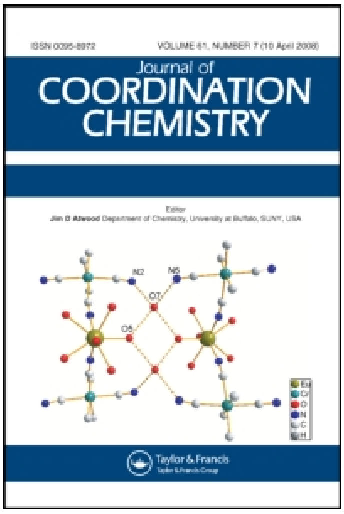

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Photochemical Reduction of Water to Hydrogen Catalyzed by Mixed-Valent Tetranuclear Platinum Complex

Ken Sakai[a]; Kazuko Matsumoto[a]
[a] Department of Chemistry, School of Science and Engineering, Waseda University, Tokyo, Japan

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PHOTOCHEMICAL REDUCTION OF WATER TO HYDROGEN CATALYZED BY MIXED-VALENT TETRANUCLEAR PLATINUM COMPLEX

KEN SAKAI and KAZUKO MATSUMOTO
Department of Chemistry, School of Science and Engineering, Waseda University, Tokyo 160, Japan

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Abstract Mixed-valent tetranuclear platinum complex, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$ (n = 4, 5, 6, 8 ; C_4H_6NO = deprotonated α-pyrrolidone), is used as a homogeneous hydrogen-producing catalyst in a photochemical model system containing EDTA as an electron donor, $Ru(bpy)_3^{2+}$ as a sensitizer and methylviologen (MV^{2+}) as an electron relay.

Keywords: Mixed-valent, tetranuclear, EDTA

INTRODUCTION

The Pt in the complex, $[Pt_4(NH_3)_8(C_4H_6NO)_4]^{n+}$, takes four oxidation states, $Pt(III)_4$, $Pt(II)_2Pt(III)_2$, $Pt(II)_3Pt(III)$ and $Pt(II)_2$ (in this lowest oxidation state, the Pt complex exists as a dimer in aqueous solution). The complexes in the higher oxidation states have been reported to generate molecular oxygen from water, while the complexes in the lower oxidation states are easily oxidized by molecular oxygen, Eqs. (1) and (2).[1,2]

$$2[Pt(III)_4(NH_3)_8(C_4H_6NO)_4]^{8+} + 2OH^- \rightleftharpoons 2[Pt(II)_2Pt(III)_2(NH_3)_8(C_4H_6NO)_4]^{6+} + 2H^+ + O_2 \quad (1)$$

$$2[Pt(II)_2Pt(III)_2(NH_3)_8(C_4H_6NO)_4]^{6+} + 2OH^- \rightleftharpoons 4[Pt(II)_2(NH_3)_4(C_4H_6NO)_2]^{2+} + 2H^+ + O_2 \quad (2)$$

On the other hand, we have found that the complexes in the lower oxidation states also produce molecular hydrogen from water in the absence of molecular oxygen. We report here our experimental data concerning the mechanism of water reduction to hydrogen and the catalytic activity of the Pt complex as a homogeneous hydrogen-producing catalyst.

EXPERIMENTAL SECTION

$[Pt(II)_2Pt(III)_2(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$ was prepared as previously described.[3] Continuous illuminations were carried out with an Ushio UXL-300W Xe lamp. The volume of the irradiated solutions was always 10 ml, which was contained in a Pyrex flask. The gas volume above the solution was ca. 14 ml. Prior to photolysis, the sample solutions were deaerated by argon bubbling. The flask was immersed in a water bath to remove IR radiation and to eliminate temperature effects. Hydrogen evolved was analyzed by gas chromatography. A GC-9A, Molecular Sieve 5A column (30 °C) and Ar as a carrier gas, was employed. The quantum yield of the hydrogen production was calculated by using a potassium ferrioxalate as a chemical actinometer.

RESULTS AND DISCUSSION

The Pt complex itself generates H_2 when dissolved into acidic water even without light irradiation. The amount of hydrogen evolved increases with H^+ concentration, Table I. The result of

TABLE I Evolution of hydrogen, detected immediately after dissolution of 1 μmol of Pt complex into 10 ml of solutions.

pH	Pt complex dissolved	H_2 evolved [μmol]
1.0	$[Pt(II)_2Pt(III)_2(NH_3)_8(C_4H_6NO)_4](NO_3)_6$[3]	0.11[a]
5.0	$[Pt(II)_2Pt(III)_2(NH_3)_8(C_4H_6NO)_4](NO_3)_6$	0.071[a]
	$[Pt(II)_2Pt(III)_2(NH_3)_8(C_4H_6NO)_4](NO_3)_6$	0[b]
	$[Pt(II)_3Pt(III)(NH_3)_8(C_4H_6NO)_4](PF_6)_3(NO_3)_2$[4]	0.24[a]
	$2[Pt(II)_2(NH_3)_4(C_4H_6NO)_2](PF_6)_2$[2]	0.042[a]
6.7	$[Pt(II)_2Pt(III)_2(NH_3)_8(C_4H_6NO)_8](NO_3)_6$	0.054[a]
9.3	$[Pt(II)_2Pt(III)_2(NH_3)_8(C_4H_6NO)_4](NO_3)_6$	0.044[a]

[a] in the absence of molecular oxygen.
[b] from a solution saturated with oxygen gas.

UV-VIS spectroscopic studies suggests that there is an interaction between the Pt complex and H^+ ion, Figure 1. No spectral change was observed by the addition of either water or $(C_2H_5)_4NClO_4$.

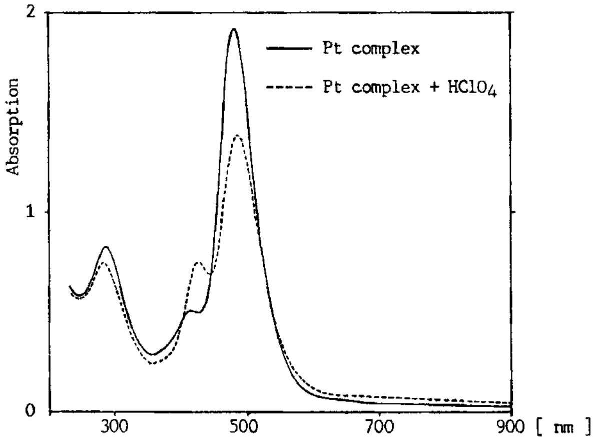

FIGURE 1 Spectral change in a UV-VIS spectrum of 0.05 mM $[Pt(II)_2Pt(III)_2(NH_3)_8(C_4H_6NO)_4](C_{12}H_{25}SO_3)_6$ in CH_2Cl_2 by the addition of $HClO_4$ (60 %).

Therefore, hydrogen-producing reaction seems to occur possibly via a protonation of the Pt complex prior to the reduction of H^+ ion.

Figure 2(a) shows the hydrogen evolution catalyzed by the Pt complex in a photochemical model system containing EDTA as an electron donor, $Ru(bpy)_3^{2+}$ as a sensitizer and MV^{2+} as an electron relay. Figure 2(c) shows that the Pt complex also has an ability to act as a sensitizer, although its activity is not so high, compared with $Ru(bpy)_3^{2+}$, Figure 2(b). Figure 2(d) shows that the rate of electron transfer becomes rather slow in the absence of MV^{2+}. It is interesting that hydrogen still evolves from a solution free of $Ru(bpy)_3^{2+}$ and MV^{2+}, Figure 2(e). By means of mass spectrometric analysis of the hydrogen evolved using D_2O, it was confirmed that the hydrogen evolved derives from water. The quantum yield of Figure 2(a) was calculated to be ca. 0.025. This value is superior to other homogeneous hydrogen-producing catalysts previously reported, such as $Rh(I)_2(1,3\text{-diisocyanopropane})_4$ ($\Phi = 0.004$).[5]

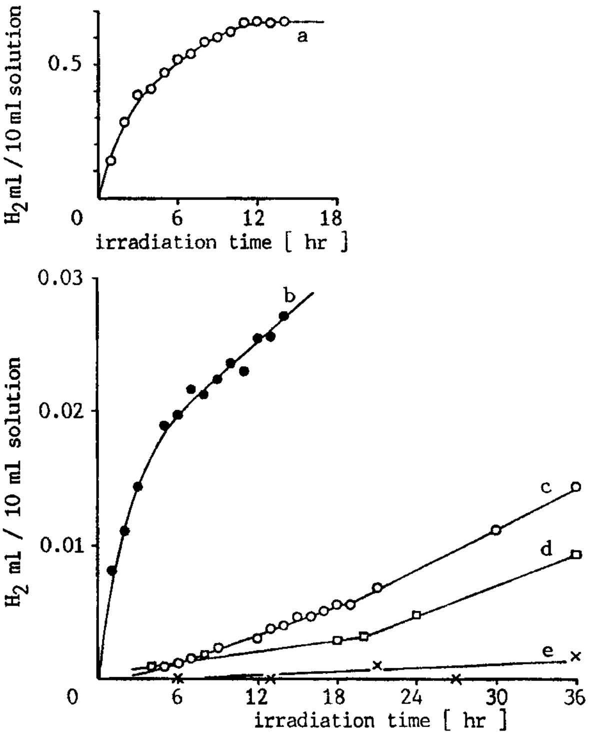

FIGURE 2 H_2 evolution from 30mM EDTA, 2mM MV^{2+}, 0.04mM $Ru(bpy)_3{}^{2+}$ and 0.1mM $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$, at pH 5.0 (adjusted with 0.03M CH_3CO_2H and 0.07M CH_3CO_2Na), irradiation with 300W Xe lamp (filtered with Pyrex glass), (a). (b), (c), (d) and (e) are H_2 evolutions from solutions free of $[Pt_4(NH_3)_8(C_4H_6NO)_4](NO_3)_6 \cdot 2H_2O$, $Ru(bpy)_3{}^{2+}$, MV^{2+} and both $Ru(bpy)_3{}^{2+}$ and MV^{2+}, respectively.

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