Triple -Decker Trinuclear Porphinatoruthenium(II) Complexes Bridged with Pyrazine or 4,4'-Bipyridine–Preparation and Electrochemical Oxidation

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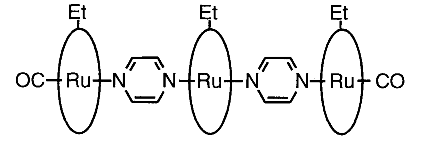
Two triple-decker trinuclear porphinatoruthenium(II) complexes bridged with pyrazine (pyr) or 4,4'-bipyridine (4,4'-bpy), [{(CO)(oep)Ru^{II}}(μ-pyr){Ru^{II}(oep)}(μ-pyr){Ru^{II}(oep)(CO)}] (H_2oep = octaethylporphine) and [{(CO)(tpp)Ru^{II}}(μ-4,4'-bpy){Ru^{II}(tpp)}(μ-4,4'-bpy){Ru^{II}(tpp)(CO)}] (H_2tpp = tetraphenylporphine), have been prepared. The first trinuclear complex was electrochemically oxidized in four steps.

A number of shish-kebab type porphinatoruthenium polymers bridged with diaza compounds have been prepared chemically[1,2] or electrochemically.[3] For an understanding of the properties of the polymers, the information about the dimer or trimer is indispensable. We have already reported the syntheses of several dinuclear porphinatoruthenium(II) complexes and their electrochemical properties.[4] In this letter, we present the syntheses and electrochemical properties of the two novel triple-decker trinuclear porphinatoruthenium(II) complexes shown below.



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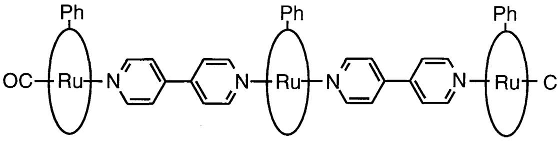

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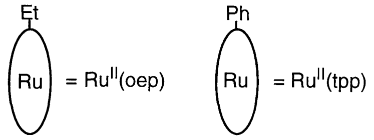

The trinuclear complexes were prepared in the following ways.[5] All the operations were carried out under an argon atmosphere with solutions that were previously deoxygenated with argon, because the target complexes, particularly complex **1**, are air-sensitive. Complex **1**: A 300 mg (0.42 mmol) sample of [Ru(oep)(CO)(EtOH)] (**3**)[6] was refluxed with five equivalents of pyrazine in 150 cm^3 of benzene for 3 h. Then [{Ru(oep)-(CO)}$_2$(pyr)] was formed, as reported previously.[4] The solution was irradiated with a high pressure mercury lamp for 30 h. The thin-layer chromatogram (TLC) on silica gel–(CH_2Cl_2–hexane (1:1 v/v)) showed two spots besides a spot at the origin. The upper spot was complex **1** and the lower spot was [Ru(oep)(pyr)$_2$] (**4**).[2] The solvent was evaporated off by passing argon at room temperature in order to avoid thermal decomposition of the complexes. The residue was dissolved in a minimum volume of CH_2Cl_2–hexane (1:1 v/v). The solution was subjected to chromatography on silica gel and developed with the same solvent. Complex **1** was obtained from the first fraction as dark-violet powder[7] when the solvent was evaporated off by passing argon. This complex could be obtained also by refluxing a benzene mixture of **3** and **4** under argon for ca. 1 h. This procedure, however, is not recommended because the chromatographic isolation of the trinuclear complex from the remaining **3** is difficult. Complex **2**: An 11 mg (0.011 mmol) sample of [Ru(tpp)(4,4'-bpy)$_2$] (**5**)[3] dissolved in benzene was mixed with a 21 mg (0.028 mmol) sample of [Ru(tpp)(CO)] (**6**)[6] dissolved in benzene, and mixture was stirred at room temperature until no more complex **5** remained when the mixture was examined by TLC. Then the mixture was subjected to silica gel–benzene column chromatography. On evaporating off the solvent from the first faction by passing argon, complex **2** was separated. The violet solid[7] thus obtained was dried under vacuum.

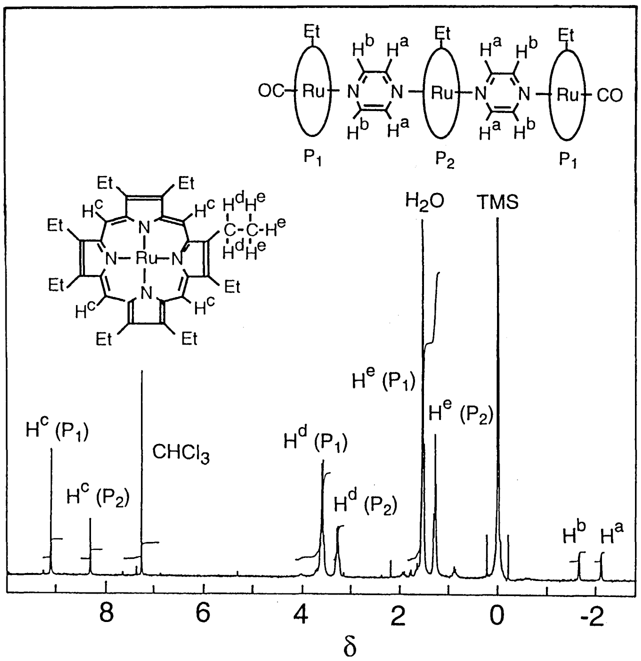

Figure 1. ^1H NMR spectrum of complex **1** in $CDCl_3$.

The ^1H NMR spectrum of **1** in $CDCl_3$ with peak assignments is shown in Figure 1. Three pairs of signals for the octaethylporphinato ring protons (H^c, H^d, and H^e) were observed. For each pair, the ratio of the integral value of the signal at lower magnetic field to that at higher magnetic field was ca. 2:1. The chemical shifts of the two doublet peaks of the bridging pyrazine protons (H^a and H^b) were considerably up-field from that of the protons of free pyrazine (8.60 ppm). The spectrum of complex **2** was very similar to that of **1**.

The voltammetric behavior of complex **1** in 0.1 mol dm^{-3} $(C_4H_9)_4N(ClO_4)$–CH_2Cl_2 was examined with a platinum disk electrode (1.7 mm diameter) at 25 °C; complexes **2** was only sparingly soluble in this solvent. The cyclic voltammogram showed four oxidation peaks (I - IV) (Figure 2a). The first peak

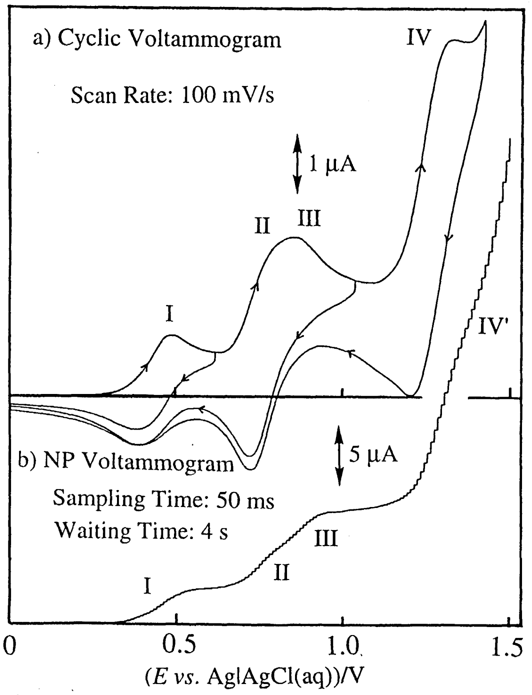

Figure 2. The cyclic voltammogram (a) and the NP voltammogram (b) of 0.3 mol m^{-3} **1** in 0.1 mol dm^{-3} $(C_4H_9)_4NClO_4$-CH_2Cl_2 at 25 °C.

is accompanied by the corresponding reduction peak on the reverse scan. But it is of quasi-Nernstian nature as seen from the peak shape and the peak separation. The broad hump that follows consists of two merged peaks (II and III) as seen more clearly in the normal pulse (NP) voltammogram (Figure 2b). At scan rates > 20 V/s or at low temperature (-30 °C), the reduction peak at ca. 0.7 V was replaced by two new waves, which corresponded to peaks II and III. This fact indicates the presence of fast chemical reactions through which the oxidation products of processes II and III decompose. Peak IV in Figure 2a is the oxidation of these decomposition products. On the contrary, the forth NP voltammetric step, IV', is the oxidation of the immediate product of step III, because the sampling time (50 ms) in the NP voltammetry is short enough to eliminate the effect of the decomposition reactions. By the same reason, the steps II and III in the NP voltammogram can be regarded as the oxidation processes virtually without the effect of the decomposition reactions.

The controlled potential coulometry of **1** at 0.6 V revealed that the first oxidation step was a one-electron process. Subsequent coulometry at 1.0 V showed that the steps II and III combined were a two-electron process. Each of steps II and III is most probably a one-electron process, in view of their almost equal limiting currents in the NP voltammogram. The height of the ill-defined step IV' seems to correspond to a three-electron process, but its exact charge number of reaction is not known.

The first one-electron oxidation should occur in the central moiety, in conformity with the symmetry of the complex. Its ruthenium atom is the more probable oxidation site rather than the porphinato ring, because the half-wave potential determined by the ln-plot analysis of the NP voltammogram, $E_{1/2}$, (0. 43 V *vs.* Ag|AgCl) is relatively near to that of the first oxidation step of [Ru(oep)(pyr)$_2$] ($E_{1/2}$ = 0. 30 V), which has been assigned to the oxidation of Ru^{II} to Ru^{III}.[1] Another piece of evidence, though indirect, for the oxidation of ruthenium is that the oxidation product of step I gave no ESR signal at -150 °C. The sites of the second and the third oxidation steps are probably the porphinato rings of the end moieties, because their $E_{1/2}$ values (0. 74 V and 0.86 V, respectively) are near to the $E_{1/2}$ (0. 72 V) of the first wave of [Ru(oep)(CO)(EtOH)], whose porphinato ring is known to be oxidized at this potential.[4] Our tentative scheme for the electrochemical oxidation processes and the sites of complex **1** is as follows:

$$[(CO)(oep)Ru^{II}\text{-pyr-}Ru^{II}(oep)\text{-pyr-}Ru^{II}(oep)(CO)]$$
$$\text{I } 0.43\text{ V} \quad \uparrow\downarrow - e^-$$
$$[(CO)(oep)Ru^{II}\text{-pyr-}Ru^{III}(oep)\text{-pyr-}Ru^{II}(oep)(CO)]^+$$
$$\text{II } 0.74\text{ V} \quad \uparrow\downarrow - e^-$$
$$[(CO)(oep^{\cdot+})Ru^{II}\text{-pyr-}Ru^{III}(oep)\text{-pyr-}Ru^{II}(oep)(CO)]^{2+}$$
$$\text{III } 0.86\text{ V} \quad \uparrow\downarrow - e^-$$
$$[(CO)(oep^{\cdot+})Ru^{II}\text{-pyr-}Ru^{III}(oep)\text{-pyr-}Ru^{II}(oep^{\cdot+})(CO)]^{3+}$$

Complex **1** gave two distinct steps II and III with a potential separation of 0.12 V in the NP voltammogram, in contradistinction to [{Ru(oep)}$_2$(pyr)] and similar binuclear complexes bridged by diaza compounds,[4] of which the steps corresponding the oxidation of the two porphinato rings are so close that they form a single two-electron step. In complex **1**, the porphinato ring of one end and the porphinato cation radical of the other end interact with each other through a center moiety to an appreciable extent, in spite of a larger distance between them.

References and Notes

1 J. P. Collman, J. T. McDevitt, G. T. Yee, C. R. Leidner, L. G. McCullough, W. A. Little, and J. B. Torrance, *Proc. Natl. Acad. Sci. U.S.A.*, **83**, 4581(1986); M. Hanack, A. Gul, and L.R. Subramanian, *Inorg. Chem.*, **31**, 1542(1992); W. Kobel and M. Hanack, *Inorg. Chem.*, **25**, 103(1986); V. marvaud and J. P. Launay, *Inorg. Chem.*, **32**, 1376(1993).

2 J. P. Collman, J. T. McDevitt, C.R. Leidner, G. T. Yee, J. B. Torrance, and W. A. Little, *J. Am. Chem. Soc.*, **109**, 4606(1987).

3 M. Saito, A. Endo, K. Shimizu, and G. P. Satô, *Chem. Lett.*, **1995**, 1079.

4 A. Endo, Y. Okamoto, K. Suzuki, J. Shimamura, K. Shimizu, and G. P. Satô, *Chem. Lett.*, **1994**, 1317.

5 The trinuclear complex bridged with pyrazine, [{(CO)(tpp)-Ru^{II}}(μ-pyr){Ru^{II}(tpp)}(μ-pyr){Ru^{II}(tpp)(CO)}], was also prepared in a similar way. It was obtained as dark-brownish-violet powder. Found: C, 72.93; H, 4.56; N, 8.83%. Calcd for $Ru_3C_{142}H_{92}N_{16}O_2$: C, 72.33; H, 3.94; N, 9.51%. However, the solubility of this complex in organic solvents was too poor to allow NMR, electrochemical and other chracterization.

6 M. Barley, J. Y. Becker, G. Domazetis, O. Dophin, and B. R. James, *Can. J. Chem.*, **61**, 2389(1983).

7 Elemental Analysis of **1** Found: C, 68.02; H, 6.56; N, 10.32%. Calcd for $Ru_3C_{118}H_{140}N_{16}O_2$: C, 66.90; H, 6.66; N, 10.60%. **2** Found: C, 73.85; H, 4.98; N, 7.98%. Calcd for $Ru_3C_{154}H_{100}N_{16}O_2$: C, 73.70; H, 4.02; N, 8.93%.