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Heteronuclear $Ru^{II}Ag^{I}$ Complexes Having a Pyrroloquinolinequinone Derivative as a Bridging Ligand

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Supporting Information

ABSTRACT: Herein, we report the synthesis of a novel heterohexanuclear complex (**1**) of a heteroaromatic cofactor, pyrroloquinolinequinone (PQQ). The crystal structure of **1** was determined to reveal that two PQQ-bridged $Ru^{II}Ag^{I}$ units were linked by two $[Ag^{I}(OTf)_2]^-$ units ($OTf = CF_3SO_3^-$). A solvent-bound $Ru^{II}Ag^{I}$ heterodinuclear complex (**2**) was formed from **1** in a coordinating solvent such as acetone to show an intense metal-to-ligand charge-transfer band at 709 nm.

Pyrroloquinolinequinone (4,5-dihydro-4,5-dioxo-1-*H*-pyrrolo[2,3-*f*]quinoline-2,7,9-tricarboxylic acid, PQQ) has been known as a redox-active heteroaromatic cofactor, which serves as a reactive site in quinoproteins such as bacterial alcohol dehydrogenases.[1] The reactivity of PQQ in catalytic alcohol oxidation in vivo is assisted by Ca^{2+} coordination by 5-oxo O, 6-pyridine N, and 7-carboxylate O atoms (ONO moiety) of PQQ (Figure 1a).[2] Because PQQ bears several potential metal-coordination sites in the structure (Figure 1b), to elucidate the characteristics of PQQ and to clarify a role of the coordinated Ca^{2+} ion in the biological activity, several metal complexes of PQQ have been synthesized and the redox behaviors of metal-bound PQQ investigated.[3,4] The properties, however, have yet to be well understood, and heteromultinuclear complexes have not been reported so far. Herein, we report the synthesis and crystal structure of a $Ru^{II}Ag^{I}$ heterohexanuclear complex (**1**) having two molecules of a PQQ derivative, a trimethyl ester of PQQ (PQQTME),[5] as a ligand. In the crystal structure, a couple of heterodinuclear units, $[\{Ru^{II}(terpy)(OH_2)\}(\mu\text{-PQQTME})\{Ag^{I}(OTf)_2\}]^+$ (terpy = 2,2′:6′,2″-terpyridine; $OTf^- = CF_3SO_3^-$), were demonstrated to be linked by two $[Ag^{I}(OTf)_2]^-$ units to form the novel heterohexanuclear complex **1**. We also investigated the optical and electrochemical properties of the heterodinuclear unit, $[\{Ru^{II}(terpy)(sol)\}(\mu\text{-PQQTME})\{Ag^{I}(OTf)_2\}]^+$ (**2**; sol = coordinating solvent), which was formed by dissolving **1** in a coordinating solvent and concomitant dissociation of the bridging $[Ag^{I}(OTf)_2]_2$ units (Scheme 1).

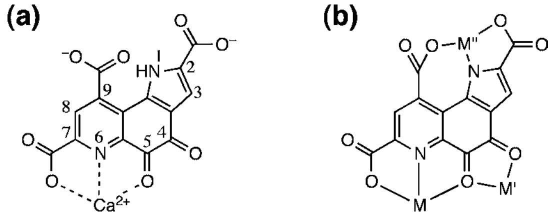
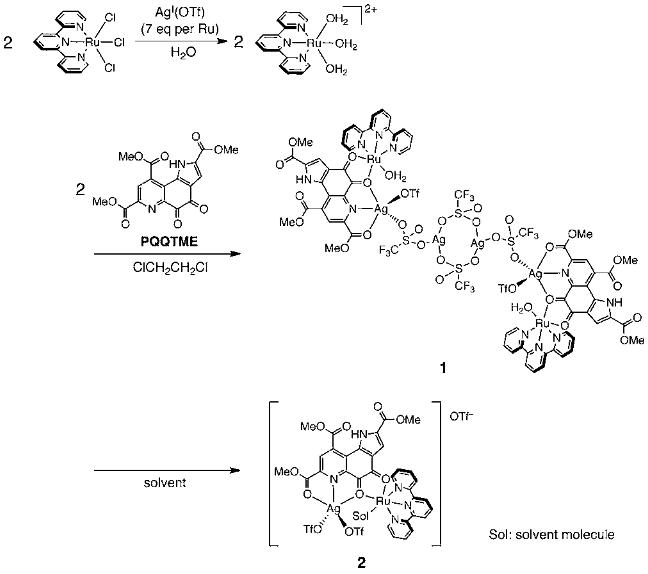


Figure 1. (a) Structure of a Ca^{2+}-bound PQQ. (b) Potential metal-coordination sites of PQQ.

Scheme 1. Synthesis of RuAg-PQQTME Complexes 1 and 2



PQQTME was synthesized with 4-amino-2-hydroxybenzoic acid as a starting material by the reported procedure.[6] The obtained PQQTME reacted in dichloroethane with $[Ru^{II}(terpy)(OH_2)_3](OTf)_2$, which was prepared by the treatment of $[Ru^{III}Cl_3(terpy)]$ with 7-fold molar excess amount of $Ag^{I}(OTf)$ per ruthenium in H_2O (Scheme 1).[7] The resulting solution was filtered, and the filtrate was slowly concentrated to obtain crystals of the heterohexanuclear bis-PQQTME complex **1** in 75% yield. The purity of **1** was confirmed by elemental analysis.[8]

The explicit structural determination of **1** was done by X-ray crystallography on a single crystal obtained by crystallization from the dichloroethane solution of the reaction mixture (Figure 2).[9] Complex **1** involves a PQQTME unit as a ligand in the asymmetric unit: The Ru^{II}(terpy) moiety coordinated to the *o*-quinone moiety of PQQTME. The bond distances between the

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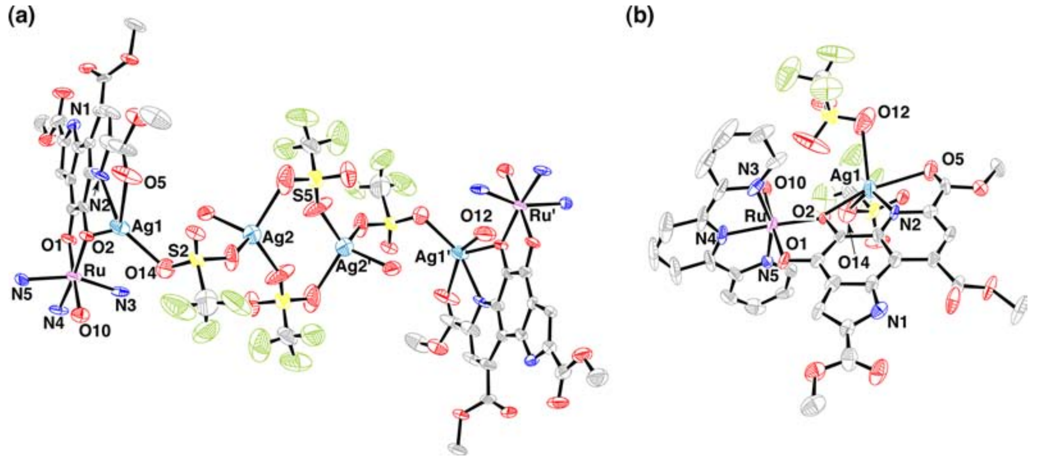

Figure 2. ORTEP drawings of the crystal structure of **1** with selected atom labeling. (a) Whole structure of **1**. The C atoms of the terpy ligand and trifluoromethyl groups, uncoordinating O atoms of OTf^- ions, and H atoms were omitted for clarity. Each atom is drawn with the thermal ellipsoid at the 30% probability. (b) Heterodinuclear unit of **1**.

Ru center and the terpy and PQQTME ligands are 1.975(6) Å for Ru−O1, 2.025(6) Å for Ru−O2, 2.059(10) Å for Ru−N3, 1.951(9) Å for Ru−N4, and 2.051(10) Å for Ru−N5. The distances strongly indicate that the electronic state of the Ru center is 2+. The last coordination site of the Ru^{II} center was occupied by an O atom with a bond distance of Ru−O10 of 2.081(9) Å, suggesting that the O atom is not a hydroxo but an aqua ligand.[10] An Ag(OTf) unit, which was derived from the excessive Ag^I(OTf) employed to remove the chloride ligands of $[Ru^{III}Cl_3(terpy)]$, was found to bind to the meridional tridentate part (ONO moiety) of PQQTME. This is the first example of a heterometallic PQQ complex whose crystal structure was determined. The Ag center resided in a distorted trigonal-bipyramidal coordination environment: The trigonal-equatorial plane consisted of two O atoms (O12 and O14) of two OTf^- ions and a N atom (N2) at the 6 position of the PQQTME ligand, and the two axial positions were occupied by two O atoms derived from the 5-oxo (O2) and 7′-ester carbonyl oxo (O5) ligands. The 5-oxo ligand (O2) was shared with both the Ru^{II} and Ag^I centers as bridging ligands. The bond lengths are 2.615(6) Å for Ag1−O2, 2.493(9) Å for Ag1−O5, 2.683(13) Å for Ag1−O12, 2.361(10) Å for Ag1−O14, and 2.343(10) Å for Ag1−N2. A comparison of the bond lengths with the reported corresponding values[11] allowed us to conclude that the oxidation state of the Ag ion was revealed to be 1+. The ion radii of Ag^I and Ca^{2+} ions are similar to each other, and the bond lengths between the Ag1 ion and the PQQ ligand in **1** were very close to the corresponding lengths between a Ca^{2+} ion and the PQQ cofactor in quinoproteins, for instance, 2.55 Å for Ca^{2+}-to-5-oxo, 2.40 Å for Ca^{2+}-to-6-nitrogen, 2.24 Å for Ca^{2+}-to-7-carboxylate, found in a crystal structure of methanol dehydrogenase.[12] In addition, two $[Ag^I(OTf)_2]^-$ units formed an eight-membered ring, which bridged two $[\{Ru^{II}(terpy)(OH_2)\}(\mu\text{-PQQTME})\{Ag^I(OTf)\}]^+$ moieties (Figures 2 and S1 in the Supporting Information, SI). In the crystal, the PQQTME ligand was found to interact with another PQQTME ligand of an adjacent molecule to form a $\pi-\pi$ stacking pair with an interplane distance of 3.47 Å (Figure S2a,b in the SI). Separately, the terpy ligand also formed a $\pi-\pi$ stacking pair with another terpy ligand in a neighboring molecule with an interplane distance of 3.42 Å (Figure S2c,d in the SI). The intermolecular $\pi-\pi$ interactions hold the crystal packing of **1**.

Dissolving complex **1** in a coordinating solvent such as acetone or CH_3CN caused dissociation of the bridging $[Ag^I(OTf)]_2$ ring to give the heterodinuclear complex **2** (Scheme 1). The ^1H NMR spectrum of **2** in acetone-d_6 showed distinctive signals by virtue of the diamagnetic character of **2** (Figure S3a in the SI). The spectrum was complicated despite the fact that the purity of the sample was confirmed by elemental analysis for complex **1**, and the signals could be derived from two species that are probably coordination isomers. By dissolving **1** in actone-d_6, two isomeric acetone-ligated complexes can be obtained, which should be distinguished by the position of the acetone ligand, as depicted in Figure S3b in the SI. The electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) spectrum of **2** in a mixed solvent of CH_3CN and water (2:3, v/v) gave a peak cluster at m/z 964.95, and the isotope distribution indicates that the detected ion contains both ruthenium and silver (Figure S4 in the SI). The computer simulation enabled the assignment of the peak cluster as $[\{Ru^{II}(terpy)\}(\mu\text{-PQQTME}^{\bullet-})\{Ag^I(OTf)\}]^+$ (calcd: m/z 964.92). The PQQTME ligand was probably reduced to be a semiquinone radical form in the course of ionization.

The UV−vis spectrum of **2** in acetone showed three intense absorption bands at 709, 465, and 379 nm (Figure 3).[13] On the basis of the time-dependent density functional theory (TD-DFT) calculations, the first and third absorption bands can be assigned to metal-to-ligand charge-transfer (MLCT) transitions from the Ru^{II} center to the PQQTME ligand (709 and 379 nm) and the second one is ascribed to another MLCT transition from the Ru^{II} center to the terpy ligand (465 nm) (Figure S7 in the SI).[14] The low-energy MLCT absorption band of the Ru^{II}-PQQTME complex indicates the highly stabilized π^* orbital of the PQQTME ligand.

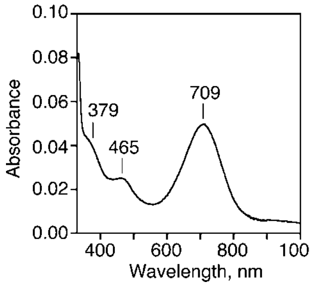

Figure 3. UV−vis spectrum of **2** in acetone at room temperature.

The redox behavior of **2** in tetrahydrofuran (THF; in the presence of 0.1 M [(*n*-butyl)$_4$N]PF$_6$ as an electrolyte) was clarified with the cyclic and differential pulse voltammograms (CV and DPV, respectively; see Figure S8 in the SI). In the electrochemical measurements, the rest potential was found to be +0.59 V vs SCE and a peak was observed at +0.50 V vs SCE in DPV. The CV of **2** showed an irreversible wave at the peak potential of +0.42 V vs SCE. The process is ascribed to the redox process of PQQTME$^{0/\bullet-}$, whose reduction potential exhibited a large positive shift relative to that of free PQQTME ($E_{1/2}$ = −0.53 V vs SCE)[15] and even that of a mononuclear Cu^{I}-PQQTME complex ($E_{1/2}$ = −0.10 V vs SCE).[3b] To confirm the assignment, we reduced complex **2** with 1 equiv of decamethylferrocene ($E_{1/2}$ = −0.04 V vs SCE)[16] in THF and measured the electron spin resonance (ESR) spectrum at 100 K (Figure S9 in the SI). In the spectrum, a signal was observed at g = 1.994, indicating the formation of a Ru^{II}-bound organic radical, that is, PQQTME$^{\bullet-}$.[3b,4] In addition, the DFT calculations also suggest that the lowest unoccupied molecular orbital (LUMO) of **2** is a π^* molecular orbital of the PQQTME ligand (Figure S10 in the SI). The large positive shift of the reduction potential of the PQQTME ligand of **2** was also caused by the coordination of both Ag^{I} and Ru^{II} centers, which resulted in a lowering of the energy level of the π^* orbital of the ligand as mentioned above.

In summary, we have succeeded in the first synthesis of a heterohexanuclear PQQTME complex (**1**), which involved both Ru^{II} and Ag^{I} centers. The crystal structure disclosed that the Ru^{II} center was coordinated by the *o*-quinone moiety of PQQTME and the Ag^{I} center was ligated with the meridional ONO unit of PQQTME. In addition, two Ru^{II}Ag^{I}PQQTME units were bridged by coordination of an eight-membered ring made of two [Ag^{I}(OTf)$_2$]$^-$ units. The electronic spectrum and electrochemical studies of the heterodinuclear Ru^{II}Ag^{I}PQQTME complex **2** derived from **1** indicate that the bimetallic complexation strongly affects the electronic characteristics of the PQQTME ligand, including a lowering of the energy level of the π^* orbital (LUMO in PQQTME) relative to that of the free PQQTME. The high reduction potential of the PQQTME ligand promises the application of **1** for oxidation of organic substrates, which can be coupled with the redox processes of the metal centers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data of **1** in CIF format, crystal packing of **1**, ^{1}H NMR spectrum of **2**, ESI-MS spectrum and CV and DPV of **2**, ESR spectrum of 1e$^-$-reduced **2**, and the details of the DFT studies of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(8) Anal. Calcd for $C_{72}H_{46}N_{10}O_{40}F_{24}S_8Ru_2Ag_4\cdot 2ClCH_2CH_2Cl\cdot 3H_2O$: C, 27.75; H, 1.84; N, 4.25. Found: C, 28.01; H, 2.11; N, 4.48. The synthetic details are described in the SI.

(9) Crystallographic data for **1**: $C_{36}H_{25}N_5O_{21}F_{12}S_4RuAg_2$, fw = 1536.66, green-brown, triclinic, $P\bar{1}$, a = 13.628(2) Å, b = 13.863(2) Å, c = 15.446(2) Å, α = 102.265(2)°, β = 100.557(2)°, γ = 96.661(2)°, V = 2766.5(7) Å^3, T = 120(2) K, Z = 2, D_c = 1.845 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, $R1$ = 0.0541 [$I > 2\sigma(I)$] and $wR2$ = 0.1377, GOF = 0.905. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 875390).

(10) The averages of bond distances of Ru^{II}−OH$_2$ and Ru^{II}−OH are in the ranges of 2.10−2.16 and 1.94−2.01 Å, respectively. For selected references, see: (a) Kobayashi, K.; Ohtsu, H.; Wada, T.; Kato, T.; Tanaka, K. *J. Am. Chem. Soc.* **2003**, *125*, 6729. (b) Yang, X.-J.; Drepper, F.; Wu, B.; Sun, W.-H.; Haehnel, W.; Janiak, C. *Dalton Trans.* **2005**, 256. (c) Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.

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(13) When the solution of **2** in acetone was kept overnight, the UV−vis spectrum was completely altered from that measured right after dissolving complex **1** in acetone (Figure S5a in the SI). The ESI-TOF-MS spectra of the acetone solution kept overnight (Figure S6 in the SI) suggested that the product giving the altered UV−vis spectrum was an acetone−adduct complex, which was obtained by the nucleophilic attack by an acetone molecule at the carbonyl C atom of the PQQTME ligand in **2** (Figure S5b in the SI). See ref 1d.

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