

C–C Bond Cleavage of Acetonitrile by a Dinuclear Copper(II) Cryptate

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Molecular recognition has been defined as a process involving both binding and selecting of substrate(s) by a given receptor molecule.¹ Polyaza cryptands, incorporating tripodal skeleton groups, possess two binding subunits located at the two poles of the structure, so they can act as good receptors for linear molecular recognition.² These cryptands are also capable of dinuclear metal coordination, and these dinuclear centers have in turn been shown to recognize various bridging anions such as μ -OH⁻,^{3,4} μ -CO₃⁻,⁵ μ -OCN⁻,⁶ μ -N₃⁻,⁷ and μ -im⁻ (im⁻ = imidazolate anion).⁸ Recently, Krämer⁹ reported that a dinuclear macrocyclic copper compound shows high recognition for the cyanide anion and can be used as a cyanide-selective electrode.

The activation of carbon–carbon bonds by transition metal complexes in homogeneous media remains a challenge in the field of organometallic chemistry.¹⁰ In most cases, metals catalyze the hydration of nitriles to amides.¹¹ However, Parkin¹² has shown recently that photolysis of [Me₂Si(C₅Me₄)₂]MoH₂ in the presence of acetonitrile results in oxidative addition of the C–C bond of acetonitrile to form [Me₂-Si(C₅Me₄)₂]Mo(Me)(CN). Jones¹³ also showed that reaction of [(dippe)NiH]₂ with benzonitrile leads to (dippe)Ni(Ph)(CN) oxidative addition. More recently, Brookhart¹⁰ reported that a cationic Rh(III) complex [Cp*(PMe₃)Rh(SiPh₃)(CH₂-Cl₂)]BAR₄' activates the carbon–carbon bonds of aryl and alkyl cyanides (R–CN, where R = Ph, (4-(CF₃)C₆H₄), (4-(OMe)C₆H₄), Me, ⁱPr, ^tBu) to produce complexes of the general formula [Cp*(PMe₃)Rh(R)(CNSiPh₃)]BAR₄'. The above activation of C–C bonds is accomplished by air-sensitive metallorganic compounds through an η^1 - or η^2 -nitrile intermediate, probably due to the high affinity of molybdenum, nickel, and rhodium for carbon atoms. We report here a novel C–C bond cleavage of acetonitrile by an air-stable dinuclear copper(II) cryptate at room temperature, where the activation of the C–C bond is due to the favorable formation of a stable cyanide bridged dinuclear copper(II) cryptate.

The dinuclear copper(II) cryptate [Cu₂L](ClO₄)₄, **1**, was prepared¹⁴ by the reaction of L and Cu(ClO₄)₂·6H₂O in methanol (L = N[(CH₂)₂NHCH₂(C₆H₄-*p*)CH₂NH(CH₂)₂]₃N). When [Cu₂L](ClO₄)₄ was dissolved in acetonitrile, and the solution was allowed to evaporate slowly at room temperature, an unexpected cyanide bridged complex [Cu₂L(CN)](ClO₄)₃·2CH₃CN·4H₂O, **2**, was obtained. An X-ray crystallographic analysis¹⁵ reveals that the two copper(II) ions in **2** are bridged by a cyanide anion (Figure 1). Each Cu(II) ion is five-coordinated with a slightly distorted trigonal bipyramid geometry, in which Cu(1) is coordinated with four nitrogen atoms on one side of L and one bridged cyanide nitrogen atom, and Cu(2) is coordinated with four nitrogen atoms from the other side of L and one bridged cyanide carbon atom. The Cu(1)–N_{cyanide} bond length (2.039(6) Å) is longer than the Cu(2)–C bond length (1.975(5) Å), while it is shorter than the other Cu–N_{cryptand} bond lengths (2.090(4)–2.160(4) Å). The two bridgehead nitrogen

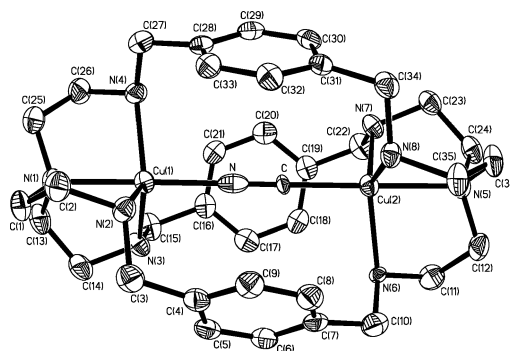


Figure 1. ORTEP drawing of the [Cu₂L(CN)]³⁺ cation in **2**. Thermal ellipsoids are drawn at the 30% level.

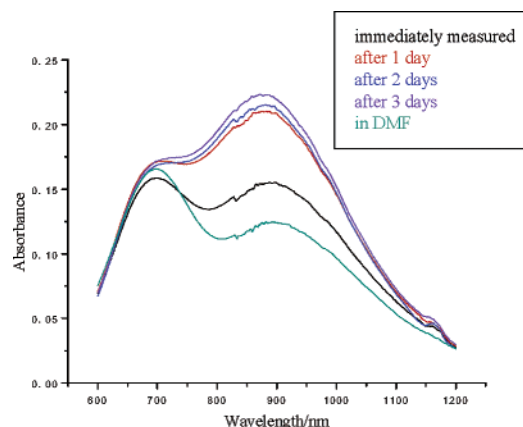


Figure 2. The electronic spectra of **1** in acetonitrile at room temperature as a function of time.

atoms, two Cu(II) ions, and cyanide anion are almost collinear with N(1)–Cu(1)–N, Cu(1)–N–C, N–C–Cu(2), and C–Cu(2)–N(2) angles of 179.3(2), 179.6(4), 179.5(5), and 179.1(2)°, respectively. The C–N distance of 1.150(6) Å and Cu(1)···Cu(2) separation of 5.163 Å are comparable to those in other cyanide bridged dinuclear copper(II) complexes.¹⁶

The electronic absorption spectra of **1** and **2** show maximum absorption bands at 699 nm in DMF and 887 nm in acetonitrile, respectively, indicating that the geometry of copper(II) is a compressed tetrahedral in **1** and a trigonal bipyramidal in **2**.¹⁷ When KCN solid was added to a solution of **1** in acetonitrile, the color of the solution changed quickly from blue to emerald green, and the maximum absorption band of the solution coincided with that for **2**, indicating that the cyanide bridged dinuclear copper(II) complex formed very quickly. To monitor the cleavage process, **1** was dissolved in acetonitrile, and the electronic absorption spectra were recorded at room temperature as a function of time. The results are shown in Figure 2. Initially, the electronic absorption spectrum shows two bands at 700 and 889 nm with similar intensity, indicating some of **1** reacts quickly to **2** in acetonitrile. After about

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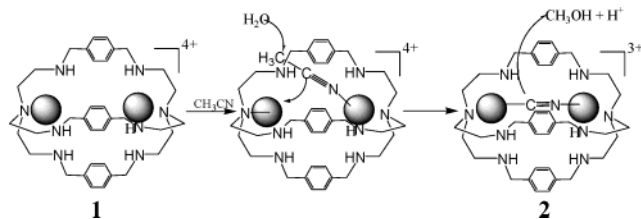


Figure 3. Possible cleavage mechanism.

1 day, the absorption spectrum is similar to that of pure **2**, indicating that complex **1** reacted completely to form complex **2**. After that, the absorption spectra did not change with further standing.

Formation of the cyanide bridged dinuclear copper complex in acetonitrile was also confirmed by ESI-MS spectroscopy on a Thermo Finigan LCQDECA XP ion trap mass spectrometer (see Supporting Information S1). Initially, an acetonitrile solution of **1** shows three peaks due to $[\text{Cu}_2\text{L}]^{3+}$, $[\text{Cu}_2\text{L}]^{2+}$, and $[\text{Cu}_2\text{L}(\text{ClO}_4)]^+$. After the solution was heated at 50 °C in a sealed tube for 1 day, the above three peaks are not observed, and three new signals attributed to $[\text{Cu}_2\text{L}(\text{CN})]^{3+}$, $[\text{Cu}_2\text{L}(\text{CN})]^+$, and $[\text{HL}]^+$ are observed. The appearance of $[\text{HL}]^+$ is probably due to the reduction of Cu(II) to copper metal during the ionization process.

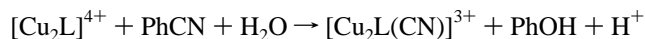
The cleavage reaction involves the C–C bond activation of acetonitrile, and we employed GC (Varian CP3800) spectra to investigate the new species formed in acetonitrile solution. The results (see Supporting Information S2) indicate that methanol is formed when an acetonitrile solution of **1** was left at room temperature in a sealed tube for 1 day. This experiment demonstrates that methanol is produced during the cleavage reaction of **1** with acetonitrile.

On the basis of the above experimental results, a likely cleavage mechanism is presented in Figure 3. In this process, the nitrogen atom of acetonitrile binds to one Cu(II) atom through its electron pair, and the other Cu(II) atom interacts with the filled π orbital of the sp-hybridized acetonitrile carbon, resulting in electron flow from the π bond to the Cu(II) atom, and this increases the “leaving ability” of cyanide and the electrophilicity of the methyl carbon, and results in cleavage by water to form methanol and cyanide bridged complex **2**.

The cleavage rate is determined spectrophotometrically at $\lambda = 890$ nm and 20 °C (see Supporting Information S3). In the presence of excess acetonitrile, the rate law can be described as $dC_A/dt = -k_{\text{obsd}}C_A$, where C_A is the concentration of **1**, and $k_{\text{obsd}} = k_2[\text{H}_2\text{O}]^\alpha$. At the lower concentration of water (0.167 M), the plot of $-\ln C_A$ versus time reveals a line in the 0–90 min time range whose slope (k) is equal to $1.52 \times 10^{-4} \text{ s}^{-1}$ ($t_{1/2} = 76$ min). After 90 min, the plot shows curvature. The reaction rates become larger along with the increasing concentrations of water, and the plots show a straight line with no curvature over 3 half-lives. These experiments clearly indicate the first-order dependence on water. The calculated second-order rate constant (k_2) and α value are $1.76(1) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ and 0.084(2), respectively.

Under similar reaction conditions, there is no reaction between $[\text{Cu}(\text{tren})](\text{ClO}_4)_2$ and acetonitrile (see Supporting Information S4);

this is a clear demonstration that the activation of the C–C bond of acetonitrile is due to the favorable formation of a stable cyanide bridged dinuclear copper(II) cryptate. This mechanism is different from those reported involving η^1 - or η^2 -nitrile intermediates.^{10,12,13} Currently, we are investigating the C–C bond activation of other alkyl and aryl cyanides by **1**. Preliminary results indicate that **1** can also cleave the C–C bond of benzonitrile at room temperature to produce phenol and the cyanide bridged complex $[\text{Cu}_2\text{L}(\text{CN})](\text{ClO}_4)_3$:



Here, the cleavage rate for benzonitrile is much faster than that for acetonitrile as the cleavage reaction appears instantaneous upon mixing **1** and benzonitrile as assessed by ESI-MS spectra.

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Supporting Information Available: Synthesis and characterization of compounds **1** and **2**, the crystallographic data for complex **2** (CIF), ESI-MS, GC, and kinetics data for complex **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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