Structural Characterization of Ruthenium–Dioxolene Complexes with Ru^{II}–SQ and Ru^{II}–Cat Frameworks

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The structural and electronic properties of $[Ru^{II}(trpy)(ClSQ)(PPh_3)]^+$ (trpy = 2,2′:6′,2″-terpyridine; ClSQ = 4-chlorobenzosemiquinonate) and $[Ru^{II}(trpy)(ClCat)(PPh_3)]$ (ClCat = 4-chlorocatecholate) have been characterized by X-ray diffractometry, UV–vis spectroscopy, ESR, and electrochemistry.

Metal complexes that absorb photons strongly in the near-infrared (NIR) region are of considerable interest for chemical and material science because of their potentials in applications such as optical data processing.[1] Ruthenium–dioxolene complexes that display strong metal-to-ligand charge transition (MLCT) in the NIR region have been applied to redox-switching devices since their MLCT bands undergo significant changes depending on the oxidation state of the ruthenium–dioxolene frameworks.[2] The characteristic NIR absorption in the ruthenium–dioxolene framework is regulated by the balance between $d\pi$ orbital energy of ruthenium and π^* orbital energy of the dioxolene ligands, that is charge distribution.[3–5] Accordingly, the actual electronic structures of Ru–dioxolene complexes are often ambiguous because of close energy levels of metal-centered d orbital and ligand-based π^* orbital.

Recently, we have shown that proton dissociation of a $Ru–OH_2$ group in $[Ru(trpy)(dioxolene)(OH_2)]^{2+}$ (trpy = 2,2′:6′,2″-terpyridine, dioxolene = 3,5-di-*tert*-butylbenzosemiquinonate and 4-chlorobenzosemiquinonate) results in electron transfer from the group to the Ru–dioxolene framework to form the correspondent Ru–oxyl radical complex $[Ru(trpy)(dioxolene)(O^{\bullet -})]$, in which the actual electronic structure of the Ru–dioxolene framework is determined by C–O bond lengths of the dioxolene ligand, binding energy of Ru 3d orbital, and ESR spectra.[6] Furthermore, an ammine complex, $[Ru(trpy)(Bu_2SQ)(NH_3)](ClO_4)$ (Bu_2SQ = 3,5-di-*tert*-butylbenzosemiquinonate), has an ability to oxidize MeOH and *i*-PrOH catalytically under very mild conditions such as the electrolysis at 0 V (vs SCE) in CH_2Cl_2.[7]

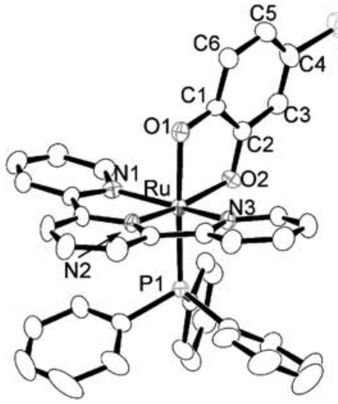

Figure 1. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

To our surprise, among various structural reports on the ruthenium–dioxolene system,[4–6,8] structural comparison of dioxolene ligands in different oxidation states has never been made within the same metal–ligand system. It should be noted, however, that the carbon–oxygen bond lengths of dioxolenes have been widely used to evaluate the oxidation state in some metal–dioxolene systems.[3] We now report, for the first time, on the structural difference in the C–O bond length between the Ru^{II}–SQ and Ru^{II}–Cat systems having the same metal–ligand framework; $[Ru(trpy)(ClSQ)(PPh_3)](ClO_4)$ ($(\mathbf{1})[ClO_4]$) (ClSQ = 4-chlorobenzosemiquinonate) and $[Ru(trpy)(ClCat)(PPh_3)]$ (**2**) (ClCat = 4-chlorocatecholate).

The ruthenium–dioxolene complex $[\mathbf{1}]^+$ was prepared by the reaction of *cis*-$Ru(trpy)(PPh_3)Cl_2$ with $ClCatH_2$ in the presence of 2 equivalent of NaOMe in MeOH followed by the oxidation with $AgClO_4$.[9] The reduction of $[\mathbf{1}]^+$ in THF with an excess amount of an aqueous sodium dithionite solution gave a reduced complex **2**. The X-ray photoelectron spectroscopy is one of the most effective method to estimate the oxidation state of Ru.[10] The $Ru(3d_{5/2})$ binding energies for $[\mathbf{1}]^+$ and **2** are observed at 280.7 and 280.3 eV, respectively, revealing that the oxidation states of $[\mathbf{1}]^+$ and **2** are Ru(II).[11]

The structures of $[\mathbf{1}]^+$ and **2** are essentially the same, that is, each complex has a distorted octahedral geometry with three nitrogen atoms of trpy, two oxygen atoms of the dioxolene ligand, and one phosphorous atom of the triphenylphosphine ligand (Figure 1).[12] The Ru–P(PPh_3) bond length of $[\mathbf{1}]^+$ (2.314(1) Å) is similar to that of **2** (2.307(2) Å). The bond lengths of three Ru–N(trpy) in $[\mathbf{1}]^+$ (2.059(4), 1.965(4), and 2.081(5) Å, respectively) are also comparable to those of **2** (2.059(6), 1.931(6), and 2.066(7) Å, respectively).

The two C–O lengths of $[\mathbf{1}]^+$ (1.289(7) and 1.304(7) Å) are apparently shorter than those of **2** (1.320(10) and 1.343(9) Å), reflecting the difference in the oxidation state at the dioxolene unit between $[\mathbf{1}]^+$ and **2**. The former is in the range of the Ru^{II}–SQ frameworks (ca. 1.29 Å),[4–6,8] and the latter is comparable to those of $Ru(Cp^*)(NO)$(2,3-naphthalenediolate) (1.342(9) and 1.345(9) Å).[13] The difference of the C–O bond length between the SQ and Cat states is also comparable to those of $Co(bpy)(Bu_2SQ)(Bu_2Cat)$ (1.297(9) Å for Bu_2SQ and 1.358(10) Å for Bu_2Cat: Bu_2Cat = 3,5-di-*tert*-butylcatecholate).[14] The difference of the Ru–O(dioxolene) bond lengths between $[\mathbf{1}]^+$ (2.092(4) and 2.082(4) Å) and **2** (2.102(5) and 2.120(6) Å) also reflects the change in the oxidation state at the dioxolene moiety.

The complex $[\mathbf{1}]^+$ exhibited a sharp isotropic ESR signal at

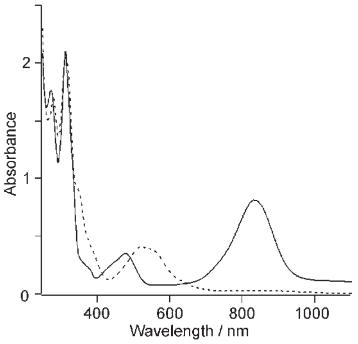

Figure 2. UV–vis spectra of the ruthenium–dioxolene complexes in CH_2Cl_2 at room temperature under N_2.[9] Solid line is $[\mathbf{1}]^+$ (8.1×10^{-5} mol dm^{-3}) and dashed line **2** (7.7×10^{-5} mol dm^{-3}).

$g = 2.00$ in CH_2Cl_2 at room temperature, whereas the catecholate complex **2** was found to be diamagnetic as expected. The complex $[\mathbf{1}]^+$ exhibited a strong absorption band at 832 nm (Figure 2),[9] whose transition energy is similar to those reported so far for Ru(trpy)(ClSQ)(OAc) (885 nm)[6] and other Ru^{II}–SQ complexes (750–950 nm).[4–8] Thus, the CT band of $[\mathbf{1}]^+$ is assigned to the MLCT transition from the dπ orbital of ruthenium(II) to the π^* orbital of the dioxolene ligand. On the other hand, the catecholate complex **2** exhibited an absorption band at 523 nm (Figure 2),[9] which must be viewed as related to the maximum absorption length reported for *cis*-Ru(trpy)(PPh_3)Cl_2 (530 nm).[15] Accordingly, the absorption band is assigned to the MLCT transition form the dπ orbital of ruthenium(II) to the π^* orbital of terpyridine ligand. The spectroscopic results strongly indicate that $[\mathbf{1}]^+$ and **2** have the Ru^{II}–SQ and Ru^{II}–Cat frameworks, respectively.

The complexes $[\mathbf{1}]^+$ and **2** both exhibited two redox couples at $E_{1/2} = -0.09$ and $+0.76$ V vs SCE, respectively. As expected from the Ru^{II}–SQ and the Ru^{II}–Cat frameworks of $[\mathbf{1}]^+$ and **2**, respectively, the equilibrium electrode potential of $[\mathbf{1}]^+$ was located at a potential between the two redox couples (+0.34 V), and that of **2** was positioned at the potential lower than the two redox couples (−0.22 V). As a result, the redox couples observed at −0.09 and +0.76 V are reasonably assigned to the Cat/SQ and Ru^{II}/Ru^{III} processes, respectively. In addition, electrochemical reduction of $[\mathbf{1}]^+$ in CH_2Cl_2 at −0.4 V gave a reduced species whose UV–vis absorption property is quite similar to that of **2**. By selecting the chloro-substituted dioxolene as the ligand, the redox potential based on the Cat/SQ couple was controlled in the region where both the reduced and the oxidized forms of the complex are stable enough to be isolated in their crystalline form.

In conclusion, we have succeeded for the first time to characterize the structural features of the Ru^{II}–SQ and Ru^{II}–Cat frameworks arising from a unique ruthenium–dioxolene system.

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9 For $[\mathbf{1}](ClO_4)$: Yield 40%. Found: C, 54.91; H, 4.11; N, 4.53%. Calcd for $C_{39}H_{29}N_3O_6Cl_2PRu{\cdot}(C_4H_{10}O_2)$: C, 55.61; H, 4.23; N, 4.52%. UV–vis: λ_{max}/nm (CH_2Cl_2) 274 (ε/dm^3 mol^{-1} cm^{-1} 21700), 313 (25900), 479 (4270), 832 (10000). ESR (CH_2Cl_2): $g = 2.00$. ESI MS (CH_2Cl_2): m/z 739 ($[M - ClO_4]^+$). For **2**: Yield 65%. Found: C, 63.36; H, 4.38; N, 5.38%. Calcd for $C_{39}H_{29}N_3O_2ClPRu$: C, 63.37; H, 3.95; N, 5.68%. UV–vis: λ_{max}/nm (CH_2Cl_2) 280 (ε/dm^3 mol^{-1} cm^{-1} 22200), 314 (27100), 523 (5250). ESI MS (CH_2Cl_2): m/z 739 ($[M]^+$).

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12 Crystal data: For $[\mathbf{1}](ClO_4){\cdot}(C_4H_{10}O_2)$: $C_{43}H_{39}N_3O_8Cl_2PRu$, $M_r = 928.75$, $T = 173$ K, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.566(1)$, $b = 16.937(1)$, $c = 20.062(2)$ Å, $\beta = 110.617(3)°$, $V = 3996.2(5)$ Å^3, $Z = 4$, μ(Mo Kα) = 6.25 cm^{-1}, Observed reflections 6368 ($I > 3\sigma(I)$), $R1$, $wR2 = 0.063$, 0.192. For **2**: $C_{39}H_{29}N_3O_2ClPRu$, $M_r = 739.17$, $T = 173$ K, monoclinic, space group $C2/c$ (No. 15), $a = 32.620(3)$, $b = 8.9988(7)$, $c = 26.998(2)$ Å, $\beta = 102.927(3)°$, $V = 7724(1)$ Å^3, $Z = 8$, μ(Mo Kα) = 5.51 cm^{-1}, Observed reflections 5501 ($I > 3\sigma(I)$), $R1$, $wR2 = 0.067$, 0.217. CCDC Nos. 245947 and 245948.

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