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Synthesis and Electrochemical Properties of Mononuclear and Binuclear Ruthenium Complexes Containing 2,2′-Bibenzimidazole

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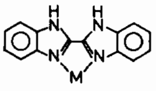
2,2′-Bibenzimidazole (BiBzImH$_2$) is of interest for its coordination ability toward transition metal ions as three different species: neutral molecule (A), monoanion (B), or dianion (C).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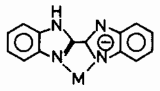
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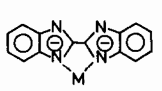
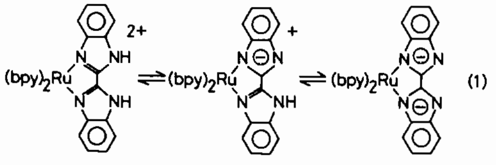

C

Moreover, the dianion (BiBzIm) functions as a bridging ligand between two metal ions to form binuclear complexes, such as [(η^5-C$_5$H$_5$)$_2$Ti]$_2$(BiBzIm) [1] and [Cu$_2$(Me$_5$dien)$_2$(BiBzIm)](BPh$_4$)$_2$ [2], where Me$_5$dien is 1,1,4,7,7-pentamethyldiethylenetriamine. The present letter reports the synthesis and electrochemical properties of mono- and binuclear ruthenium complexes containing 2,2′-bibenzimidazole.

The [Ru(bpy)$_2$(BiBzImH$_2$)](ClO$_4$)$_2$ complex (*1*) (bpy = 2,2′-bipyridine) was prepared by the equimolar reaction of Ru(bpy)$_2$Cl$_2$·2H$_2$O with BiBzImH$_2$ in 50% aqueous ethanol, followed by the addition of a small excess amount of NaClO$_4$. *Anal.* Calcd for C$_{34}$H$_{26}$N$_8$Cl$_2$O$_8$Ru·2H$_2$O: C, 46.26; H, 3.43; N, 12.70%. Found: C, 46.12; H, 2.99; N, 12.82%. Λ_M = 339 Ω^{-1} cm^2 M^{-1} in CH$_3$CN (5.0 × 10^{-4} M). The electronic absorption spectra of *1* in 50% aqueous methanol at various pH are depicted in FiG. 1, which indicates that the absorption band around 460 nm assignable to ruthenium-to-ligand π^* charge transfer transition is shifted to lower energy with an isosbestic point at 487 or 513 nm as the pH value increases. This result confirms that the dication of *1* (*1a*) in solution undergoes two successive deprotonations to exist as an equilibrium mixture with the monocation (*1b*) and neutral species (*1c*), as shown in eqn. (1).



(1)

From the pH dependence of the absorption spectra in 50% aqueous methanol, the acid dissociation constants, pK$_{a1}$ and pK$_{a2}$, for *1* were calculated as 5.7 and 10.1, respectively. Complex *1* has, therefore, a diacidic character, and the fully deprotonated complex [Ru(bpy)$_2$(BiBzIm)] may further act as a bidentate ligand. Actually, [Ru(bpy)$_2$(BiBzIm)] prepared *in situ* by mixing [Ru(bpy)$_2$(BiBzImH$_2$)]-(ClO$_4$)$_2$ with sodium methoxide in methanol reacted with Ru(bpy)$_2$Cl$_2$·2H$_2$O and Ru(phen)$_2$Cl$_2$ (phen = 1,10-phenanthroline) to give binuclear ruthenium complexes, [(bpy)$_2$Ru(BiBzIm)Ru(bpy)$_2$](ClO$_4$)$_2$ (*2*) and [(bpy)$_2$Ru(BiBzIm)Ru(phen)$_2$](ClO$_4$)$_2$ (*3*), respectively. *2*: *Anal.* Calcd for C$_{54}$H$_{40}$N$_{12}$Cl$_2$O$_8$Ru$_2$: C, 51.55; H, 3.21; N, 13.36%. Found: C, 51.00; H, 2.93; N, 13.35%. Λ_M = 321 Ω^{-1} cm^2 M^{-1} in CH$_3$CN (5.0 × 10^{-4} *M*). *3*: *Anal.* Calcd for C$_{58}$H$_{40}$N$_{12}$Cl$_2$O$_8$Ru$_2$: C, 53.34; H, 3.09; N, 12.89%. Found: C, 52.94; H, 2.63; N, 12.90%. Λ_M = 298 Ω^{-1} cm^2 M^{-1} in CH$_3$CN (5.0 × 10^{-4} *M*).

The cyclic voltammogram of *1* in CH$_3$CN showed a reversible Ru(II)/Ru(III) couple with E$_{1/2}$ = +1.11 V *vs.* SCE and ΔE$_p$ = 70 mV. On the other hand, *2* exhibits two pairs of anodic and cathodic waves at E$_{1/2}$ = +0.74 and +1.04 V *vs.* SCE (Fig. 2), both of which are quasi-reversible, as evidenced by the facts that ΔE$_p$ = 95 mV in each case. Similar electro-

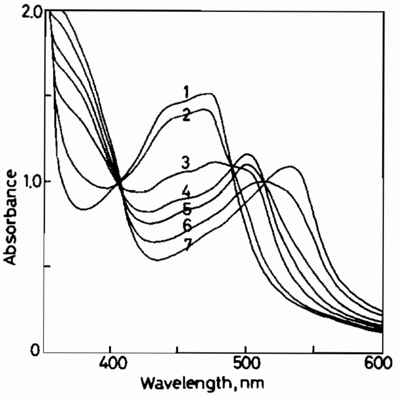


Fig. 1. Absorption spectra of [Ru(bpy)$_2$(BiBzImH$_2$)](ClO$_4$)$_2$ (1.2 × 10^{-4} *M*) in 50% aqueous methanol at 25 °C as a function of pH: (1) 3.89, (2) 4.63, (3) 6.04, (4) 8.30, (5) 9.39 (6) 10.50, (7) 11.60.

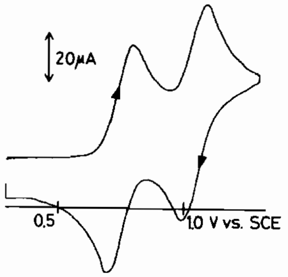


Fig. 2. Cyclic voltammogram of [(bpy)$_2$Ru(BiBzIm)Ru(bpy)$_2$](ClO$_4$)$_2$ in acetonitrile containing 0.1 *M* (n-C$_4$H$_9$)$_4$NClO$_4$ as a supporting electrolyte; the sweep rate of 200 mV/s.

chemical behavior ($E_{1/2}$ = +0.73 and +1.02 V *vs.* SCE, and ΔE_p = 70 mV in each case) was observed for *3*. Thus, the electrode reactions of binuclear complexes *2* and *3* may be formulated as,

$$[\mathrm{Ru(II)}\text{–}\mathrm{Ru(II)}]^{2+} \rightleftharpoons [\mathrm{Ru(II)}\text{–}\mathrm{Ru(III)}]^{3+} + e^-$$
$$[\mathrm{Ru(II)}\text{–}\mathrm{Ru(III)}]^{3+} \rightleftharpoons [\mathrm{Ru(III)}\text{–}\mathrm{Ru(III)}]^{4+} + e^- \qquad (2)$$

where [Ru–Ru] stands for the cationic moieties of the binuclear complexes. The mixed-valence Ru(II)–Ru(III) complexes formed during the course of oxidation of *2* and *3* are relatively stable in CH_3CN. From the differences between the first and second half wave potentials in *2* and *3*, the comproportionation constants, K_{con},* of the equation

$$[\mathrm{Ru(II)}\text{–}\mathrm{Ru(II)}]^{2+} + [\mathrm{Ru(III)}\text{–}\mathrm{Ru(III)}]^{4+} \overset{K_{con}}{\rightleftharpoons} 2[\mathrm{Ru(II)}\text{–}\mathrm{Ru(III)}]^{3+} \qquad (3)$$

were calculated to be 9.8 × 10^4 for both complexes. The K_{con} value obtained is larger than those reported for other ruthenium–bpy systems, $[(bpy)_2Ru^{II}(bpyrm)Ru^{III}(bpy)_2]^{5+}$ (1.1 × 10^3) [3], and $[Cl(bpy)_2Ru^{II}(pyr)Ru^{III}(bpy)_2Cl]^{3+}$ (1 × 10^2) [4], where bpyrm = 2,2'-bipyrimidine and pyr = pyrazine. This is suggestive of a great destabilizing interaction between Ru(II)–Ru(II) or Ru(III)–Ru(III) in our complexes, because the K_{con} value may reflect the destabilizing interaction rather than intrinsic stabilization of the Ru(II)–Ru(III) complex by electron delocalization [5].

Near-infrared spectra may be expected to give direct insight into the extent of electron delocalization between two ruthenium sites [6]. Thus, the absorption spectra were measured on the electrochemical oxidation of *2*. The result is depicted in Fig. 3, which shows the occurrence of three new bands at 712 (ϵ 1.7 × 10^3 M^{-1} cm^{-1}), 1062 (ϵ 1.3 × 10^3 M^{-1} cm^{-1}), and 1950 nm (ϵ 3.4 × 10^3 M^{-1} cm^{-1}) after exhaustive electrolysis at +0.90 V *vs.* SCE, where the mixed-valence Ru(II)–Ru(III) complex should exist. Upon complete oxidation at +1.30 V *vs.* SCE to afford the fully oxidized Ru(III)–Ru(III) complex, the 712 nm band is shifted to 754 nm with intensifying, while the remaining two bands in the near infrared region completely disappear. The 712 and 754 nm bands may be assigned to ligand π-to-ruthenium(III) charge transfer transitions [7].

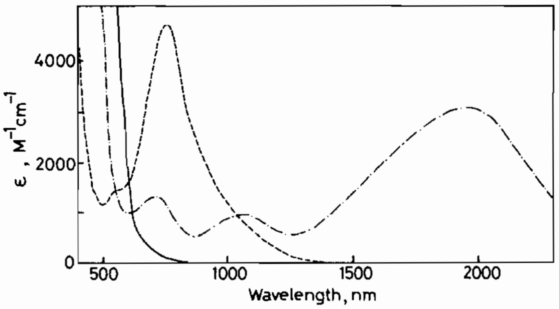


Fig. 3. Absorption spectra of $[(bpy)_2Ru(BiBzIm)Ru(bpy)_2](ClO_4)_2$ on the electrochemical oxidation in acetonitrile containing 0.1 *M* $(n\text{-}C_4H_9)_4NClO_4$ as a supporting electrolyte: ——, before electrolysis; –•–•–, after exhaustive electrolysis at +0.90 V; – – –, after exhaustive electrolysis at +1.30 V *vs.* SCE.

On the other hand, the 1950 and 1062 nm bands may both arise from intervalence transitions within the mixed-valence binuclear complex; the former probably corresponds to Ru(II) t_{2g} → Ru(III) t_{2g} and the latter to Ru(II) t_{2g} → Ru(III) e_g transitions, as described for Prussian blue [8]. Further work is in progress to elucidate the spectral properties of the mixed valence Ru(II)–Ru(III) complexes.

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*The value of K_{con} was obtained by the formula $E_{1/2}$(second) − $E_{1/2}$(first) = 0.0591 log K_{con}.