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Synthesis and Properties of Tris(2,2′-bibenzimidazole)ruthenium(II) Dication, $[Ru(BiBzImH_2)_3]^{2+}$

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Tris(2,2′-bipyridine)ruthenium(II) di-cation, $[Ru(bpy)_3]^{2+}$, has received much attention as an attractive candidate for electro- and photo-catalysts in solar energy conversion [1]. The substitution of various groups into the bipyridine ring of $[Ru(bpy)_3]^{2+}$ has been shown to alter the electrochemical and photochemical properties [2]. Recently, tris(2,2′-bipyrazine)ruthenium di-cation, $[Ru(bpz)_3]^{2+}$, has been reported to be a better photocatalyst than $[Ru(bpy)_3]^{2+}$ [3]. It is thus of interest to examine the effect of ligands on the spectral and excited state properties of ruthenium complexes. The author reports here the synthesis and properties of tris(2,2′-bibenzimidazole)ruthenium(II) di-cation, $[Ru(BiBzImH_2)_3]^{2+}$.

Experimental

Materials

2,2′-Bibenzimidazole($BiBzImH_2$) was prepared as described in the literature [4]. Acetonitrile was dried over phosphorus pentoxide for spectral measurements and further dried over calcium hydride before use in electrochemical measurements. Solvents for emission measurements were distilled twice. Other materials were reagent grade and were used as supplied.

Synthesis of the Complex, $[Ru(BiBzImH_2)_3](ClO_4)_2$

A suspension of $RuCl_3 \cdot 3H_2O$ (0.5 g, 2.21 mmol) in glycerol (25 cm^3) was heated to 100 °C under nitrogen until the color of the solution became green. To the resulting solution was added solid $BiBzImH_2$ (1.71 g, 7.30 mmol), and the mixture was heated at 150 °C for a further 10 h. The red-brown solution was filtered hot and allowed to stand at room temperature. After the dilution of the filtrate with ethanol/water (1:1 v/v, 50 cm^3), sodium perchlorate (1 g, 7.2 mmol) was added, to give a red precipitate which was collected and recrystallized from ethanol/water (4:1 v/v), 60% yield. *Anal.* Calcd for $C_{42}H_{30}N_{12}Cl_2O_8Ru$: C, 50.31; H, 3.02; N, 16.77%. Found: C, 50.49; H, 2.86; N, 16.88%. $\Lambda_M = 302\ \Omega^{-1}\ cm^2\ mol^{-1}$ (5.0×10^{-4} mol dm^{-3} in CH_3CN).

Physical Measurements

The ^1H NMR spectra were recorded on a JNM-PMX 60SI spectrometer with tetramethylsilane (TMS) as an internal standard. Electric conductivities were measured by using a Yokogawa Model 4255A Universal Bridge. Electronic spectra were recorded on a Shimadzu UV-210A double-beam spectrophotometer equipped with a 1 cm quartz cell. Cyclic voltammetry was measured by using a Hokuto Denko HA-301 potentiostat-galvanostat, a Hokuto Denko HF-201 function generator and a Yokogawa Model 3086 x–y recorder as described previously [5]. The number of electrons in the oxidation of the complex was obtained by the potential-step method [6]. All emission spectra at room temperature and 77 K were measured with a Hitachi 650-10 fluorescence spectrophotometer. Emission data were uncorrected for the spectral sensitivity of the system. Emission lifetime measurements were obtained using a home-made nitrogen laser as a pulsed light source (pulse width 10 ns). The solutions for emission measurements were degassed by freeze-pump-thaw cycles three times and sealed under vacuum.

Results and Discussion

The new complex $[Ru(BiBzImH_2)_3](ClO_4)_2$, is soluble in acetone, acetonitrile, and methanol and sparingly soluble in water. The molar conductivity in CH_2CN is 302 Ω^{-1} cm^2 mol^{-1}, which is consistent with the 2:1 electrolyte. The ^1H NMR spectrum of $[Ru(BiBzImH_2)_3]^{2+}$ in $CD_3CN/(CD_3)_2SO$ (4:1 v/v) shows two doublets and two triplets for the benzimidazole protons of $BiBzImH_2$ (Fig. 1), which indicates that each $BiBzImH_2$ is acting as a bidentate ligand. In the molecular model of $[Ru(BiBzImH_2)_3]^{2+}$ each $H^{4\ \mathrm{or}\ 4'}$ proton lies close to a benzene ring of another $BiBzImH_2$ molecule and is presum-

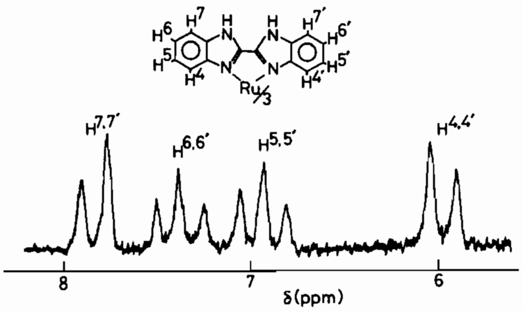

Fig. 1. ^1H NMR spectrum of $[Ru(BiBzImH_2)_3](ClO_4)_2$ in the region of benzimidazole protons in $CD_3CN/(CD_3)_2SO$ (4:1 v/v).

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TABLE I. Absorption and Emission Maxima of the Ru(II) Complexes.

Complex	absorption[a]	emission[b]	
	λ_{max}, nm	λ_{max}, nm	lifetime, μs
$[Ru(bpy)_3]^{2+}$ [c]	454	584, 628	5.30
$[Ru(bpy)_2(BiBzImH_2)]^{2+}$ [d]	463	616, 659	3.00
$[Ru(BiBzImH_2)_3]^{2+}$	483	650, 708	1.00

[a]In CH_3CN at room temperature. [b]In ethanol–methanol (4:1 v/v) at 77 K. [c]Ref. [13]. [d]Ref. [11].

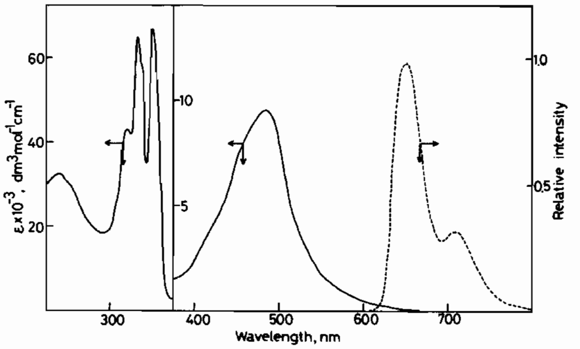

Fig. 2. Absorption spectrum of $[Ru(BiBzImH_2)_3](ClO_4)_2$ (———) in CH_3CN at room temperature and its emission spectrum (------) in ethanol–methanol (4:1 v/v) at 77 K.

ably exposed to a shielding due to ring currents (see Fig. 1 for the numbering system). Therefore, the high-field doublet at δ 5.98 (J_{4-5} = 8 Hz) is assigned to the $H^{4,4'}$ protons and the low field doublet at δ 7.85 (J_{6-7} = 8 Hz) to the $H^{7,7'}$ protons. The irradiation of the high-field doublet results in a collapse of the triplet at δ 6.94 to a doublet. This decoupling experiment leads to an assignment of the triplet at δ 6.94 as $H^{5,5'}$ protons and the triplet at δ 7.39 as $H^{6,6'}$ protons ($J_{4-5} = J_{5-6} = J_{6-7}$ = 8 Hz, $J_{4-7} = J_{5-7} \approx 0$ Hz). This assignment is compatible with that for $[M(bpy)_3]^{n+}$ (M = Os, Ru, and Fe) [7]. The N–H proton signal could not be detected.

The absorption spectrum of $[Ru(BiBzImH_2)_3](ClO_4)_2$ in CH_3CN is shown in Fig. 2. The low energy absorption band at 483 nm may be assigned to a metal-to-ligand charge transfer (MLCT) transition and three bands with maxima at 350, 331, and 242 nm to $BiBzImH_2$ intraligand transitions by referring the spectrum of $[Ru(bpy)_3]^{2+}$ [8]. While the color of $[Ru(BiBzImH_2)_3](ClO_4)_2$ in aqueous CH_3CN solution was affected by the solution pH, a quantitative study has been prevented by the precipitation of the complex*.

$[Ru(BiBzImH_2)_3](ClO_4)_2$ does not emit at room temperature, which is distinct from the emission property of $[Ru(bpy)_3]^{2+}$ [1]. When the temperature is lowered to 77 K, the emission is observed at 650 and 708 nm (Fig. 2) and has a lifetime of 1.00 μs, which can be assigned to a MLCT transition by comparing with that of $[Ru(bpy)_3]^{2+}$ [1] and $[Ru(bt)_3]^{2+}$ (bt = 2,2'-bi-2-thiazoline [9]. The emission energy and the lifetime decrease with increasing the number of $BiBzImH_2$ for a series of $[Ru(bpy)_n(BiBzImH_2)_{3-n}]^{2+}$ (Table I).

The decrease of lifetime on increasing the number of $BiBzImH_2$ may be attributed to a rapid non-radiative deactivation of the excited states, in which the excitation energy may be vibrationally dissipated to the solvent medium through the N–H bonds of the $BiBzImH_2$ ligand.

The cyclic voltammogram of $[Ru(BiBzImH_2)_3]^{2+}$ in CH_3CN shows a reversible one-electron Ru(II)/Ru(III) couple with $E_{1/2}$ = +0.80 V *vs.* SCE. However, no reversible reduction steps were observed in the range from 0 to –2.0 V. The Ru(II)/Ru(III) oxidation potential of $[Ru(BiBzImH_2)_3]^{2+}$ is considerably lower than that of $[Ru(bpy)_3]^{2+}$ (+1.29 V *vs.* SCE in CH_3CN [10]), suggesting that the donor property of $BiBzImH_2$ is stronger than that of bpy. This is consistent with the results of absorption and emission spectra.

Addition of water or methanol to a solution of $[Ru(BiBzImH_2)_3](ClO_4)_2$ in CH_3CN leads to the gradual cathodic shift of the Ru(II)/Ru(III) oxidation potential (Fig. 3) and a small decrease of absorbance at 483 nm in the absorption spectra, although the oxidation potential and absorbance of $[Ru(bpy)_3]^{2+}$ remain almost constant in the same experimental conditions. A similar potential shift is observed for $[Ru(bpy)_2(BiBzImH_2)]^{2+}$. This may indicate that the N–H bonds in the $BiBzImH_2$ ligand can specifically interact with solvents (water or methanol) through the hydrogen-bonding, followed by the electron-pair donation from solvent molecules and then the increase of electron density of the Ru(II) ion. The deprotonation of $BiBzImH_2$ ligand by

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*The precipitated species may be regarded as the neutral complex, $[Ru(BiBzImH_2)(BiBzImH)_2]$, formed by deprotonation of $[Ru(BiBzImH_2)_3]^{2+}$.

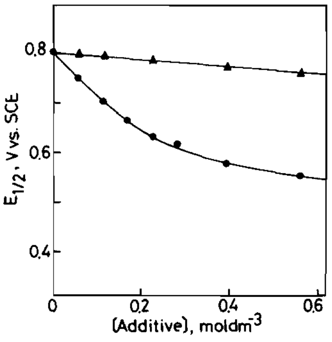

Fig. 3. The effect of additives (water (—●—); methanol (—▲—)) on the Ru(II)/Ru(III) oxidation potential, $E_{1/2}$, of $[Ru(BiBzImH_2)_3](ClO_4)_2$ (1.0×10^{-3} mol dm^{-3}) in CH_3CN.

base [11] is regarded as the limiting case of this interaction. A similar specific interaction has been recently reported for the ruthenium(II) ammine complexes [12].

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