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Oxygen Evolution by Means of Water Oxidation Catalyzed by Mononuclear Ruthenium-Ammine Complexes

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Water oxidation was achieved catalytically by the use of mononuclear ruthenium-ammine complexes and using Ce(IV) as an oxidant. Cyclic voltammetric studies of the mononuclear ruthenium-ammine complexes $[Ru(NH_3)_5Cl]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{3+}$, have been carried out using Basal Plane Pyrolytic Graphite (BPG) coated with poly(*p*-styrenesulfonate), Nafion, or Kaolin clay. The electrochemical properties of these ruthenium-ammine complexes show that they can be used as two-electron oxidants for water oxidation. It has also been found that these complexes oxidize water to evolve oxygen in the presence of excess Ce(IV) under homogeneous as well as heterogeneous conditions. The oxygen evolution by means of water oxidation was confirmed by using the $H_2{}^{18}O$ isotope in the reaction medium. The water oxidation process was found to be dependent on the ionic strength of the medium. Higher acidic conditions gave higher O_2 yields. Heterogeneous catalysis with the Ru complex adsorbed in Kaolin clay was as effective as the homogeneous one. The water oxidation reaction catalyzed by ruthenium-ammine complexes was also discussed.

The oxidation of water to molecular oxygen is of great importance as a means of converting light energy into chemical energy, because, among the possible methods of solar energy storage, its conversion into the energy of chemical fuels seems to be one of the most promising.[1,2] In order to realize such light-to-chemical energy conversion systems, the use of water as an electron donor, i.e., water oxidation, is a crucial point, as in the photosynthesis in nature. Oxygen evolution is significantly more difficult to accomplish than hydrogen evolution because four electrons must be transferred in the reaction (Eq. 1):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

The photogeneration of oxygen from water is an essential part of green-plant photosynthesis, where the oxygen evolves as a result of water photooxidation in the active center of the photosystem II, with the participation of Mn ions.[3] However, the mechanism of Mn catalytic action is still unclear. The difficulty of creating such models lies in the need to couple the four-electron oxidation of water (Eq. 1) with the one-electron chemistry of the photoredox process.[4] Several types of oxygen evolving catalysts have been identified,[5] but these catalysts are far from ideal, and there are many problems associated with their use in model photochemical systems.[4–8] In recent reports,[9–13] it has been shown that the soluble polynuclear metal complexes work as homogeneous[9–11] as well as heterogeneous catalysts[12–14a] to oxidize water to oxygen.

Recently, Collin and Sauvage[15] have prepared several complexes of ruthenium(II) which contain two molecules of sterically hindering diimine as ligands; they have studied the catalytic activity of the complexes toward water oxidation. None of these complexes display catalytic activity for oxygen formation from water in the presence of excess cerium(IV). Based on their observations, they concluded that a multimetallic system is required to achieve water oxidation to oxygen. Until now it has seemed quite rational to think that only the polynuclear complexes are candidates for the water oxidation because the reaction is a four-electron process. However, the present authors have found, for the first time, that mononuclear ruthenium-ammine complexes catalyze oxygen evolution by means of water oxidation in the homogeneous[14b] as well as in the heterogeneous state; they wish to report their findings in this paper.

Experimental

$[Ru(NH_3)_5Cl]^{2+}$ (Aldrich Chemicals) was used as received, while $[Ru(NH_3)_5(H_2O)]^{3+}$ was prepared by modifying the reported procedure.[16] A hot solution of silver trifluoroacetate, prepared by dissolving 0.079 g of Ag_2O in a 4 ml aqueous solution of 2 M trifluoroacetic acid (1 M=1 mol dm^{-3}), was added to 0.1 g of $[Ru(NH_3)_5Cl]^{2+}$. The AgCl precipitate was digested by heating and stirring for several minutes. The AgCl precipitate was then removed by filtration, and the solution was cooled to room temperature. The pH of the solution was adjusted to about pH 3 by the drop-by-drop addition of 3 M NaOH. The solid $[Ru(NH_3)_5(H_2O)]^{3+}$ complex was isolated by adding solid NH_4PF_6 (about 0.5 g) to the solution, which was then filtered and washed with ethanol and finally with ether. The Kaolin clay (Nakarai Chemicals) was used in this investigation without further treatment. Kaolin clay with the $[Ru(NH_3)_5(H_2O)]^{3+}$ catalyst adsorbed was prepared by mixing the known amounts of the clay and the catalyst in deionized water. The mixture was stirred until complete adsorption was noticed. The clay was filtered after adsorption, washed with deionized water, and dried in air. The adsorbed complex was not desorbed upon dipping into fresh water.

Cyclic voltammograms were run using a Function Generator HB-104 model and a Potentiostat/Galvanostat HA-301 model of Hokuto Denko, Ltd. A basal plane pyrolytic graphite (BPG) electrode coated with poly(*p*-styrenesulfonate), Nafion, or Kaolin clay was used as the working electrode; platinum wire, as the counter electrode, and a Saturated Calomel Electrode (SCE), as the reference electrode. The supporting electrolyte was 0.5 M H_2SO_4.

A water oxidation experiment was carried out under an argon atmosphere by mixing the mononuclear ruthenium-ammine complex and excess ammonium cerium(IV) nitrate.[10,13] The gas evolved by the reaction was analyzed by the use of the Gas Chromatogram (Shimadzu GC 4C, 1.5-m column of Molecular Sieve 5A and an argon carrier). The amount of O_2 evolved was corrected by subtracting the amount of O_2 coming from the dissolved air. The water oxidation was confirmed by using $H_2{}^{18}O$ in the reaction medium, and a Quadrupole Mass Spectrometer from the Ulvac Corporation (MSQ-150A) was used to analyze the gas evolved.

Results and Discussion

The solution chemistry of ruthenium ammine complexes has been studied extensively.[17] These complexes are widely used as quenchers[18] for the excited state of $[Ru(bpy)_3]^{2+}$. The electrochemical behavior of the ruthenium-ammine complexes has also been investigated;[19] however, attention has not been focused on the redox chemistry involving the higher oxidation states, e.g., Ru(IV) and Ru(V).

Cyclic voltammograms obtained for $[Ru(NH_3)_5Cl]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{3+}$ are given in Fig. 1. When the uncoated BPG was used to record the cyclic voltammograms in the potential region from 0.5 to 1.5 V vs. SCE, a large catalytic current attributable to the electrochemical water oxidation was observed. However, a better cyclic voltammogram was obtained when the BPG was modified with poly(*p*-styrenesulfonate), Nafion, or Kaolin clay.

For both the ruthenium-ammine complexes, the $[Ru(NH_3)_5Cl]^{2+/+}$ and $[Ru(NH_3)_5(H_2O)]^{3+/2+}$ couples were observed in the potential region from −0.5 to 0.3 V vs. SCE (Fig. 1). Figure 1 shows that there are two oxidative peaks in the potential region from 0.5 to 1.5 V vs. SCE, peaks which are reversible in the reductive scan for the $[Ru(NH_3)_5Cl]^{2+}$ and $[Ru(NH_3)_5(H_2O)]^{3+}$ complexes. However, the reductive waves were not clear because of the larger catalytic current caused by water oxidation.

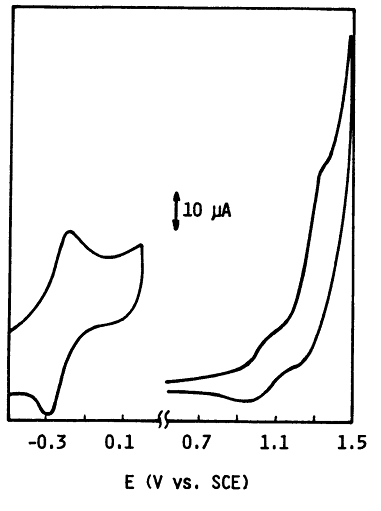


Fig. 1. Cyclic voltammogram of $[Ru(NH_3)_5Cl]^{2+}$ in 0.1 M H_2SO_4 at Nafion coated BPG at a scan rate of 50 mV s^{-1}.

The $[Ru(NH_3)_5Cl]^{2+/+}$ couple appears at −0.25 V vs. SCE. The other two peaks in the potential region from 0.5 to 1.5 V vs. SCE indicate the formation of $[Ru^{V}(NH_3)_5Cl]^{4+}$ by a series of one-electron oxidation of $[Ru^{III}(NH_3)_5Cl]^{2+}$ (Eq. 2). Similar results were observed for the $[Ru(NH_3)_5(H_2O)]^{3+}$ complex. However, the peak potentials are slightly shifted to less positive values than those for the $[Ru(NH_3)_5Cl]^{2+}$ complex. It has already been reported[19] that the formal potentials of the $[Ru(NH_3)_5Cl]^{2+/+}$ and $[Ru(NH_3)_5(H_2O)]^{3+/2+}$ couples are almost the same. Based on the present results, the various redox processes occurring in the chloropentammine ruthenium complex may be said to be as given in Eq. 2:

$$\underset{-0.25\text{ V}}{[Ru^{II}(NH_3)_5Cl]^{+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}} [Ru^{III}(NH_3)_5Cl]^{2+} \underset{1.06\text{ V}}{\underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}}$$

$$[Ru^{IV}(NH_3)_5Cl]^{3+} \underset{1.28\text{ V}}{\underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}} [Ru^{V}(NH_3)_5Cl]^{4+} \qquad (2)$$

For both the complexes, fairly large peak separations (100 mV) were observed. They may be caused by the rapid reduction of the higher-oxidation-state ruthenium by water or by the polymer coating rather than by electrochemical reduction. Such processes have already been observed in our own earlier works[10,11] with dinuclear ruthenium complexes. It has also been reported that the $[Ru(NH_3)_5Cl]^{+}$ complex undergoes rapid aquation with a rate constant of 4.7 s^{-1} (Eq. 3), which corresponds to a half-life of 0.15 s:[20]

$$[Ru(NH_3)_5Cl]^{+} + H_2O \rightarrow [Ru(NH_3)_5(H_2O)]^{2+} + Cl^{-} \qquad (3)$$

The monomeric ruthenium complexes easily form higher-oxidation-state Ru(V) complexes upon chemical oxidation, and the redox potentials of the ruthenium complexes show that they can be used as oxidants for water oxidation. These monomeric ruthenium complexes can act as two-electron oxidants and, therefore, might be able to bring about the four-electron oxidation of water to oxygen only on the surface of a suitable catalyst. However, oxygen evolution was observed visibly in a homogeneous solution upon the addition of excess Ce(IV) to the monomeric ruthenium complexes, without the addition of any external oxygen evolution catalyst. Gas bubbles were observed in solution soon after the addition of excess Ce(IV), and the chromatographic results (Fig. 2) show that the gas evolved is oxygen. Water oxidation was confirmed by mass spectrometry using water containing $H_2{}^{18}O$ isotopes. Oxygen was confirmed by the peaks at m/z=32, 34, and 36, which correspond to $^{16}O_2$, $^{18}O^{16}O$, and $^{18}O_2$ respectively. Both the gas-chromatograph and mass-spectral data clearly showed that oxygen is

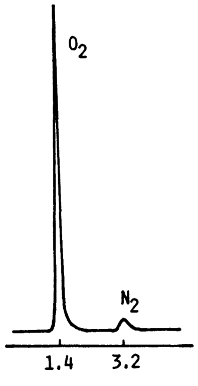


Fig. 2. Gas chromatogram of the gas evolved by reaction of $[Ru(NH_3)_5Cl]^{2+}$ in water in the presence of Ce(IV). Carrier gas, argon; column, Molecular Sieve 5 A; 200 µl of the evolved gas was injected for the measurement.

Table 1. Oxygen Evolution by Water Oxidation under Homogeneous Conditions Using $[Ru(NH_3)_5Cl]^{2+}$ at 25 °C

Ru : Ce(IV) (molar ratio)	O_2 evolved	
	(µl)	Turnover number
1 : 50	26	1.04
1 : 100	56	2.29
1 : 200	166	6.86
1 : 300	203	8.36

$[Ru(NH_3)_5Cl]^{2+}$, 2 µmol. Solution volume, 10 ml; reaction time, 90 min.

Table 2. Oxygen Evolution by Water Oxidation under Homogeneous Conditions Using $[Ru(NH_3)_5Cl]^{2+}$ at 25 °C: Concentration Variation of the Catalyst

Ru complex (10^{-4} M)	O_2 evolved	
	(µl)	Turnover number
6.70	64	2.63
3.35	131	5.41
2.01	166	6.86

Ru: Ce(IV)=1 : 200 (molar ratio). $[Ru(NH_3)_5Cl]^{2+}$, 2 µmol; reaction time, 90 min.

evolved by the water oxidation. The experimental results of the homogeneous catalysis of water oxidation by monomeric ruthenium complexes were treated with great caution because the decomposition product of the compounds is often ruthenium oxide, which is catalytically active for water oxidation.[21,22] The Ru complex was stable in water, even in the presence of excess Ce(IV), as was confirmed by visible spectroscopy. Gas bubbles were observed immediately after Ce(IV) had been added to the complex solution. These results indicate that the Ru complex itself is active in the catalysis.

The amount of oxygen evolved in 90 minutes with different Ru : Ce(IV) ratios (molar ratio) under homogeneous conditions are given in Table 1. When the Ru: Ce(IV) (molar ratio) was changed from 1 : 50 to 1 : 300, the oxygen evolution increased with the increase in the Ce(IV) concentration. The results shown in Table 1 indicate that the monomeric ruthenium complex works as a catalyst in the water oxidation process. Table 2 shows that when the ruthenium complex concentration is decreased from 6.7×10^{-4} to 2.01×10^{-4} M the oxygen evolution is increased 2.6 times. However, Table 3 shows that the increase in the ionic strength leads to the decrease in the oxygen evolution. The four-electron oxidation of water must be realized through the interaction of two intermediate mononuclear ruthenium complexes. Such interaction would be hindered by increasing the ionic strength. It is clear that the effect of the concentration change on

Table 3. OxygenEvolution by Water Oxidation Using $[Ru(NH_3)_5Cl]^{2+}$ under Homogeneous Conditions at 25 °C: Ionic Strength Variation

Ionic strength[a)]	O_2 evolved	
	(µl)	Turnover number
0.48	166	6.86
0.58	135	5.56
0.98	84	3.47
1.48	70	2.89
2.48	50	2.04

a) Adjusted with KNO_3. Ru : Ce(IV)=1 : 200 (molar ratio). $[Ru(NH_3)_5Cl]^{2+}$, 2 µmol; solution volume, 10 ml; reaction time, 90 min.

Table 4. Oxygen Evolution by Water Oxidation Using $[Ru(NH_3)_5Cl]^{2+}$ under Homogeneous Conditions at 25 °C

Ionic strength[a)] : 2.11			Ionic strength[a)] : 3.11		
Ru complex (10^{-4} M)	O_2 evolved		Ru complex (10^{-4} M)	O_2 evolved	
	(µl)	Turnover number		(µl)	Turnover number
6.67	64	2.64	6.67	40	1.66
3.33	56	2.31	3.33	45	1.84
2.0	67	2.76	2.0	45	1.84

a) Adjusted with KNO_3. $[Ru(NH_3)_5Cl]^{2+}$, 2 µmol; Ru: Ce(IV)=1 : 200 (molar ratio); reaction time, 90 min.

water oxidation shown in Table 2 is attributable to the ionic strength effect. The change in the concentration of the ruthenium complex did not have any important effect on the water oxidation process under a constant ionic strength (Table 4).

The effect of acid on the water-oxidation process was also studied; the data are given in Table 5. When the HNO_3 concentration was increased to 0.2 M, an increase in the oxygen evolution with the HNO_3 concentration was observed. In an acidic solution, $[Ru(NH_3)_5Cl]^{2+}$ readily undergoes aquation accompanied by the formation of the water-substituted pentammine ruthenium complex; the higher rate of oxygen evolution can be explained on the basis that the water molecule in the coordination sphere is involved in the water oxidation process. When $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$ was used as the catalyst for water oxidation,[9,23)] it was explained that the water ligands in the dinuclear ruthenium complex take part in the water oxidation reaction.

As catalysts for water oxidation, the $[Ru(NH_3)_5(H_2O)]^{3+}$ complex was used in a homogeneous state, and the Kaolin clay-adsorbed complex, in a heterogeneous state. The amount of oxygen evolved in 90 minutes with different concentration of Ce(IV), using the homogeneous as well as the heterogeneous state $[Ru(NH_3)_5(H_2O)]^{3+}$ in water oxidation, are given in Table 6. The effect of the concentration of the complex adsorbed in the clay in the heterogeneous catalysis was also studied; the results are given in Table 7. A comparison of the results of Table 6 (homogeneous system) and Table 2 will show that the $[Ru(NH_3)(H_2O)]^{3+}$ is a better catalyst than the chloropentammineruthenium complex. One reason for the better catalytic activity of the aquapentammine complex can be the fact that the water molecules in the coordination sphere are involved in the water oxidation process, as has been explained before. It should also be noted that the $[Ru(NH_3)_5(H_2O)]^{4+/5+}$ couple is less positive than the chloropentammine complex and that the Ce(IV) will more readily oxidize the water complex than the chloro complex, thus producing the higher-oxidation-state ruthenium complex. From the electrochemical data, it is clear that the ruthenium-ammine complexes can act as a two-electron oxidants for water oxidation. In order to evolve one molecule of oxygen by water oxidation, two molecules of a ruthenium complex are needed. The addition of excess Ce(IV) to a solution of a mononuclear ruthenium-ammine complex should lead to the oxidation of the complex to give Ru(V) complex; then, the two molecules of the Ru(V) complex will oxidize water to oxygen.

When $[Ru(NH_3)_5Cl]^{2+}$ is used as a catalyst for water oxidation, the water will coordinate at first to the $[Ru^{V}(NH_3)_5Cl]^{4+}$ higher-oxidation-state complex, and then the two molecules of the water-coordinated intermediate should lead to oxygen evolution. Such a seven coordination in the intermediate step has been suggested for the Ru(IV) and Ru(III) complexes (d^4 and d^5 ions) in the oxidation-reduction reactions of monomeric ruthenium-ammine complexes.[24,25)] It is probable that the Cl^- ligand will be oxidized by the Ru(V) metal center or by the Ce(IV), which will lead to the formation of the water substituted ruthenium complex. Considering that the coordinated water molecule is involved in the water-oxidation reaction, as has been reported for the dinuclear ruthenium complex,[7,19)] the following reaction scheme is proposed to explain the oxygen evolution by the monomeric ruthenium-ammine complex. Two molecules of the water coordinated monomeric Ru(V) complex would lead to the formation of a peroxo-bridged dinuclear ruthenium complex, Ru-O-O-Ru, and then the intermediate would release one molecule of oxygen. Such a peroxo-bridged ruthenium intermediate complex is not known; however, the oxo-bridged dinuclear

Table 5. Oxygen Evolution by Water Oxidation under Homogeneous Conditions Using $[Ru(NH_3)_5Cl]^{2+}$ at 25 °C

HNO_3 (M)	O_2 evolved	
	(μl)	Turnover number
0.0	166	6.86
0.01	189	7.79
0.05	238	9.80
0.1	252	10.41
0.2	286	11.82

$[Ru(NH_3)_5Cl]^{2+}$, 2 μmol. Ru:Ce(IV)=1:200 (molar ratio); solution volume, 10 ml; reaction time, 90 min.

Table 6. Oxygen Evolution by Water Oxidation under Homogeneous and Heterogeneous Conditions at 25 °C with $[Ru(NH_3)_5(H_2O)]^{3+}$

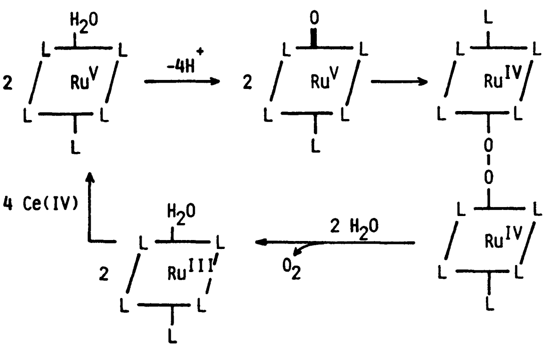
$[Ru(NH_3)_5(H_2O)]^{3+}$ in water (homogeneous)			$[Ru(NH_3)_5(H_2O)]^{3+}$ in Kaolin clay (heterogeneous)		
Ru: Ce(IV) (molar ratio)	O_2 evolved		Ru: Ce(IV) (molar ratio)	O_2 evolved	
	(μl)	Turnover number		(μl)	Turnover number
1:100	243	10.04	1:200	362	14.96
1:200	287	11.87	1:400	378	15.58
1:300	308	12.73	1:500	436	18.01
1:400	358	14.77			

$[Ru(NH_3)_5(H_2O)]^{3+}$, 2 μmol; Kaolin clay, 100 mg; solution volume, 5 ml; reaction time, 90 min.

Table 7. Oxygen Evolution by Water Oxidation under Heterogeneous Conditions Using $[Ru(NH_3)_5(H_2O)]^{3+}$ Adsorbed on Kaolin Clay

Kaolin clay	O_2 evolved	
mg	(μl)	Turnover number
100	378	15.58
300	389	16.05
500	453	18.63

Ru : Ce(IV)=1 : 400 (molar ratio). $[Ru(NH_3)_5(H_2O)]^{3+}$, 2 μmol; solution volume, 5 ml; reaction time, 90 min.



ruthenium complex, $[(NH_3)_5RuORu(NH_3)_5]^{4+}$, is known.[26]

Porter[27] suggested that manganese(IV) complexes of porphyrin might oxidize water and that this water-oxidation reaction might be expected to occur via an intermediate oxygen bridged dinuclear complex. So far, the generation of oxygen with such systems has remained ambiguous, and there are no substantiated reports in which a metalloporphyrin has been used to oxidize water to oxygen. The oxygen evolution in the photosystem II is expected to occur via oxygen-bridged dinuclear species.[3,28] Recently, the formation of an O-O bond as an intermediate has been proposed to explain the oxygen evolution by water oxidation using multimetal complex systems,[9,10,13,23] which would support the above mentioned intermediate formation.

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