

## Heterogenous Water Oxidation by an Amide-bridged Dinuclear Ruthenium Complex adsorbed on Ion-exchange Resins

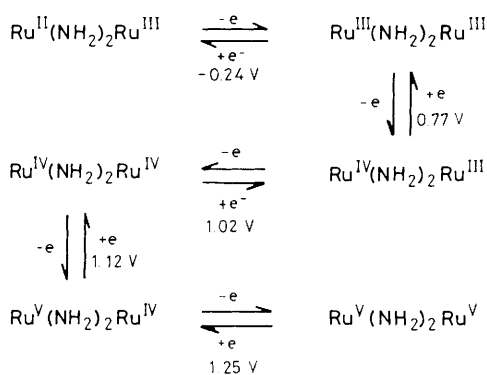
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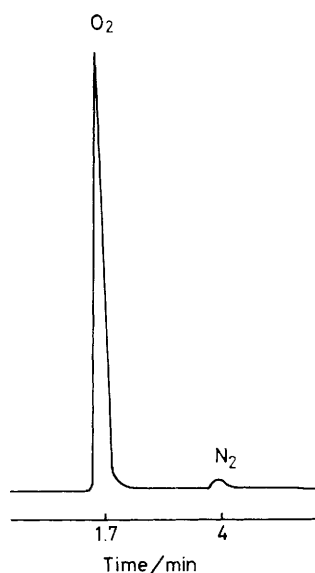
An amide-bridged dinuclear ruthenium complex adsorbed on ion-exchange resins has been prepared and used as a solid phase catalyst in water oxidation to evolve oxygen.

Oxygen evolution by water oxidation has been a difficult process to study. According to our present knowledge, oxygen evolves during photosynthesis in the heterogeneous phase of a Mn protein of photosystem II as a result of water oxidation,<sup>1</sup> and many model systems aimed at storing solar energy have tried to mimic this natural process.<sup>2</sup> Recent reports have

shown<sup>3</sup> that metal oxides (*e.g.* PtO<sub>2</sub> and RuO<sub>2</sub>) are able to catalyse the oxidation of water using a strong one-electron oxidant such as Ru(bpy)<sub>3</sub><sup>3+</sup> (bpy = bipyridine). However, the main difficulty in achieving water oxidation lies in coupling one-electron redox chemistry with four-electron redox chemistry, which is necessary for the formation of oxygen from



Scheme 1



**Figure 1.** Gas chromatogram of the gas evolved by the Amberlite, IR-120B resin-adsorbed amide-bridged dinuclear ruthenium complex in water in the presence of  $\text{Ce}^{\text{IV}}$ . Carrier gas: argon; column: 5 Å molecular sieves; 200  $\mu\text{l}$  gas injected for test; Ru–Ru:  $\text{Ce}^{\text{IV}}$  = 1:400 (molar ratio).

water. Recent reports have shown<sup>4,5</sup> that soluble oxo-bridged dinuclear ruthenium complexes are capable of acting as four-electron catalysts for the oxidation of water to give oxygen without the addition of external catalyst. However, the catalyst turnover number is not high and the total yield of oxygen obtainable from such systems remains low.<sup>5</sup> It has also been found<sup>5</sup> that oxo-bridged dinuclear ruthenium complexes adsorbed on ion-exchange resin (Amberlite, IR-120B), in the heterogeneous phase, were not effective catalysts for water oxidation. We have shown, however, that an amide-bridged dinuclear ruthenium complex is capable of oxidizing water more efficiently than the previously reported catalysts.<sup>5</sup> In order to construct a biomimetic water oxidation system, we used a different approach utilizing the heterogeneous phase of polymer systems to realise the four-electron water oxidation process. When the amide-bridged dinuclear ruthenium complex was adsorbed into ion-exchange resins, it acted as a solid phase catalyst for water oxidation. Such a solid catalyst system would be valuable for separating oxidation and reduction sites in a solar energy conversion system. We now report the preparation of this ion-exchange resin-adsorbed dinuclear

**Table 1.** Water oxidation by amide-bridged dinuclear ruthenium complex adsorbed on Amberlite, IR-120B resin (Ru–Ru) under argon at room temperature (20°C).

Molar ratio Ru–Ru <sup>a</sup> : $\text{Ce}^{\text{IV}}$	Total amount of oxygen evolved/ $\mu\text{l}$	Turnover number of ruthenium complex
1:100	135	1.6
1:250	631	7.7
1:400	947	11.5
1:400	1412	11.4 <sup>b</sup>

<sup>a</sup> The amount of Ru–Ru adsorbed into the Amberlite, IR-120B resin (500 mg) in the experiment is  $3.4 \times 10^{-6}$  mol. <sup>b</sup> Homogeneous water oxidation using amide-bridged dinuclear ruthenium complex. The amount of Ru–Ru in homogeneous solution is  $5.1 \times 10^{-6}$  mol.

ruthenium complex and its catalytic activity towards oxidation.

The ion-exchange resins, Amberlite, IR-120B and Diaion, CR-10 containing  $-\text{SO}_3^-\text{Na}^+$  and  $-\text{N}(\text{CH}_2\text{CO}_2\text{Na})_2$ , respectively, were used to adsorb the dinuclear ruthenium complex  $[(\text{NH}_3)_4\text{Ru}(\text{NH}_2)_2\text{Ru}(\text{NH}_3)_4]\text{Cl}_4$ , which was prepared according to the reported procedure.<sup>6</sup> The ion-exchange resin and the dinuclear complex were added to deionized water and the mixture was stirred for 2–3 hours until complete adsorption of the complex into the resin was observed. The resins containing the adsorbed complex were then filtered and washed with deionized water and dried in air, and adsorption of the complex was confirmed by the reflectance spectra of the resins. The dinuclear complex adsorbed into the resins is stable on standing in air for several months and is not desorbed from the resin beads even in acidic and basic aqueous solutions, or in the presence of salts like KCl, NaCl, and  $\text{Ce}^{\text{IV}}$ .

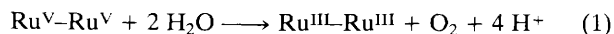
The cyclic voltammograms were recorded using basal plane pyrolytic graphite (BPG) in the potential region from  $-0.5$  V to  $1.4$  V vs. standard calomel electrode (s.c.e.) in aqueous  $0.1$  M  $\text{H}_2\text{SO}_4$ . The oxidation of solvent occurs in a higher potential region. However, the chemically modified BPG coating poly(styrene sulphonate), gave a well defined cyclic voltammogram in water in the same potential region. The cyclic voltammogram in water shows five oxidation peaks which are reversible in the reductive scan with a peak separation of 60–80 mV. The  $\text{Ru}^{\text{III}}(\text{NH}_2)_2\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}(\text{NH}_2)_2\text{Ru}^{\text{III}}$  couple appears at  $-0.24$  V vs. s.c.e., and the further four peaks in the positive region clearly explain the formation of  $\text{Ru}^{\text{V}}(\text{NH}_2)_2\text{Ru}^{\text{V}}$  by a series of one-electron oxidations of the  $\text{Ru}^{\text{III}}(\text{NH}_2)_2\text{Ru}^{\text{III}}$  complex (Scheme 1). The observed redox properties of the amide-bridged ruthenium dinuclear complex show a close resemblance with the redox properties of monomeric ruthenium complexes<sup>7</sup> and oxo-bridged dinuclear ruthenium complexes.<sup>5</sup>

The aqueous solution containing a known amount of amide-bridged dinuclear ruthenium complex adsorbed into the resin beads was deaerated by bubbling through argon gas for two hours. An excess of ammonium ceric nitrate was added to the mixture after deaeration, and the mixture was stirred at room temperature (20°C). The gas evolved by the water oxidation reaction was analysed by g.c. using a 1.5 m column of 5 Å molecular sieves and argon carrier. The amount of oxygen evolved was calculated by subtracting the oxygen content due to the residual air that was contained in the reaction vessel from the total oxygen observed. The gas chromatogram obtained for the amide-bridged dinuclear ruthenium complex adsorbed on Amberlite, IR-120B, Figure 1, shows that the gas evolved is oxygen. The water oxidation process has been confirmed by the peaks at  $m/z$  32 and 34

which correspond to  $^{16}\text{O}_2^+$  and  $^{18}\text{O}^{16}\text{O}^+$  respectively, in the reaction carried out in the presence of  $\text{H}_2^{18}\text{O}$ .

The dinuclear ruthenium complex adsorbed on Amberlite, IR-120B resin gave oxygen in water upon the addition of  $\text{Ce}^{\text{IV}}$  and a maximum turnover number of 11.5 (947  $\mu\text{l}$  oxygen) was observed using a 1:400 molar ratio of the resin-adsorbed complex and  $\text{Ce}^{\text{IV}}$  (Table 1). When the Diaion, CR-10 resin was used, no oxygen was evolved. This may be due to the effective reduction of the  $\text{Ru}^{\text{V}}\text{-Ru}^{\text{V}}$  species by the imino-diacetate binding site in the Diaion, CR-10 resin. It has been found that the amide-bridged dinuclear ruthenium catalyst underwent decomposition in the homogeneous as well as in the heterogeneous state during the water oxidation process with a maximum turnover number of 11.5. A blank experiment was carried out with the ion-exchange resin and  $\text{Ce}^{\text{IV}}$ , and no oxygen was observed in this system.

The higher oxidation state dinuclear ruthenium complex in the ion-exchange resin,  $\text{Ru}^{\text{V}}\text{-Ru}^{\text{V}}$ , produced upon addition of an excess of  $\text{Ce}^{\text{IV}}$  to the solution phase, oxidizes water to evolve oxygen, equation (1). Thus the heterogeneous catalytic water oxidation by the resin-adsorbed dinuclear ruthenium



complex not only mimics photosynthetic oxygen evolution, but may also lead to interesting applications in the construction of photoenergy conversion systems by coupling with photochemical reactions.

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