A Novel Ruthenium–Quinonoid Complex. Structural, Spectroscopic, and Electrochemical Characterization of Ruthenium(II) Bis(2,2′-bipyridine) Chloranilate

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[Ru(bpy)$_2$(CA)]•EtOH (**1**) (CA^{2-} = chloranilate) has been characterized by X-ray diffractometry, electrochemistry, UV–vis, IR, and Raman spectroscopy. Spectroscopic and theoretical characterization reveal that the chloranilate ligand allows for the fine-tuning of the electronic property of **1**.

The ruthenium complexes containing π-acidic co-ligands such as α-diimines (bpy, phen, etc.) systems are important because they efficiently control the energy of metal dπ levels.[1] Among their potential applications, photosensitizers, biological model study, DNA intercalation are well studied.[2] On the other hand, chloranilic acid (H$_2$CA) is a family of dihydroxybenzoquinone derivatives that behaves as a typical bidentate ligand for transition-metal ions.[3] In addition to a wide range of its analytical applications, dihydroxybenzoquinone derivatives have frontier orbitals with energies comparable to those of the transition-metal ions, and the nature of the reduced and oxidized species may depend on the metal ions and the coordination environment.[4] In spite of their unique potential properties, to our knowledge, the expected non-innocent properties have rarely been exploited for ruthenium complexes up to the present time.[5] A common feature of the metal–quinone chemistry is delocalization of active electrons between the metal and the quinonoid ligand. A strong covalence involving this type of ligands has been suggested for the corresponding ruthenium–polypyridine complexes, giving rise to an interesting discussion concerning the assignment of the redox states and valence localization. Along this line, we report here a detailed investigation on the structural, spectroscopic, and electrochemical behavior of the [Ru(bpy)$_2$(CA)]•EtOH (**1**).

An equimolar mixture of *cis*-[RuCl$_2$(bpy)$_2$] (bpy = 2,2′-bipyridine) with the dideprotonated form of the chlolanilic acid yielded **1**. Purple crystals of **1** were produced from the DMF/ethanol solution.[7] The molecular structure of **1** is shown in Figure 1.[6] The ruthenium(II) ion is chelated by two bipyridine and one chloranilate ligand. The two bipyridines are equivalent, and Ru–N distances at positions trans to other bipyridine nitrogens (2.055(2) Å) are longer than those at positions trans to chloranilate oxygens (2.022(2) Å). The bipyridine rings are approximately coplanar, and the ruthenium–chloranilate moiety is also essentially planar. The symmetrical coordination of the CA^{2-} dianion and the difference in the lengths between coordinated and uncoordinated C–O distances (C(1)–O(1): 1.282(4) Å, C(3)–O(2): 1.220(6) Å) suggest that CA^{2-} dianion is in the *o*-quinone form, where C–O bonds of equal length are located in ortho position. In practice, the IR spectrum of **1** shows two characteristic bands at 1518 and 1606 cm^{-1}.[7] These bands are assigned to $\nu_{\text{C–O}}$ and $\nu_{\text{C=O}}$ for chemically distinct sites, respectively, confirming the *o*-quinone form of the chloranilate. Interestingly, bipyridine ligands of adjacent complex molecules stack to form a one-dimensional chain in the crystal structure. The closest interatomic separation between bipyridine atoms is 3.420(6) Å between C(8) and C(10) of the corresponding ligand related by the inversion center at the origin of the unit cell. Moreover, the chains assemble together to make a channel parallel to the chain direction. Interstitial ethanol molecules are introduced to the channel by the hydrogen-bonding interaction (Figure 2). The ethanol molecule is disordered at two positions in the crystal. A hydrogen bond can be detected between the ethanol molecules, and the non-coordinated oxygen (2.816(3) Å) and a weak CH···O hydrogen-bonding interaction stabilizes the interstitial ethanol molecule (C(4)–O(3): 3.253(14) Å, C(7)–O(3): 3.46(5) Å). The electronic spectrum of **1** consists of several absorptions, composite bands around 524, 360, 335, and 296 nm in UV and visible region (Figure 3a). The spectra in various kind of solvents and KBr mull were also measured for **1**.[7] The diffuse reflectance spectrum is similar to that in DMF. The lower energy band (19100 cm^{-1}) is thought to be a ruthenium(II)-to-ligands charge-transfer band, and there is a strong electronic effect of the coordinated chloranilate. In order to elucidate this point, Raman spectra were measured

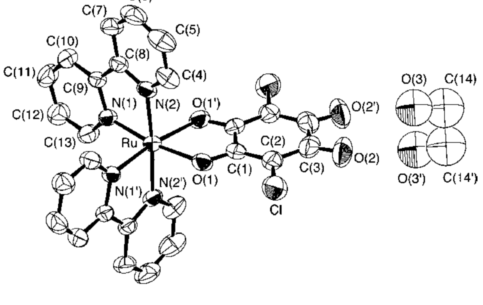

Figure 1. Molecular structure of **1**. The hydrogen atoms are omitted for clarity.

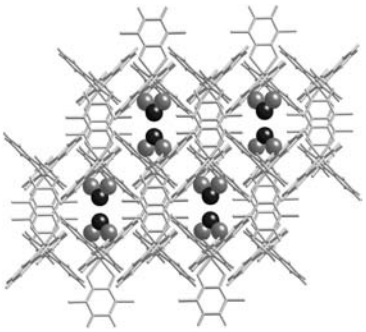

Figure 2. Assembled structure of **1**.

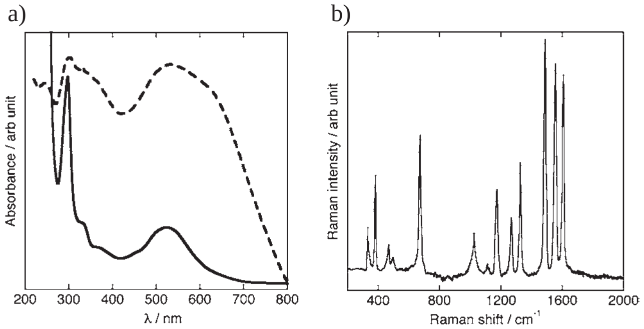

Figure 3. (a) Electronic spectra of **1** in DMF solution (full line) and solid state (broken line). (b) Raman spectrum of **1**.

(Figure 3b). The enhanced peaks at 1600, 1550, 1481, 1320, 1263, 1168, 670, and 378 $\mathrm{cm^{-1}}$ in the spectrum obtained at $\lambda_{\mathrm{ex}} = 514.5$ nm are characteristic of bipyridine vibrational modes that are observed for related $\mathrm{Ru^{II}}$–bpy complexes, reinforcing our assignment of the charge-transfer band in the visible region.[1b,5a] Further a typical cyclic voltammogram for **1** is shown in Figure 4. A reversible wave was observed at 0.170 V vs. ferrocenium/ferrocene ($\mathrm{Fc^+/Fc}$), (0.570 V vs. NHE), the value of which fits the linear correlation between the redox potentials and the $\mathrm{Ru^{II}}$–bpy MLCT wavenumbers for previously reported $\mathrm{[Ru(bpy)_2L]}$ complexes, eq 1.[5c]

$$E\ (\mathrm{cm^{-1}}) = 5242\ E\ (\mathrm{Ru^{III/II}},\ \mathrm{V\ vs.\ NHE}) + 16130 \qquad (1)$$

The E ($\mathrm{Ru^{III/II}}$) value is consistent with the red shift of the Ru–bpy MLCT band, reflecting the influence of the coordinated $\mathrm{CA^{2-}}$ ligand. Furthermore, theoretical calculation results[1a] support the assignment of the visible bands in terms of ruthenium(II)-to-ligands charge-transfer transitions predicted at 445–460 nm, involving three occupied and three unoccupied orbitals. Two of the occupied orbitals are predominantly $\mathrm{d}\pi$-metal orbitals with small contribution of orbitals of $\mathrm{CA^{2-}}$ [MO indexes 139 and 140], and the other orbital is the highest occupied MO [MO index 141] with remarkable contribution of orbitals of chloranilate. The unoccupied orbitals [MO indexes 142, 143, and 144] consist of π^*(chloranilate) and π^*(bpy) orbitals.[7] The three $\mathrm{d}\pi$ orbitals in the occupied orbitals are unstabilized by the electrostatic effect of $\mathrm{CA^{2-}}$, and the energy levels of the occupied ones are close to each other resulting in lower energy shift of the Ru–bpy MLCT band. The transition probabilities from 141 to the π^*(bpy) orbitals are much smaller than those from 139 and 140 because of symmetrically unfavorable overlapping, and thus, there is no character of $\mathrm{CA^{2-}}$ in the Raman spectrum. The calculation also reveals that the dipole moment for the ruthenium complex is as great as 36 D, which suggests a larger contribution of an ionic electronic structure $\mathrm{(Ru(bpy)_2{}^{2+})(CA^{2-})}$ in the ground state. Interestingly, we have found a blue shift for this CT band upon increasing solvent polarity, reflecting that stabilization of the polar ground state is greater than those for CT excited states in solvents with higher polarity.[7]

In conclusion, the present work demonstrates that chloranilic acid forms a stable mixed-ligand complex with bis(bipyridine)ruthenium(II), displaying a broad electronic band at lower energy associated with metal-to-ligands charge-transfer transitions. Moreover, the chloranilate ligand allows for the fine-tuning of the electronic structure of **1**. By the choice of a suitable non-innocent ligand, novel metal–quinone system will be constructed. In this case, it forms mononuclear ruthenium(II) complex with metal-free quinonoid end. Unutilized *o*-quinone may act as metalloligand unit to build up homo/hetero dinuclear or polynuclear complexes.

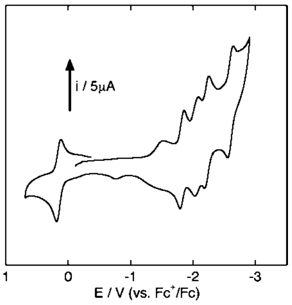

Figure 4. Cyclic voltammogram of **1** in $n\text{-}\mathrm{Bu_4NClO_4}$–DMF solution ($\mathrm{Ag/Ag^+}$ reference electrode was employed).

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6 Crystal data for $\mathrm{C_{28}H_{22}N_4O_5Cl_2Ru}$,[7] $M_\mathrm{r} = 666.48$, monoclinic, space group $C2/c$ (no. 15), $a = 11.847(4)$, $b = 15.514(3)$, $c = 14.996(3)$ Å, $\beta = 104.89(2)°$, $V = 2663.7(1)$ Å^3, $T = 296$ K, $Z = 4$, $\mu(\mathrm{Mo\,K\alpha}) = 0.837\ \mathrm{mm^2}$, 4057 reflections collected, 3888 unique ($R_\mathrm{int} = 0.0374$). $R_1 = 0.0407$ ($F^2 > 2\sigma(F^2)$); $wR_2 = 0.1176$ (all data); GOF = 0.947. CCDC 646535.

7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.