

## Novel Cu(I) Dinuclear Complexes Containing $\mu_2$ - $\eta^2$ , $\eta^2$ -Type Benzoquinone Ligand

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Quinonoid compounds are one of the most versatile redox-active organic molecules and have played a pivotal role in electron- and proton-transfer reactions.<sup>1</sup> Among compounds including these molecules, a combination of two redox pairs, copper(I)/copper(II) and *p*-benzoquinone (BQ)/hydroquinone (HQ), is the most interesting due to its biological roles<sup>2</sup> and catalytic activities<sup>3</sup> in addition to its rich electrochemistry.<sup>4</sup> Although BQ is a potentially bidentate olefin ligand to provide multinuclear complexes (Scheme 1), copper(I)–BQ complexes reported thus far are very rare,<sup>5</sup> which are expected to afford not only important information for intermediates in the Cu–BQ catalytic system but also rich redox chemistry based on a variety of formal oxidation states for both the metal centers and the ligand moiety. Herein we report the synthesis and structures of a novel copper(I) complex family containing a  $\mu_2$ - $\eta^2$ ,  $\eta^2$ -type BQ ligand, [Cu<sub>2</sub>(syn- $\mu_2$ - $\eta^2$ ,  $\eta^2$ -BQ)(OAc)<sub>2</sub>] (**1**), {[Cu<sup>I</sup><sub>2</sub>(anti- $\mu_2$ - $\eta^2$ ,  $\eta^2$ -BQ)Cl<sub>2</sub>(py)<sub>2</sub>]}<sub>n</sub> (**2**), and {[Cu<sub>2</sub>(syn- $\mu_2$ - $\eta^2$ ,  $\eta^2$ -BQ)(4,4'-bpy)]·0.5HQ}<sub>n</sub> (**3**), where compound **1** and **3** are first examples of syn-type Cu<sub>2</sub>–BQ complex.

A key to success in the synthesis of the syn-type Cu<sub>2</sub>–BQ complex **1** is the use of dimetallic copper(II) acetate, [Cu<sup>II</sup><sub>2</sub>(OAc)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>], and HQ as oxidant and reductant, respectively. The reaction of [Cu<sup>II</sup><sub>2</sub>(OAc)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] with HQ (1.2 equiv) in ethanol affords a red solution. Slow evaporation of the ethanol affords **1** as air-stable red plates (yield 95%).<sup>6</sup> The anti-type complex **2** is obtained by the replacement of two bridging acetate anions of **1** with chloride anions. The addition of pyridine and chloroform to the ethanol solution of **1** affords **2** as red prisms in one month (41%),<sup>7</sup> where chloroform acts as a supplier of chloride anions. On the other hand, a coordination polymer **3** was successfully obtained by linking **1** with 4,4'-bipyridine as a linear bidentate linker. The reaction of **1** with 4,4'-bipyridine and excess HQ results in the formation of **3** as air-stable red plates (35%).<sup>8</sup> All compounds were characterized by the X-ray crystallography.

The molecular structure of **1** is shown in Figure 1. The BQ ligand coordinates two Cu atoms in a syn- $\mu_2$ - $\eta^2$ ,  $\eta^2$  fashion. The two Cu atoms are bridged by one BQ and two acetates, forming a dicopper core (Cu<sub>2</sub>). The axial positions of the Cu<sub>2</sub> core are occupied by the weakly coordinated oxygen atoms from the neighboring Cu<sub>2</sub> units (Cu1–O6' 2.273(9) Å, Cu2–O1'' 2.294(8) Å). It is worth noting that the alkenic bonds of the BQ of **1** (C2–C3 1.42(2) Å, C5–C6 1.37(2) Å) are significantly longer than that of the free BQ (1.322 Å).<sup>9</sup> Measurements of the magnetic susceptibility of **1** at ambient temperature show diamagnetism, which corresponds to monovalent copper cations.

Figure 2 shows the molecular structure of **2**, where the BQ ligand sits in an anti- $\mu_2$ - $\eta^2$ ,  $\eta^2$  fashion. The Cu center has a distorted

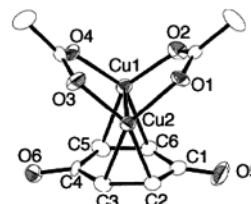


Figure 1. Molecular Structure of **1**. Cu–Cu distance is 2.730(3) Å.

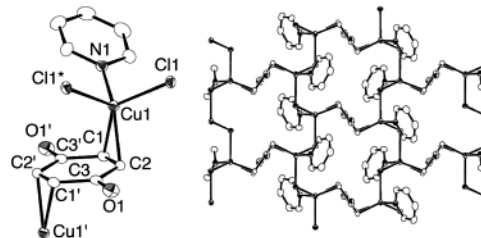


Figure 2. Molecular Structure of **2**.

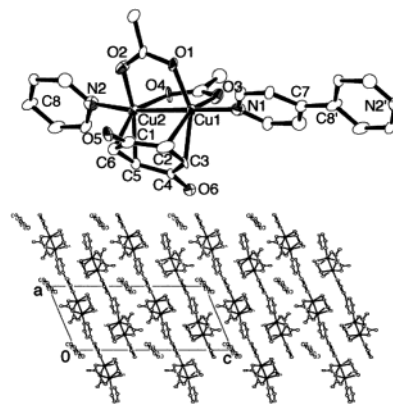
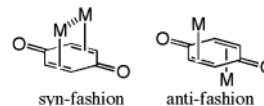


Figure 3. Molecular Structure of **3**. Cu–Cu distance is 2.733(3) Å.

### Scheme 1



tetrahedral environment with the two chloride atoms, one nitrogen atom, and an alkenic moiety from the BQ. The chloride anion also bridges the two Cu ions, forming a two-dimensional layer (Figure 2). The alkenic bonds of the BQ of **2** (1.383(3) Å) are also longer than that of the free BQ (1.322 Å).<sup>9</sup>

The molecular structure of **3** is shown in Figure 3. The Cu<sub>2</sub> dimetallic unit is constructed in a way similar to that of **1**. Like **1** and **2**, the alkenic bonds of the BQ of **3** (C2–C3 1.37(2) Å, C5–

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C6 1.41(2) Å) are longer than that of the free BQ (1.322 Å).<sup>9</sup> In the case of **3**, the axial positions of the Cu<sub>2</sub> unit are occupied by nitrogen atoms from the 4,4'-bpy to construct a one-dimensional coordination chain. To satisfy the crystal packing, one free HQ is contained per two Cu<sub>2</sub> units, hydrogen-bonded to carboxylate groups from the bridging acetate. (Figure 3).

One of the remarkable features of these Cu–BQ complexes is observed in their <sup>13</sup>C NMR studies. The <sup>13</sup>C CPMAS NMR spectra show the extremely large upfield shifts of the alkenic carbon atoms of the BQ (87.31 ppm for **1**, 95.46 ppm for **2**, and 88.72 ppm for **3**) compared to that of the metal-free BQ (136.55 ppm, CDCl<sub>3</sub> solution), indicative of the bond-order decrease in the alkenic bond, consistent with the trend in the crystallographic results. There have been to date some examples of <sup>13</sup>C NMR studies for copper(I)–olefin complexes,<sup>10</sup> in which the spectra show the upfield shifts of the alkenic carbon atoms compared with those of metal-free olefin. However, the magnitude of the upfield shifts for common copper(I)–olefin complexes are small because of weak  $\pi$ -back-donation from Cu(I) to the olefin ligand. To the best of our knowledge, these Cu–BQ complexes show the largest upfield shifts on coordination for the alkenic carbon atoms of the copper(I)–olefin complex ( $\Delta\delta = -49.24$  ppm for **1**,  $-41.09$  ppm for **2**, and  $-47.83$  ppm for **3**). Two electron-withdrawing carbonyl groups on each olefin bond in the BQ ligand enhance  $\pi$ -back-donation, which could be a principal reason for the large upfield shifts.

Compound **1** is soluble in polar organic solvents, such as methanol, ethanol, acetonitrile, and THF. The <sup>13</sup>C NMR chemical shifts of **1** in CD<sub>3</sub>OD are in good agreement with those in solid state and show 87.14 ppm chemical shift of the alkenic carbon atoms ( $\Delta\delta = -49.41$  ppm). The <sup>1</sup>H NMR spectrum of **1** in CD<sub>3</sub>-OD shows two peaks ( $\delta = 4.925$  (4H) and 1.819 (6H)), corresponding to hydrogen atoms from BQ and AcO<sup>-</sup>, respectively. The chemical shift of hydrogen atoms of  $\pi$ -coordinated BQ also shows the extremely large upfield shift compared to that of the metal-free BQ ( $\delta = 6.800$  ppm in CDCl<sub>3</sub> solution,  $\Delta\delta = -1.875$  ppm), corresponding to the results of <sup>13</sup>C NMR.

One of the best methods to elucidate the electronic structure is density functional theory (DFT) calculation on the *discrete* model compound based on the X-ray structure. However, **1** is not suitable for such a model compound because two adjacent Cu<sub>2</sub> cores are too close in the crystal packing with the result that the axial positions of the Cu<sub>2</sub> core are occupied by oxygen atoms from the neighboring Cu<sub>2</sub> units. Meanwhile, in the crystal of **3**, the axial positions of the Cu<sub>2</sub> core are occupied by nitrogen atoms from 4,4'-bpy (Figure 3), and there is no appreciable interaction between the two nearest-neighbor Cu<sub>2</sub> cores. Accordingly, we carried out the DFT calculation on the model compounds [Cu<sub>2</sub>(syn- $\mu_2$ - $\eta^2$ , $\eta^2$ -BQ)(OAc)<sub>2</sub>(py)<sub>2</sub>] (**3'**).<sup>11</sup>

The frontier orbitals for **3'** show that the HOMO is a  $\sigma^*$  orbital of the Cu<sub>2</sub> core; the LUMO is an antibonding orbital formed from a  $\pi^*$  orbital of the BQ and a  $\delta$  orbital of the Cu<sub>2</sub> core and mainly localized on the  $\pi^*$  orbital (Figure S1 in Supporting Information). The notable results of this calculation are the molecular orbitals for the HOMO-1 and -2, which obviously show the  $\pi$ -back-donation from  $\delta$  or  $\delta^*$  orbitals of the Cu<sub>2</sub> unit to  $\pi^*$  orbitals of the BQ. On this basis, the trend in upfield shifts of <sup>13</sup>C NMR of **3** is well reproduced by the calculation of the <sup>13</sup>C NMR on **3'** (Figure S2 in Supporting Information).<sup>13</sup>

This study represents the syntheses and structures of Cu(I) complexes containing the  $\mu_2$ - $\eta^2$ , $\eta^2$ -type benzoquinone ligand, which are synthesized by the redox reaction of a copper–quinonoid pair and may indicate a significant intermediate in the Cu–BQ catalytic system. Above all, we successfully synthesized the one-dimensional coordination polymer containing the Cu<sub>2</sub>–BQ cores, which is our first step toward the construction of microporous coordination network with reactive or catalytic sites. Moreover, this study is regarded as one of the good examples in Cu(I)–olefin families with the enhanced  $\pi$ -back-donation.

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**Supporting Information Available:** Frontier orbitals and calculation shifts of <sup>13</sup>C NMR for **3'**, <sup>13</sup>C CPMAS NMR spectra (PDF), and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) [Cu<sub>2</sub>(syn- $\mu_2$ - $\eta^2$ , $\eta^2$ -BQ)(OAc)<sub>2</sub>] (**1**). Anal. Calcd for C<sub>10</sub>H<sub>10</sub>Cu<sub>2</sub>O<sub>6</sub>: C, 34.00; H, 2.85. Found: C, 34.00; H, 2.77. Crystal data for **1**: monoclinic, *P*<sub>2</sub>/c, *a* = 10.45(1) Å, *b* = 7.565(7) Å, *c* = 15.61(2) Å,  $\beta$  = 103.45(1)°, *V* = 1200(1) Å<sup>3</sup>, *T* = 298 K, *Z* = 4, *R* = 0.070, *R*<sub>w</sub> = 0.067.
- (7) {[Cu<sub>2</sub>(anti- $\mu_2$ - $\eta^2$ , $\eta^2$ -BQ)Cl<sub>2</sub>(py)<sub>2</sub>]}<sub>n</sub> (**2**). Anal. Calcd for C<sub>8</sub>H<sub>8</sub>CuNOCl: C, 41.39; H, 3.04; N, 6.03. Found: C, 41.46; H, 3.02; N, 5.76. Crystal data for **2**: monoclinic, *P*<sub>2</sub>/c, *a* = 10.471(4) Å, *b* = 6.166(4) Å, *c* = 13.777(9) Å,  $\beta$  = 110.312(8)°, *V* = 834.5(9) Å<sup>3</sup>, *T* = 298 K, *Z* = 4, *R* = 0.0290, *R*<sub>w</sub> = 0.0395.
- (8) {[Cu<sub>2</sub>(syn- $\mu_2$ - $\eta^2$ , $\eta^2$ -BQ)(4,4'-bpy)]·0.5HQ]}<sub>n</sub> (**3**). Anal. Calcd for C<sub>23</sub>H<sub>21</sub>Cu<sub>2</sub>N<sub>2</sub>O<sub>7</sub>: C, 48.94; H, 3.75; N, 4.96. Found: C, 48.87; H, 3.73; N, 5.04. Crystal data for **3**: monoclinic, *P*<sub>2</sub>/c, *a* = 11.965(5) Å, *b* = 7.090(2) Å, *c* = 26.60(2) Å,  $\beta$  = 112.783(5)°, *V* = 2080(1) Å<sup>3</sup>, *T* = 298 K, *Z* = 4, *R* = 0.0714, *R*<sub>w</sub> = 0.0917.
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- (11) The geometric structure of **3'** was taken from X-ray crystal structure of **3** by the substitution of parent pyridines for pyridyl groups from 4,4'-bpy. The molecular orbital (MO) of **3'** was calculated within B3LYP functional along with the 6-31G\* bases (ref 12), using the Gaussian 98 program on an IBM RS/6000 workstation.
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- (13) In the calculation of the <sup>13</sup>C NMR chemical shielding of **3'**, the 6-31G\* basis was applied in the B3LYP method. For the <sup>13</sup>C NMR chemical shielding in the molecule, the chemical shielding constants were calculated in the coupled perturbed Hartree–Fock (CPHF) method with the gauge including atomic orbital (GIAO). The calculated chemical shift  $\delta$  for <sup>13</sup>C is defined by  $\delta = \sigma - \sigma_{\text{ref}}$ , where  $\sigma$  and  $\sigma_{\text{ref}}$  are the chemical shieldings in question and the reference, respectively. The calculated chemical shift is given relative to the reference, tetramethylsilane (TMS). For TMS, we also used the 6-31G\* basis in the B3LYP method, and calculated the shielding constants in CPHF method with GIAO.

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