Oxidative C—H and C—C Bond Cleavage by a (2,2′-Bipyridine)Copper(I) Chloride Complex

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Acetonitrile is easily oxygenated at ambient reaction conditions to copper(II) oxalate [Cu(bpy)(ox)]$_n$ mediated by copper(I) chloride in the presence of 3,5-di-*tert*-butylcatechol and 2,2′-bipyridine. In the case of other nitriles (e.g., propionitrile), instead, the unusual and selective 1,4-extradiol cleavage of 3,5-di-*tert*-butylcatechol occurs to give copper(II) *tert*-butylmaleate [Cu(bma)(bpy)(H$_2$O)]$_n$ in good yield.

Scheme 1. The Formation of Complex **1**

Copper(I) chloride in the presence of amines constitutes an efficient and also industrially important oxidizing/oxygenating system with dioxygen.[1] The stoichiometry of the reaction of CuCl and amines with O$_2$ is Cu/O$_2$ = 4:1, leading to [CuCl(amine)]$_4$O$_2$.[2] The industrially used oxidative coupling of phenols to aromatic polyethers[3] or diphenoquinone[4] is an important process, and catalysts of this type have biological importance too because they mimic tyrosinase,[5] catechol oxidase,[6] and catechol dioxygenase.[7]

We and others have found previously that catechols can be oxidized to *o*-quinones[8] or cleaved to *cis,cis*-muconic acids[9] by dioxygen in the presence of copper catalysts. It is also known that catechols can be aminated to give *o*-aminophenols,[10] and we looked for possible catalysts for this reaction. During the course of these studies, we observed surprisingly that the solvent acetonitrile used had been oxygenated. When copper(I) chloride in the presence of 3,5-di-*tert*-butylcatechol (dtbcH$_2$) or 3,5-di-*tert*-butyl-1,2-benzoquinone and 2,2′-bipyridine (bpy) in acetonitrile as the solvent is reacted with dioxygen (Scheme 1), the pale-green compound of [Cu(bpy)(ox)]$_n$ (**1**) (ox = oxalate) is obtained after recrystallization in 46% yield. Complex **1** is paramagnetic, with electron paramagnetic resonance (EPR) parameters of $g_{\parallel}$ = 2.173 and $g_{\perp}$ = 2.070 at 77 K. The structure of [Cu(bpy)(ox)]$_n$ was proved by spectroscopic data and X-ray crystal structure determination (Figure 1), and the data found were slightly different from those observed earlier.[11] The 2,2′-bipyridine(μ-1,2,3,4-oxalato)copper complex is composed of polymeric chains of [Cu(bpy)]$^{2+}$ ions bridged by

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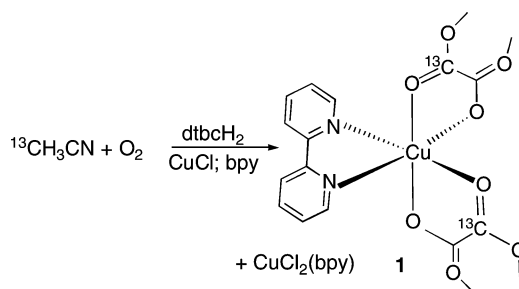(3) Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 505–517.
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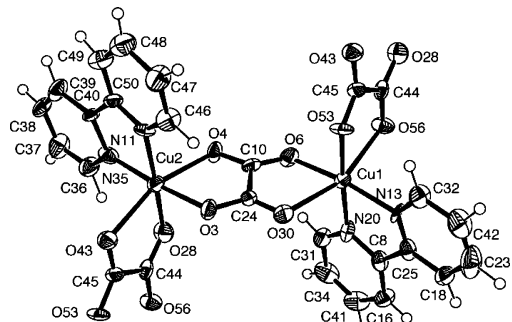
Figure 1. The molecular structure of **1** with selected bond distances (Å) and angles (deg): Cu(1)−O(6) 1.9556(7), Cu(1)−O(53) 1.993(8), Cu(1)−N(13) 2.029(7), Cu(1)−N(20) 2.024(10), Cu(1)−O(30) 2.327(7), Cu-(1)−O(56) 2.317(7), Cu(2)−N(35) 1.942(10), Cu(2)−N(11) 1.999(8), Cu(2)−O(28) 1.980(9), Cu(2)−O(3) 2.005(7), Cu(2)−O(43) 2.310(8), Cu(2)−O(4) 2.300(7), O(6)−Cu(1)−O(53) 91.1(4), O(6)−Cu(1)−O(30) 76.8(3), N(13)−Cu(1)−N(20) 80.5(4), N(35)−Cu(2)−N(11) 81.3(4), O(28)−Cu(2)−O(43) 77.8(3), O(3)−Cu(2)−O(4) 79.1(3). See also the Supporting Information.

**Scheme 2.** The Formation of Complex **2**
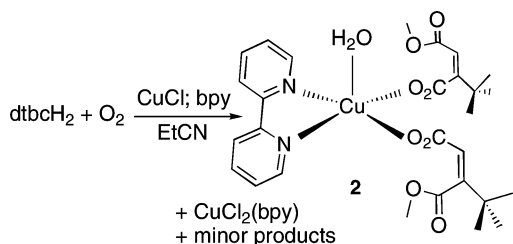
oxalate anions. The neighboring two copper centers have slightly different geometries. The results show that acetonitrile has been oxygenated to oxalate under very mild conditions by the copper dioxygen complex(es) formed, which is unprecedented.

When, instead of acetonitrile, propionitrile, isobutironitrile, or benzilnitrile was used as the solvent, no oxygenation of the solvent was observed. Instead, the dtbcH$_2$ was oxygenated to the copper(II) *tert*-butylmaleate complex [Cu(bma)(bpy)-(H$_2$O)]$_n$ (**2**) (bmaH$_2$ = *tert*-butylmaleic acid) (Scheme 2) in 42% yield. It forms a polymer where the *tert*-butylmaleate acts as a bridging ligand between the Cu(II) centers (Figure 2). The complex is paramagnetic with EPR parameters of $g_{||}$ = 2.270, $g_\perp$ = 2.050, and $^{Cu}A_{||}$ = 177 G at 77 K. The spectrum is axial with a g value consistent with a distorted square-pyramidal CuN$_2$O$_2$O′ chromophore present with a τ
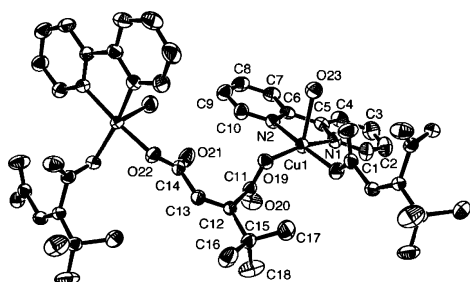
Figure 2. The molecular structure of **2** with selected bond distances (Å) and angles (deg): Cu(1)−N(1) 2.003(2), Cu(1)−N(2) 1.992(2), Cu(1)−O(19) 1.9691(1), Cu(1)−O(22_4) 1.952(2), Cu(1)−O(23) 2.371(2), N(1)−Cu-(1)−O(19) 165.74(9), N(2)−Cu(1)−O(22) 172.87(9), N(1)−Cu(1)−O(23) 94.90(10), O(19)−Cu(1)−O(23) 99.17(9). See also the Supporting Information.
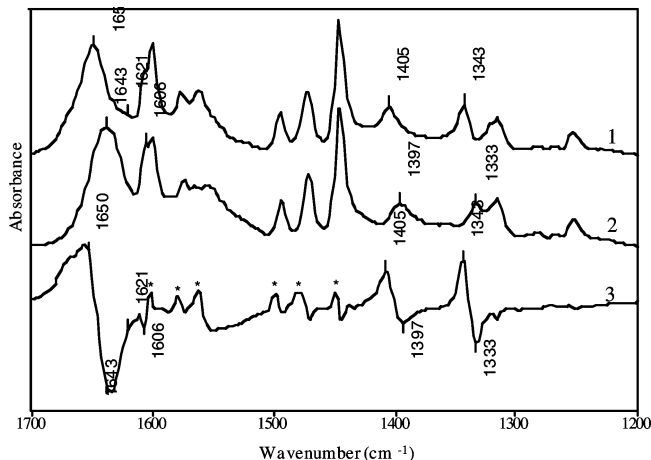
Figure 3. Result of the spectral subtraction (3) of the unlabeled (1) and ^{18}O-labeled (2) complexes. (*Since the bpy bands are exhibiting small frequency shifts in different complexes, it was difficult to compensate them fully.)

value of 0.12.[12] Its UV−vis spectrum shows bands at λ_{max} = 260 (log ε = 3.78), 302 (4.03), and 423 (1.61) nm and IR absorptions of $\nu_{CO2(as)}$ = 1645 and $\nu_{CO2(s)}$ = 1374 cm^{-1}, proving monodentate carboxylate coordination. The two monodentate carboxylato groups of the maleate are in basal positions [Cu−O 1.952(2) and 1.9691(19) Å] together with the two N atoms of bpy [Cu−N 1.992(2) and 2.003(2) Å]. The carboxylate groups are coordinated to another copper(II) ion, forming a linear polymer. In the apical position is an O atom of a water molecule with a Cu−O distance of 2.371(2) Å. The half amount of the copper ions weighted in was obtained as CuCl$_2$(bpy), and its molecular structure was proved by IR spectrum and X-ray analysis and found to be identical with former literature data.[13]

In order to prove that acetonitrile has been oxygenated, we carried out the reaction with ^{13}CH$_3$CN and ^{18}O$_2$ as well. Analysis of the infrared and Raman spectra of the products using ^{13}C- and ^{18}O-labeled compounds gave an answer to this question.

The IR spectra in the CO$_2$ stretching region are presented in Figure 3. The most isotope-sensitive bands were the CO stretching modes, which are summarized in Table 1.

DFT quantum chemical calculations were made for the bidentate coordinated oxalate ligand to Cu^{2+} with a general C_{2v} point group common for both asymmetrically labeled oxalate ions. The isotope-sensitive band positions were determined from the difference spectra of **1**−**1a** and **1**−**1b**, where the bands of different isotopes appeared in the opposite directions (see, e.g., Figure 3). In all cases, the second derivatives were also compared to obtain more accurate band positions and frequency shifts.

The highest-frequency IR band (ν_7) at 1650, 1643, and 1644 cm^{-1} for the **1**, **1a**, and **1b** complexes, respectively, exhibited isotope shifts 7 (9) and 6 (11) cm^{-1} for ^{18}O and ^{13}C labeling where, in parentheses, the calculated band displacements are given.

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Table 1. Infrared CO Stretching Frequencies (cm^{-1}) of Coordinated Oxalate Ion

no	$[Cu(bpy)(ox)]_n$ (**1**)		complex using $^{12}CH_3CN + {}^{18}O_2$ (**1a**)		complex using $^{13}CH_3CN + {}^{16}O_2$ (**1b**)		assignments[a]
	observed	calculated	observed	calculated	observed	calculated	
v_7	1650	1659	1643 (7)	1650 (9)	1644 (6)	1648 (11)	CO_2 asym stretch
v_1	1621	1625	1606 (15)	1611 (11)	1591 (30)	1588 (37)	CO_2 asym stretch
v_2	1405	1427	1397 (8)	1414 (13)	1373 (32)	1413 (14)	CO_2 asym stretch
v_8	1343	1326	1333 (10)	1302 (24)	1329 (14)	1313 (13)	CO_2 asym stretch

[a] Assignments based on DFT calculations simplified as $Cu({}^{16}O_2{}^{12}C{}^{12}C{}^{16}O_2)Cu$ (**1**), $Cu({}^{16}O_2{}^{12}C{}^{12}C{}^{18}O_2)Cu$ (**1a**), and $Cu({}^{16}O_2{}^{13}C{}^{12}C{}^{16}O_2)Cu$ (**1b**) labeled complexes. In parentheses, the isotope shifts are listed.

The next band (v_1) around 1600 cm^{-1} has a complex structure due to the solid-state splitting, and in addition, it overlaps with bpy ligand vibration. The band showed a strong (15 cm^{-1}) isotope shift for **1a** and an even stronger one (30 cm^{-1}) for the **1b** complex. The calculated shifts were 13 and 37 cm^{-1} for ^{18}O- and ^{13}C-labeled complexes, respectively.

The medium IR band at 1405 cm^{-1} showed the strongest isotope shift for the ^{13}C isotopic species (over 32 cm^{-1}), which is the v_2 asymmetric CO_2 stretching, while the calculated isotope shift was only 14 cm^{-1}. Due to the rather complex nature of the spectra, we are still not sure about the assignment of the band at 1373 cm^{-1} for the ^{13}C isotope species.

Following the acetonitrile oxidation reaction by UV−vis spectroscopy (SFigure 2, Supporting Information), it can be seen that a band at ∼400 nm evolves and after a certain time decreases. 3,5-Di-*tert*-butyl-1,2-benzoquine is formed and then reduced by the substrate back to the catechol again just acting as an electron-transfer mediator. The mechanism of the stoichiometric formation of complexes **1** and **2** is at the moment not fully understood. Copper(I) chloride in the presence of amines with O_2 forms complexes of $[CuCl-(amine)]_4O_2$.[17] The methyl group is oxygenated to the formyl group and then to the carboxylate group. The cyano group is then hydrolyzed to the carboxylato group, resulting in oxalate, which coordinates to the copper(II) centers.[18] In the case of propionitrile as the solvent, 3,5-di-*tert*-butylcatechol undergoes a 1,4-oxidative cleavage of the aromatic ring, giving the copper(II) maleate complex **2**.[21] The mild oxygenation of the C−H bond in acetonitrile to oxalate represents to our knowledge the first case for this type of reaction under very mild conditions,[22] and the 1,4-oxidative cleavage of 3,5-di-*tert*-butylcatechol leading to *tert*-butyl-maleate is the first straightforward and selective reaction of catechol oxygenation of this kind. The role of 3,5-di-*tert*-butylcatechol in the oxygenation of acetonitrile to oxalate is to be an electron-transfer mediator in a coupled catalytic system as found in many cases in the oxidation of organic substrates by dioxygen or dihydrogen peroxide.[23]

Supporting Information Available: Full synthetic details of all of the compounds, CIF files, and O_2-uptake experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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