

A Dinuclear Zinc Complex, $[\text{Zn}_2(\mu\text{-H}_2\text{THBQ})(\text{TPA})_2](\text{ClO}_4)_2$, [TPA = Tris(2-pyridylmethyl)amine; $\text{H}_2\text{THBQ}^{2-} = 2,3,5,6\text{-Tetrahydroxy-1,4-benzoquinonate}$], Exhibiting Two-proton Coupled Two-electron Donating Ability

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The reaction of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with TPA and H_4THBQ in methanol gave air-sensitive crystalline powder $[\text{Zn}_2(\mu\text{-H}_2\text{THBQ})(\text{TPA})_2](\text{ClO}_4)_2$ (**1**). An equimolar reaction of **1** with 1,4-benzoquinone (BQ) in acetonitrile under Ar atmosphere quantitatively produced 1,4-hydroquinone and $[\text{Zn}_2(\mu\text{-RHOD})(\text{TPA})_2](\text{ClO}_4)_2$ (**2**) as a result of the 2H^+ , 2e proton-coupled electron-transfer (PCET) reaction.

Quinones, which occur widely in nature as well as biological system, are important functional material in an extensive area of industry.¹ Their diverse functions in biology and industry appertain to their abilities of electron and proton transfer. This fascinating proton-coupled redox property has been stimulating synthetic coordination chemists to create an operative molecule-based material that consists of polynuclear transition-metal complexes bearing quinone-frame ligand(s).² This is because such metal complexes could potentially show several interesting functionalities such as magnetism, intramolecular electron transfer, multiredox processes, redox-related catalytic activity, thanks to a variety of formal oxidation states not only for the metal centers but also for the ligand.³ From the view point of proton-coupled electron transfer (PCET),⁴ 2,3,5,6-tetrahydroxy-1,4-benzoquinone (H_4THBQ) is one of the most fascinating ligands, because the quinone can bridge two metal ions in the form of $[\text{M}(\mu\text{-H}_2\text{THBQ})\text{M}]$ which is in principle further capable of giving up two protons and two electrons to generate dinuclear species $[\text{M}(\mu\text{-RHOD})\text{M}]$, where RHOD^{2-} is rhodizionate. In fact, Miller et al. have recently reported dinuclear complex $[\text{Fe}_2(\mu\text{-H}_2\text{THBQ})(\text{TPA})_2]^{2+}$, which exhibits dual magnetic functions of a spin crossover with hysteresis and a ferromagnetic exchange.⁵ Although this structural motif $[\text{M}(\mu\text{-H}_2\text{THBQ})\text{M}]$ is expected to apply into other transition metals, to our best knowledge, no such example has been reported so far. In order to examine proton and electron donation ability of the $\mu\text{-H}_2\text{THBQ}$ unit, redox inactive zinc(II) was selected to construct the $[\text{M}(\mu\text{-H}_2\text{THBQ})\text{M}]$ core in this study. We herein report the first example of two-proton coupled two-electron donation ability of the newly synthesized complex $[\text{Zn}_2(\mu\text{-H}_2\text{THBQ})(\text{TPA})_2](\text{ClO}_4)_2$ (**1**).⁶ Another zinc complex $[\text{Zn}_2(\mu\text{-RHOD})(\text{TPA})_2](\text{ClO}_4)_2$ (**2**), which was obtained by a reaction of **1** with BQ, was also characterized by X-ray crystallography.

The cationic structure $[\text{Zn}_2(\mu\text{-H}_2\text{THBQ})(\text{TPA})_2]^{2+}$ determined by X-ray crystallography⁷ is shown in Figure 1, whose structural features are very similar to the Fe(II) derivative report-

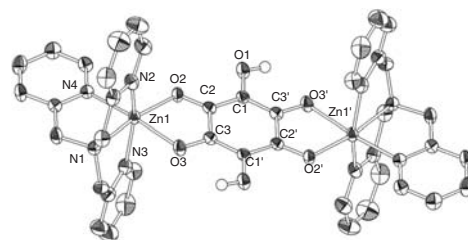


Figure 1. Perspective view of the complex cation $[\text{Zn}_2(\mu\text{-H}_2\text{THBQ})(\text{TPA})_2]^{2+}$ in **1**·4DMF.

ed by Miller. Complex **1**·4DMF resides on a crystallographically imposed center of symmetry, relating the primed and unprimed atoms. Each Zn(II) ion in the dinuclear core has a distorted octahedral geometry with the four N atoms of TPA and the two O atoms of $\text{H}_2\text{THBQ}^{2-}$ in the cis positions. Since the C1–O1 [$=1.365(4)$ Å] and the C2–C3 [$=1.533(3)$ Å] bonds of the C_6O_6 bridging ring are fixed as a single bond, two π electrons are treated as being delocalized on the three carbons C3, C1 and C2', resulting in the formation of 1.5 bond order for the C2–O2 [$=1.278(5)$ Å] and the C3–O3 [$=1.251(4)$ Å] bond pairs. The C–C (av 1.438 Å) and C–O (av 1.298 Å) bond distances in the C_6O_6 ring are very comparable to averaged C–C and C–O bond distances of metal-free H_4THBQ (av C–C = 1.438 Å, av C–O = 1.317 Å).⁸

The UV–vis spectrum measured in acetonitrile showed characteristic intense bands at 361 nm ($\epsilon = 30.8 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 232 nm ($\epsilon = 31.6 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), which are assigned to $\text{H}_2\text{THBQ}^{2-}$ -centered absorption, as well as a strong band centered at 255 nm ($\epsilon = 26.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), which is assigned to the TPA ligand absorption. Its green color in the solid state gradually changed to red in open air after several days, but the original green color in an acetonitrile solution immediately changed to deep red after being exposed to air. The oxidation process was monitored by BQ titration by means of UV–vis and ESI mass measurements. As shown in Figure 2, adding BQ into an acetonitrile solution containing **1** decreased the $\text{H}_2\text{THBQ}^{2-}$ -centered absorption and exhibited new characteristic bands at 450 and 496 nm. This spectral change was maintained until completion of adding equimolar of BQ with isosbestic points at 277, 311, and 390 nm, indicating that this reaction proceeded quantitatively without an intermediate species. The ESI mass spectrum of an acetonitrile solution of **1** (Figure S1 in Supporting Information)⁹

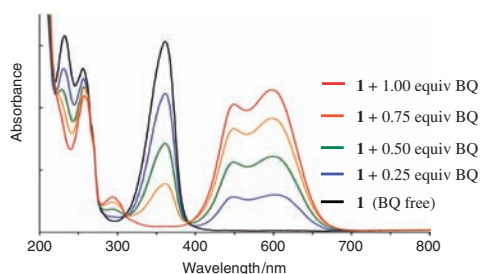


Figure 2. UV-vis spectral changes of **1** with adding BQ in CH₃CN.

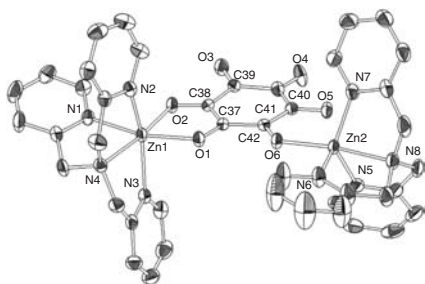


Figure 3. Perspective view of the complex cation [Zn₂(μ-RHOD)(TPA)₂]²⁺ in 2·3CH₃CN.

showed the strongest peak at $m/z = 981.1$ corresponding to [Zn₂(μ-H₂THBQ)(TPA)₂](ClO₄)⁺. On the other hand, this peak completely disappeared in the reaction mixture of **1** and BQ (=1:1), instead, a new peak appeared at $m/z = 979.1$, which was tentatively assigned to [Zn₂(μ-RHOD)(TPA)₂](ClO₄)⁺ as a result of 2H⁺, 2e PCET (Figure S2).⁹

To confirm the occurrence of 2H⁺, 2e PCET from the H₂THBQ²⁻ unit of **1** to BQ, RHOD²⁻-bridged dizinc complex [Zn₂(μ-RHOD)(TPA)₂](ClO₄)₂ (**2**) was independently synthesized¹⁰ as the authentic sample and was fully characterized (Figure 3).¹¹ The dinuclear unit [Zn₂(μ-RHOD)(TPA)₂]²⁺ has a lower symmetry than that of **1**; Zn1 has a distorted octahedral geometry and Zn2 is a trigonal bipyramidal with the occupation of O6 and N8 at its axial positions. Concerning bond distances of the C₆O₆ bridging ring, as expected, the distances of 1.215(4) and 1.208(4) Å (C39–O3 and C40–O4) and 1.518(4) Å for the C39–C40 are treated as a double bond and a single bond, respectively. However, the bond distance of 1.433(4) Å for the C37–C42 is longer than that expected for a localized double bond of rhodizone, indicative of the partial delocalization of two π electrons on the C38, C37, C42, and C41 carbons. This is also supported by the fact that the distances of 1.456(4) Å for the C37–C38 and 1.468(5) Å for the C41–C42 are slightly shorter than that expected for the ideal C–C single bond, and further, the remaining four C–O bonds [1.240(4)–1.275(4) Å] are of C–O 1.5 bond order. The averaged C–C (=1.475 Å) and C–O (=1.243 Å) bond distances in the C₆O₆ ring are very comparable to averaged C–C and C–O bond distances of metal-free H₂RHOD (av C–C = 1.460 Å, av C–O = 1.252 Å).¹² Since the two negative charges on the ring are partially delocalized on the adjacent O1, O2 and O5, O6 pairs, the coordination sites of the two Zn(II) ions are different from those of **1**.

Finally, the UV-vis spectrum of a 1:1 mixture of **2** and 1,4-hydroquinone in acetonitrile was measured (Figure S3).⁹ As expected, the spectrum was perfectly consistent with that of the re-

action mixture of **1** and BQ. This result and the presence of isosbestic points during the BQ titration led us to the conclusion that complex **1** functioned as a 2H⁺, 2e PCET donor for BQ to generate 1,4-hydroquinone, and thus this PCET took place in one step. It is most likely that complex **2** was produced as a result of the metal migration that occurred immediately after the PCET.

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References and Notes

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- 6 Synthetic procedure obtaining **1** is described in Supporting Information. Anal. Calcd for C₄₂H₄₂Cl₂N₈O₁₆Zn₂ (**1**·2H₂O): C, 45.18; H, 3.79; N, 10.04%. Found: C, 44.92; H, 3.95; N, 9.88%. Selected IR data (KBr): 3540, 3386, 1605, 1527, 1442, 1375, 1296, 1088 cm⁻¹. ¹³C NMR (125 MHz in *d*₃-acetonitrile): δ 61.74, 125.05, 125.69, 130.21, 141.16, 148.30, 155.20, 166.80.
- 7 Single crystals suitable for X-ray crystallography were obtained by recrystallization of **1** from DMF. Crystal data for **1**·4DMF: C₅₄H₆₆Cl₂N₁₂O₁₈Zn₂, $M_r = 1372.83$, triclinic, $a = 8.9806(13)$ Å, $b = 12.2669(17)$ Å, $c = 14.781(2)$ Å, $\alpha = 76.263(2)^\circ$, $\beta = 74.129(2)^\circ$, $\gamma = 71.428(3)^\circ$, $V = 1464.3(4)$ Å³, $T = 298$ K, space group *P*1̄ (#2), $Z = 1$, $\mu(\text{Mo K}\alpha) = 0.994$ mm⁻¹, of the 8918 which were collected, 6409 reflections with $I > 2\sigma(I)$ were used for calculation. Refinement converged with $R_1 = 0.0657$ and $wR_2 = 0.1694$, GOF = 1.054. CCDC-751665.
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- 9 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- 10 Synthetic procedure obtaining **2** is described in Supporting Information. Anal. Calcd for C₄₂H₄₀Cl₂N₈O₁₆Zn₂ (**2**·2H₂O): C, 45.26; H, 3.62; N, 10.05%. Found: C, 45.08; H, 3.57; N, 10.43%. Selected IR data (KBr): 3433, 1611, 1512, 1438, 1316, 1272, 1086 cm⁻¹. ¹³C NMR (125 MHz in *d*₃-acetonitrile): δ 60.10, 125.51, 125.97, 141.83, 149.05, 155.59, 175.60.
- 11 Single crystals suitable for X-ray crystallography were obtained under by recrystallization of **2** from acetonitrile. Crystal data for **2**·2CH₃CN: C₄₈H₄₅Cl₂N₁₁O₁₄Zn₂, $M_r = 1201.59$, orthorhombic, $a = 15.2483(10)$ Å, $b = 41.812(3)$ Å, $c = 16.5509(11)$ Å, $V = 10552.3(12)$ Å³, $T = 120$ K, space group *Pnma*, $Z = 8$, $\mu(\text{Mo K}\alpha) = 1.086$ mm⁻¹, of the 58826 which were collected, 12286 reflections with $I > 2\sigma(I)$ were used for calculation. Refinement converged with $R_1 = 0.0532$ and $wR_2 = 0.1317$, GOF = 1.041. CCDC-751666.
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