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# Preparation of Binuclear Octaethylporphinatoruthenium(II) Complexes Bridged with Diaza Compounds and Their Electrochemical Oxidation

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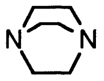
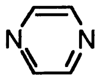
Binuclear octaethylporphinatoruthenium(II) complexes bridged with five diaza compounds (L), [{$Ru^{II}$(oep)(CO)}$_2$(μ-L)] ($H_2$oep = 2,3,7,8,12,13,17,18-octaethylporphin) have been synthesized. They are oxidized through two two-electron steps at a platinum electrode in $CH_2Cl_2$.

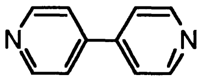
Since the Creutz-Taube complex was reported, many related binuclear and polynuclear ruthenium complexes bridged with diaza compounds have been synthesized.[1-10] However, binuclear porphinatometal complexes with a bridging diaza compound are very few. Some coordination polymers have been prepared,[11-13] and the formation in solution of a binuclear complex of iron(II) was observed;[14] the binuclear complexes so far isolated are [{$Rh^{III}$(p)(Cl)}$_2$(μ-L)] with $H_2$p = $H_2$oep and 5,10,15,20-tetraphenylporphin, and L = 4,4'-bipyridine (4,4'-bpy), 1,2-bis(4-pyridyl)ethane (bpe), and *trans*-1,2-bis(4-pyridyl)ethylene) (tbpe).[15] In this letter, we report syntheses of five kinds of binuclear octaethylporphinatoruthenium(II) complexes with five kinds of diaza compounds shown below, *i.e.*, 1,4-diazabicyclo-[2,2,2]octane (dabco), pyrazine (pyr), 4,4'-bpy, bpe, tbpe, together with their electrochemical oxidation processes.



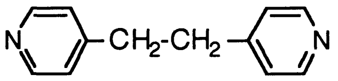
**dabco**



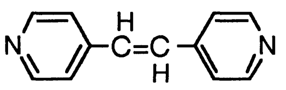
**pyr**



**4,4'-bpy**



**bpe**



**tbpe**

Each complex was formed simply by adding an excess of the bridging ligand to a benzene solution of [Ru(oep)(EtOH)(CO)](**1**), which had been prepared according to the literature method.[16] Except for the case of dabco, the binuclear complex was separated from the excess ligand by means of column chromatography (silica gel-benzene), and the purified samples were dried under a vacuum after the solvent was evaporated off. When an excess of dabco was added, the binuclear complex(**2**) precipitated at once as dark red crystals, which were collected and washed with chloroform; they were then dried under vacuum. The yields were 90% or larger. The $^1$H NMR spectra of the binuclear complexes in $CDCl_3$ showed the characteristic peak or peaks of the bridging diaza moiety (Table 1). The elemental analyses of C, H, and N were also in good agreement with the calculated values for the binuclear complexes. Found: C,65.54; H,6.98; N,9.59%. Calcd for $Ru_2C_{80}H_{100}N_{10}O_2$ (**2**): C,66.92; H,7.02; N,9.75%. Found: C,66.64; H,6.65; N,9.87%. Calcd for $Ru_2C_{78}H_{92}N_{10}O_2$ (**3**): C,66.76; H,6.56; N,9.99%. Found: C,68.26; H,6.66; N,9.46%. Calcd for $Ru_2C_{84}H_{92}N_{10}O_2$ (**4**): C,68.18; H,6.54; N,9.46%. Found: C,68.20; H,6.76; N,9.06%. Calcd for $Ru_2C_{86}H_{100}N_{10}O_2$ (**5**): C,68.50; H,6.68; N,9.29%. Found: C,68.12; H,6.50; N,9.13%. Calcd for $Ru_2C_{86}H_{98}N_{10}O_2$ (**6**): C,68.59; H,6.56; N,9.30%.

The cyclic voltammograms of the binuclear complexes in 0.1 mol dm$^{-3}$ $(C_4H_9)_4N(ClO_4)$ (TBAP)-$CH_2Cl_2$ at a platinum disk electrode (2 mm diameter) are alike; they showed apparently two oxidation waves (Fig. 1). No reduction waves were observed within the potential window. Their normal pulse voltammograms exhibited two oxidation steps of almost equal heights, the first being well-defined, but the second drawn-out. The limiting currents of the first steps were the same as total height of the two oxidation steps of **1** of the same concentration. Each of these two oxidation steps actually consists of two, merging one-electron steps, as already suggested by the cyclic voltammogram of 4, whose second wave indeed split into two overlapping waves. Controlled-potential coulometry of **3** and **4** revealed that their first oxidation steps were of a two-electron process. Although coulometry at a potential of the second step was unsuccessful owing to complications caused by some regeneration process of the oxidation products, the second step is most probably a two-electron process in view

Table 1. Chemical shifts (δ) of $^1$H NMR spectra of binuclear complexes ($[\{Ru(oep)(CO)\}_2(\mu\text{-}L)]$) in $CDCl_3$ at room temperature

| Complex | | δ | | | |
|---|---|---|---|---|---|
| | | oep$^{2-}$ | | | L |
| | | meso-*H* | $-C\underline{H}_2CH_3$ | $-CH_2C\underline{H}_3$ | |
| [Ru(oep)(EtOH)(CO)] | (**1**) | 9.94(s) | 4.03(q) | 1.93(t) | - |
| L = dabco | (**2**) | 9.24(s) | 3.69(q) | 1.54(t) | -6.34(s) |
| = pyr | (**3**) | 9.26(s) | 3.71(q) | 1.63(t) | -1.50(s) |
| = 4,4'-bpy | (**4**) | 9.57(s) | 3.80(q) | 1.72(t) | 3.93(d),0.35(d) |
| = bpe | (**5**) | 9.63(s) | 3.85(m) | 1.77(t) | 4.15(d),0.06(d),0.04(s) |
| = tbpe | (**6**) | 9.64(s) | 3.85(m) | 1.77(t) | 4.69(s),4.35(d),0.56(d) |

s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

of the wave height.

Their mid-potentials, $E_m = (E_{p,a} - E_{p,c})/2$ ($E_{p,a}$ and $E_{p,c}$ are the anodic and the cathodic peak potentials, respectively), are listed in Table 2.

When a solution of **3** in 0.3 mol $dm^{-3}$ TBAP-$CH_2Cl_2$ was exhaustively electrolyzed at 1.0 V and then its ESR spectrum was recorded at 293 K, an isotropic signal at $g = 1.9997$ was observed. At 77 K this signal exhibited fine structure ($D = 3.24 \times 10^{-3}\ cm^{-1}$, $E = 0\ cm^{-1}$). Similar results were obtained for **4** ( $D = 1.33 \times 10^{-3}\ cm^{-1}$, $E = 0\ cm^{-1}$). These fine structures strongly suggest that the sites of the first oxidation are the two porphinato rings.

No direct information about the sites of the second oxidation was available because of the complication owing to the regeneration reaction, as mentioned above. Nevertheless, the sites of the second oxidation will probably be the two central atoms, because the potential differences between the first and second steps

$$[\{Ru^{II}(oep)(CO)\}\text{-L-}\{Ru^{II}(oep)(CO)\}]$$
$$E_1 \ \rightleftharpoons \ -e^-$$
$$[\{Ru^{II}(oep^{+\bullet})(CO)\}\text{-L-}\{Ru^{II}(oep)(CO)\}]$$
$$E_2 \ \rightleftharpoons \ -e^-$$
$$[\{Ru^{II}(oep^{+\bullet})(CO)\}\text{-L-}\{Ru^{II}(oep^{+\bullet})(CO)\}]$$
$$E_3 \ \rightleftharpoons \ -e^-$$
$$[\{Ru^{III}(oep^{+\bullet})(CO)\}\text{-L-}\{Ru^{II}(oep^{+\bullet})(CO)\}]$$
$$E_4 \ \rightleftharpoons \ -e^-$$
$$[\{Ru^{III}(oep^{+\bullet})(CO)\}\text{-L-}\{Ru^{III}(oep^{+\bullet})(CO)\}]$$

Scheme 1. Electrochemical oxidation of the binuclear complexes.

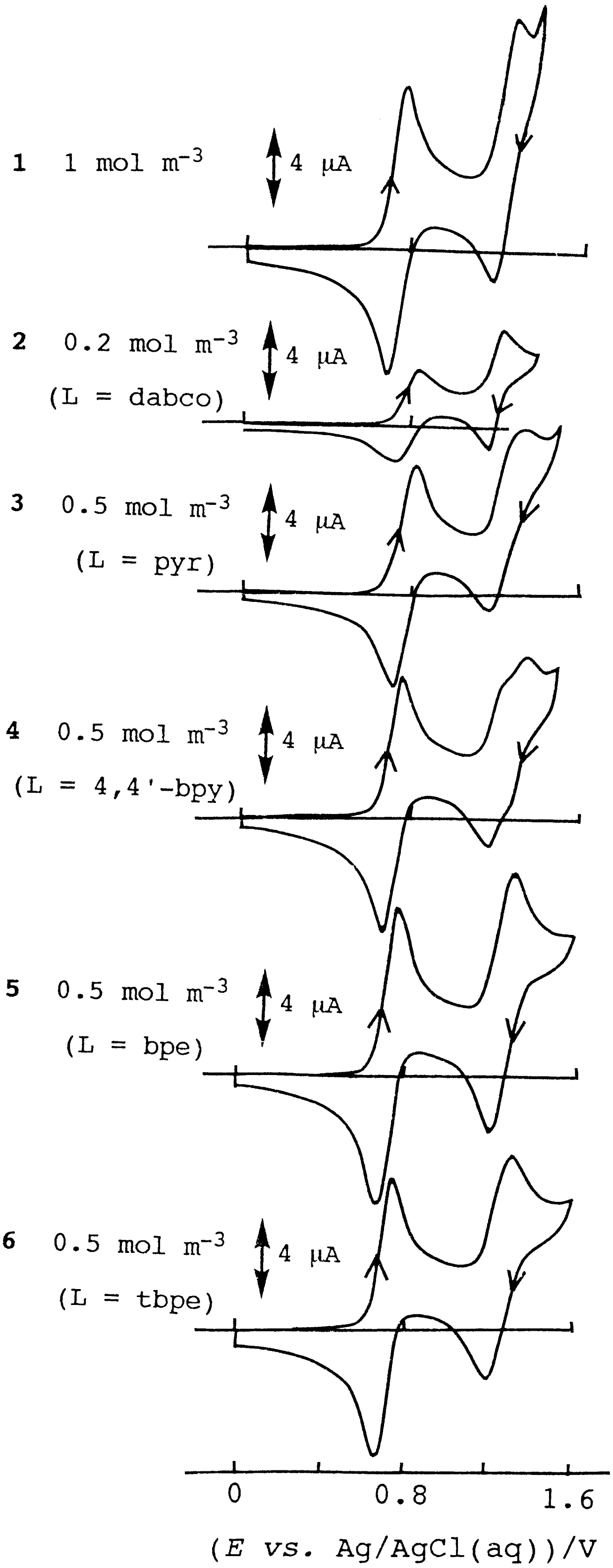


Fig. 1. Cyclic voltammograms of **1** ~ **6** in 0.1 mol $dm^{-3}$ TBAP-$CH_2Cl_2$ at 25 °C. Scan rate=100 mV/s.

Table 2. The mid-potentials (*vs.* Ag|AgCl(aq)$^{a)}$) of the binuclear complexes in 0.1 mol dm$^{-3}$ TBAP-$CH_2Cl_2$ at 25 °C

| Complex | $E_m(1)$/V | $E_m(2)$/V | $\{E_m(2)-E_m(1)\}$/V |
|---|---|---|---|
| **1** | 0.72 | 1.24 | 0.52 |
| **2** | 0.77 | 1.19 | 0.42 |
| **3** | 0.80 | 1.25 | 0.45 |
| **4** | 0.73 | 1.31 | 0.54 |
| **5** | 0.72 | 1.26 | 0.54 |
| **6** | 0.72 | 1.28 | 0.56 |

a)-0.56 V *vs.* the ferricinium/ferrocene potential in this medium.

(Table 2) were much larger than 0.29 ±0.05 V, the empirical value for the processes in which a porphinato cation radical formed at the first step is oxidized to the dication at the second.$^{17)}$ This view is supported by the conclusion drawn from the studies of substituent effects on the oxidation potentials of several mononuclear porphinato ruthenium complexes coordinated with CO that their second oxidation occurs at the central atom.$^{18,19)}$

The oxidation processes of these binuclear complexes can be represented by Scheme 1. Here, $E_2 \approx E_1$ and $E_4 \approx E_3$ except for **4**, i.e., the interaction between the oxidation sites through the bridging diaza moiety is very small compared to the cases of Creutz-Taube complexes.$^{1)}$

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