potential coulometry revealed that this reaction did occur. It also corroborated the above stoichiometry.

Coulometry. A green solution containing a known small excess of chlorate ions was electrolyzed with a mercury pool electrode at a potential of the first plateau (−0.1 V) and the polarograms were recorded intermittently by suspending the electrolysis and letting the solution stand for a while. The polarogram remained almost unchanged until a certain quantity of electricity, Q_1, was consumed. The magnitude of the diffusion current of step A, $I_{d,A}$, began to diminish in proportion to the advancement of elec-

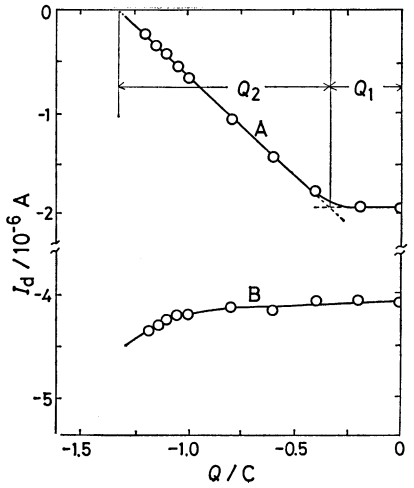

Fig. 3. Coulometric curves of 1.0 mol m^{-3} [Ru(Hedta)(H_2O)]·$4H_2O$+0.110 mol m^{-3} $NaClO_3$ in 0.2 mol dm^{-3} sodium acetate-acetic acid buffer at 25 °C. Reduction potential=−0.1 V. A, diffusion current at −0.1 V. B, diffusion current at −0.4 V. The current and quantity of electricity for reduction are considered to be negative.

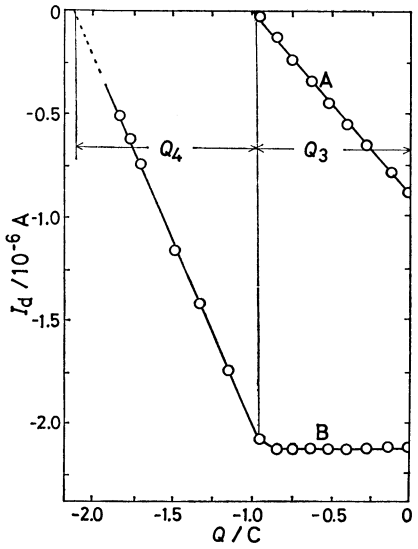

Fig. 4. Coulometric curves of 1.0 mol m^{-3} [Ru(Hedta)(H_2O)]·$4H_2O$+0.104 mol m^{-3} $NaClO_3$ in 0.2 mol dm^{-3} sodium acetate-acetic acid buffer at 25 °C. Reduction potential=−0.4 V. A, diffusion current at −0.1 V. B, diffusion current at −0.4 V. The current and quantity of electricity for reduction are considered to be negative.

trolysis, whereas the diffusion current of step B, $I_{d,B}$ (total step height less $I_{d,A}$), remained fairly constant (Fig. 3). Another quantity of electricity, Q_2, was consumed before the completion of the electrolysis; the polarogram and UV-visible spectrum of the solution were then the same as those of Ru(III)L. During the first stage of the electrolysis, Ru(III)L produced by the reduction of the mixed valence dimer was reoxidized by the chlorate ions, so that Q_1 was equal to the quantity of electricity that was required for the six-electron reduction of the excess chlorate ions. The roundness of $I_{d,A}$-Q curve reflects the slowness of the reoxidation process. When no more chlorate ions were present, the process was simply the reduction of the mixed-valence dimer, as was indicated by the fact that Q_2 was equal to the quantity of electricity corresponding to the one-electron reduction of half the amount of Ru(III)L originally contained in the solution.

The electrolysis at a potential of the second plateau (−0.4 V) showed that Ru(IV)–Ru(III) reacted with Ru(II)L. In this case, $|I_{d,A}|$ decreased linearly from the beginning until a quantity of electricity, Q_3, was consumed, when step A disappeared (Fig. 4). During this stage, $I_{d,B}$ remained constant and no oxidation step was observed. On further electrolysis, $|I_{d,B}|$ began to decrease and the oxidation step of Ru(II)L began to grow, both in proportion to the advancement of electrolysis. For the completion of the electrolysis another quantity of electricity, Q_4, was consumed. The quantity of electricity Q_3 was equal to that required for the six-electron reduction of all the chlorate ions added to the solution and Q_4 to that required for the one-electron reduction of Ru(III)L which was originally contained in the solution. At this potential the mixed-valence dimer undergoes a three-electron reduction to Ru(II)L, which reacts both with the excess chlorate ions and with the dimer to regenerate Ru(III)L during the first stage:

$$\text{Ru(IV)-Ru(III)} + 3e^- \longrightarrow 2\text{Ru(II)L}, \quad (2)$$

$$6\text{Ru(II)L} + ClO_3^- \longrightarrow 6\text{Ru(III)L} + Cl^-, \quad (3)$$

$$\text{Ru(II)L} + \text{Ru(IV)-Ru(III)} \longrightarrow 3\text{Ru(III)L}. \quad (4)$$

When no more Ru(IV)–Ru(III) and chlorate ions are present, the reduction is simply that of Ru(III)L to Ru(II)L (the second stage).

The coulometric data are summarized in Table 1; the last two columns are the results for the isolated dimer, which will be discussed later. These data reconfirm the above-mentioned stoichiometry of the reaction between Ru(III)L and ClO_3^-.

Characterization of the Green Complex. The isolated green complex is readily soluble in water. The titration curve of the solution with a standard sodium hydroxide solution showed a single pH jump corresponding to the dissociation of carboxylic protons; there was no second pH jump characteristic of the dissociation of the proton of aqua ligand, as observed in the case of Ru(III)L.[12] The amount of the dissociable protons was 1.0 mol per 1 mol of ruthenium. The solution of the complex was passed through a column of an H-form cation-exchange resin, and the eluate was titrated with a standard alkali solution. The results indicated that 1.5 mol of hydrogen ions per 1 mol of ruthenium was present in the eluate, *i.e.* the complex contained 0.5 mol of cations (sodium ions) per 1 mol of ruthenium. These results, together with those of the elemental analysis, are in fair agreement with the values calculated for Na[(Hedta)-RuORu(Hedta)]·$10H_2O$ (molar mass 999.7 g mol^{-1}).

Table 1. Controlled potential coulometry in 0.2 mol dm^{-3} acetate buffer

Sample	Ru(III)L+$NaClO_3$				Green complex	
(E *vs.* SCE)/V	−0.1		−0.4		−0.5	
	$-Q_1$/C	$-Q_2$/C	$-Q_3$/C	$-Q_4$/C	$-Q_3'$/C	$-Q_4'$/C
Obsd	0.33	1.00	0.94	1.15	0.95	1.91
Calcd	0.332[a]	1.02[b]	0.967[c]	1.35[d]	$Q_3'/Q_4'=0.497$	

a) $6F\{n(ClO_3^-)-n(\text{Ru(III)L})/12\}$. b) $Fn(\text{Ru(III)L})/2$. c) $6Fn(ClO_3^-)$. d) $Fn(\text{Ru(III)L})$. F is the Faraday constant and n(X) is the initial amount of substance X.

Table 2. UV-visible spectral data

Compound	λ_{max}/nm (ε/mol^{-1} m^2)			
[(Hedta)RuORu(Hedta)]$^-$ [a]			392 (1790)	630 (38)
[Ru(Hedta)(H_2O)][a]			280 (250)	
[(bpy)$_2$ClRuORuCl(bpy)$_2$]$^{3+}$ [b]	246 (4200)	300 (4600)	470 (1970)	
[(bpy)$_2$ClRuORuCl(bpy)$_2$]$^{2+}$ [b]	244 (6590)	289 (3900)	627 (1790)	
[Ru(bpy)$_2$Cl$_2$]$^+$ [c]	298 (2480)	310 (2240)	380 (565)	

a) In aqueous 0.2 mol dm^{-3} acetate buffer, pH=4.7. b) Ref. 1, in acetonitrile. c) J. N. Braddock and T. J. Meyer, *Inorg. Chem.*, **12**, 723 (1973).

Found: Ru, 20.24; C, 23.94; H, 3.87; N, 5.72; Na, 2.31; rest, 43.98%. Calcd for Ru, 20.22; C, 24.03; H, 4.64; N, 5.60; Na, 2.30; O, 43.21%. The above results show that the overall reaction between Ru(III)L and chlorate ion can be written as follows:

$$12[\text{Ru(edta)}(H_2O)]^- + ClO_3^- \longrightarrow 6[\text{(edta)RuORu(edta)}]^{3-} + Cl^- + 6H^+ + 9H_2O. \quad (5)$$

The IR spectrum (KBr disk) was almost the same as that of Ru(III)L. The absorption bands of coordinated carboxyl groups (1630 cm^{-1}) and of protonated carboxyl groups (1725 cm^{-1}) was observed. According to Hewkin and Griffith,[14] Wing and Callahan,[15] and Filippo *et al.*,[16] for a linear Ru–O–Ru species, a weak, infrared-active asymmetric stretching band should appear in the range of 800 cm^{-1}—900 cm^{-1} (for a non-linear Ru–O–Ru system, at a lower frequency). Attempts to identify this band failed because many small bands covered this region.

The UV-visible spectrum of the green complex was the same as that of the Ru(III)L–ClO_3^- reaction mixture and showed two absorption bands (Table 2). According to Meyer *et al.*[1] an intense, low energy band at about 650 nm is characteristic of the oxo-bridged Ru(III) dimers and this band is considerably blue-shifted for the one-electron oxidized species, *i.e.* the corresponding Ru(IV)–O–Ru(III) dimers.†††† It is most likely that the intense band at 392 nm indicates the presence of the Ru(IV)–O–Ru(III) system in the green complex.

The polarogram of the isolated green complex was the same as that presented in Fig. 1b, except that the height of the second step was a little larger than twice the first step height and varied from sample to sample. The isolated green complex is not very stable and decomposes in the presence of the air and/or light.

The coulometric curves of the reduction at −0.5 V were similar to those in Fig. 4. But in this case the quantity of electricity consumed during the first stage, Q'_3, should be equal to that required for the one-electron reduction of the dimer to Ru(III)L, since no excess chlorate ions were present and reaction(3) was not involved. The quantity of electricity consumed during the second stage, Q'_4, should be that required for the reduction of Ru(III)L to Ru(II)L. Consequently the ratio Q'_3/Q'_4 must be 1/2, as was the case (Table 1).

The molar mass calculated from the coulometric data was 996 g mol^{-1}, while that calculated from the pH titration data was 996.4 g mol^{-1}. These were in good agreement with the calculated value (999.7 g mol^{-1}) for the monosodium decahydrate. However, the thermogravimetric data and coulometric data on other samples, which are not cited in Table 1, indicated that the number of the waters of crystallization might be variable (probably from 8 to 10) according to the condition of crystallization and storage.

The green complex was paramagnetic, and the value of χV_m, corrected for diamagnetism, was 2.34×10^{-8} m^3 mol^{-1} at 23 °C. The magneton number, $\boldsymbol{m}/\underline{\boldsymbol{m}}_B$, was 2.10. This value will be compatible with the existence of one unpaired electron. Dunitz and Orgel[17] have reported that $[Cl_5RuORuCl_5]^{4-}$, a linearly oxo-bridged Ru(IV) dimer, was diamagnetic. In their extensive study of Ru(III)–O–Ru(III) systems Meyer *et al.*[1] explained the magnetic data in terms of the delocalization through the bridging oxide ion and pointed out that the relative stability of [(bpy)$_2$ClRuORuCl(bpy)$_2$]$^{3+}$ is reasonable because the electron lost comes from a π^* level. In the present case too, the observed magneton number can be attributed to the presence of one unpaired electron in the lowest π^* MO delocalized over both ruthenium centers.

Ezerskaya and Solovykin[3,4] reported that a dimer was formed by the oxidation of K[RuCl(Hedta)] with hydrogen peroxide or oxygen. The spectral and polarographic data[4] suggest that their complex was the

†††† "Ru(IV)–O–Ru(III)" is only a formal representaion; the two ruthenium centers are equivalent.[1]

same as or very similar to the present green complex. These authors described the compound as a μ-oxo and μ-peroxo double bridged dimer. But their arguments do not seem to be very convincing. Although no direct evidence is available for the oxo single bridge in the present case, μ-peroxo structure is less plausible than μ-oxo structure in explaining the stoichiometry, electrochemical behavior, and the results of pH titration.

Yoshino *et al.*[5] reported a green substance obtained by oxidizing Ru(III)L either anodically at a platinum electrode, chemically with several oxidizing agents, or photochemically in the presence of oxygen. The substance was later characterized by Uehiro[6] to be the acid form of the present complex: H[(Hedta)RuORu-(Hedta)]·6.5H_2O. His spectral and magnetic data are essentially the same as ours.

Oxidation of Ru(III)L at a Platinum Electrode and with Hydrogen Peroxide. The cyclic voltammogram of Ru(III)L in the acetate buffer with a platinum wire electrode over a range of −0.4 V to +0.5 V showed coupled oxidation and reduction peaks corresponding to Ru(III)L+e^-=Ru(II)L. When the anodic sweep was extended, a shoulder rose on the anodic current at +0.7 V and a new reduction peak at +0.25 V appeared; this reduction peak was attributable to the reduction of the Ru(IV)–O–Ru(III) dimer, since the same peak was observed on the cyclic voltammogram of the green solution prepared by the oxidation of Ru(III)L with chlorate ions. These results confirm the observation of Yoshino *et al.* that the green dimer could be obtained by anodic oxidation of Ru(III)L with platinum electrode. The reduction potential of the dimer at platinum electrode was much more positive than the half-wave potential of the polarographic step A, probably owing to faster decomposition of the Ru(III)–Ru(III) dimer on the platinum surface than on mercury.

The oxidation of Ru(III)L with hydrogen peroxide was reexamined. The UV-visible spectrum and the polarogram of the oxidized solution was the same as those of the solution obtained by the oxidation with chlorate ions. The stoichiometry, however, was complicated. If hydrogen peroxide acted as a two-electron oxidizing agent, $n(H_2O_2)/n(\mathrm{Ru(III)L})$ should be 0.25, whereas the experimental ratio determined from the end-points of the amperometric and spectrophotometric titrations was 0.3. Very likely, partial decomposition of hydrogen peroxide took place owing to the catalytic action of the dimer.[3] No further study was made on this reaction.

Preliminary Study on the Kinetics of the Oxidation of Ru(III)L with Chlorate Ions. The kinetics was examined by measuring the increase of the absorbance at 630 nm and by measuring the growth of the polarographic diffusion current of step A in a weakly acid solution.

If the rate of increase of the concentration of the dimer is proportional to the concentrations of both Ru(III)L and chlorate ions, *i.e.*,

$$dx/dt = k(a-2x)(b-x/6),$$

then

$$[6/(12b-a)] \ln [a(b-x/6)/b(a-2x)] = kt, \quad (6)$$

where x is the concentration of the dimer at time t, and a and b are the initial concentrations of Ru(III)L and chlorate ions, respectively. The value of x was determined either spectrophotometrically or polarographically. In both cases, the experimental plots of the left-hand side of Eq. 6 against time were quite linear up to about 80% of the completion of the reaction. The values of k thus obtained were fairly constant. The average value of the second-order rate constant was 5.3_2 mol^{-1} dm^3 s^{-1} at 25 °C in 0.2 mol dm^{-3} acetate buffer of pH 4.7.

It is rather surprising that this complicated reaction followed a simple second-order rate equation. Uehiro[6] in his study of the oxidation of Ru(III)L with $[Mn(edta)(H_2O)]^-$ observed that the rate equation was compatible with a mechanism that involved the dimerization of Ru(III)L followed by the electron transfer. Since the range of the initial concentration of Ru(III)L was quite limited (1 to 2 mol m^{-3}) in the present study, the above result is not conclusive.

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