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Mechanistic Studies of C–C Bond Cleavage of Nitriles by Dinuclear Metal Cryptates

Li-Zi Yang,^[a] Yu Li,^[a] Xiao-Mei Zhuang,^[a] Long Jiang,^[a] Jia-Mei Chen,^[a]
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Abstract: We previously reported that dinuclear copper(II) cryptate $[\text{Cu}_2\text{L}]^{4+}$ cleaves the C–C bond of acetonitrile at room temperature to produce a cyano-bridged dinuclear cryptate and methanol, whereby the reaction mechanism has not yet become clear. We have now systemically investigated this reaction, and four cryptates, $[\text{Cu}_2\text{L}](\text{ClO}_4)_4$ (**1**), $[\text{Zn}_2\text{L}](\text{ClO}_4)_4$ (**2**), $[\text{Cu}_2\text{L}(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_4$ (**5**), and $[\text{Cu}_2\text{L}(\text{OH})(\text{OH}_2)]-$

$(\text{ClO}_4)_3$ (**6**) are reported here. Cryptates **1** and **2** can cleave the C–C bonds of acetonitrile, propionitrile, and benzonitrile at room temperature under open atmospheric conditions to give cyano-bridged cryptates $[\text{Cu}_2\text{L}(\text{CN})]-$

Keywords: C–C activation • copper • cryptands • reaction mechanisms • zinc

$(\text{ClO}_4)_3$ (**3**) and $[\text{Zn}_2\text{L}(\text{CN})](\text{ClO}_4)_3$ (**4**), respectively, and the corresponding alcohol. In contrast, **5** and **6** do not show any C–C bond activation of nitriles, as the interior axial positions of Cu^{II} in **5** and **6** are occupied by water/ OH^- . The C–C bond cleavage of (*S*)-(+)-2-methylbutyronitrile by **2** produced (*R*)-(-)-2-butanol only; that is, the cleavage reaction proceeds through an $\text{S}_{\text{N}}2$ pathway (Walden inversion).

Introduction

Activating and transforming covalent bonds are key processes in organic and organometallic chemistry. Recent studies indicate that supramolecular receptors bearing appropriate reactive groups in addition to binding sites may act like enzymes to activate and transform the binding substrate under mild conditions.^[1] In general, supramolecular activation and transformation involve two steps: first, recognition of a substrate by a receptor; second, transformation of the bound substrate into product within the receptor–substrate complex. Polyaza cryptands which incorporate tripodal skeleton groups have two binding subunits located at the two extremities of the structure, as well as their dinuclear metal cryptates, have been shown to act as good receptors for the rec-

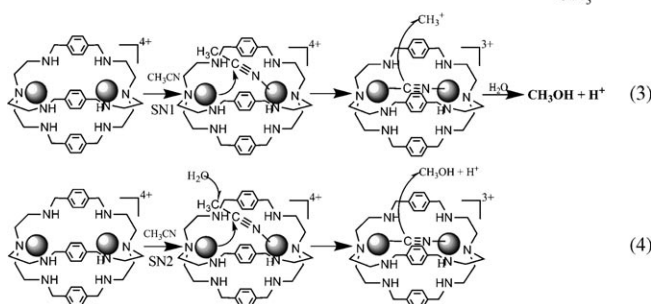
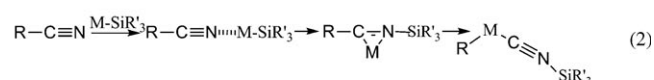
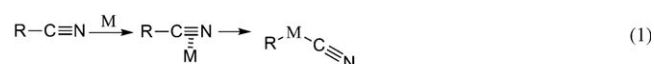
ognition of various molecules and anions.^[2] The recognition interaction of a receptor with a substrate may activate a reactant containing a substrate group, and transform the reactant into the receptor–substrate complex and product.

The inherent stability of carbon–carbon σ bonds makes their cleavage by transition metal complexes a daunting challenge,^[3b,e] and successful cases have been mainly observed in systems assisted by ring strain or chelation.^[4] In the case of nitriles, metals mostly catalyze their hydration to amides.^[5] However, recent studies indicate that the C–C bonds of nitriles (note that C–C bond herein refers only to the C–C bond adjacent to the $\text{C}\equiv\text{N}$ moiety) can be cleaved by some air-sensitive organometallic complexes under various reaction conditions.^[3] Mechanistic studies indicate that the cleavage of C–C bonds of nitriles by such complexes occurs mainly through two distinct pathways (Equations (1) and (2) in Scheme 1).^[3k] In Equation (1), oxidative addition of a C–C bond of a nitrile to a low-valent metal center affords an alkyl(aryl) cyano complex. For instance, Jones et al. have reported reactions of $[(\text{dippe})\text{NiH}]$ (dippe = bis(dialkylphosphanyl)ethane) with acetonitrile and benzonitrile via an η^2 -nitrile Ni^0 intermediate to generate $[(\text{dippe})\text{Ni}(\text{Me})(\text{CN})]$ and $[(\text{dippe})\text{Ni}(\text{Ph})(\text{CN})]$, respectively.^[3e,q] In Equation (2), insertion of a cyano group into the metal–silicon bond via a 2-nitrile intermediate generates an alkyl(aryl) silylisocyanide complex, and in this process, observed by Brookhart and co-workers,^[3o,p] insertion of a cyano group

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200901610>.



Scheme 1.

into a Rh^{III} -silyl bond in RhSiR'_3 forms the η^2 -nitrile intermediate, which undergoes de-insertion of silyl isocyanide to afford the C–C cleavage complex $[(\text{R})\text{Rh}(\text{CNSiR}'_3)]$. The above cleavage of C–C bonds achieved by air-sensitive organometallic compounds via an η^2 -nitrile intermediate is probably due to the high affinity of nickel and rhodium for carbon atoms.

Previously, we demonstrated that the receptor of dinuclear copper(II) cryptate $[\text{Cu}_2\text{L}](\text{ClO}_4)_4$ (**1**) can cleave the C–C bond of acetonitrile at room temperature to produce a stable receptor–substrate complex of a cyano-bridged dinuclear cryptate and methanol.^[6] The above cleavage reaction can occur by two possible pathways: $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$. On the $\text{S}_{\text{N}}1$ pathway, $[\text{Cu}_2\text{L}]^{4+}$ first cleaves the C–C bond of CH_3CN to give CH_3^+ and CN^- , followed by transformation of CH_3^+ into CH_3OH in the presence of water (Equation (3) in Scheme 1). Indeed, cleavage of CH_3CN into CH_3^+ and CN^- by a mononuclear Cu^{II} complex has been previously reported.^[7] On the other hand, simultaneous cleavage of the C–C bond of CH_3CN by $[\text{Cu}_2\text{L}]^{4+}$ and water via an $\text{S}_{\text{N}}2$ pathway can also afford $[\text{Cu}_2\text{L}(\text{CN})]^{3+}$ and CH_3OH (Eq. (4) in Scheme 1). Our previously reported experimental results^[6] did not allow us to determine whether the C–C bond cleavage reaction proceeds according to Equation (3) or Equation (4). Additionally, we also experienced difficulty in replicating this reaction.^[8]

Following up on our previous studies on the recognition and activation of small guest molecules by cryptates and protonated cryptands,^[6,9] and in order to clarify the mechanism of C–C bond cleavage by $[\text{Cu}_2\text{L}]^{4+}$, as well as to discover the missing subtle aspect that would lead to such radically different results, we have systemically investigated the reactivity and mechanism of **1** and $[\text{Zn}_2\text{L}](\text{ClO}_4)_4$ (**2**) in the C–C bond cleavage of a variety of nitriles.

Results and Discussion

Crystal structures of $[\text{Zn}_2\text{L}(\text{CN})](\text{ClO}_4)_3$ (4**) and $[\text{Cu}_2\text{L}(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_4$ (**5**):** The structure of $[\text{Cu}_2\text{L}(\text{CN})](\text{ClO}_4)_3$ (**3**) was previously reported.^[6] Single-crystal X-ray crystallographic analysis reveals that **4** has a similar structure to **3** (Figure 1a), in which two Zn^{II} ions are bridged by a disordered cyanide ligand with each atom site of the CN group comprising 50 % C and 50 % N. Each Zn^{II} ion in **4** is five-coordinate, bonded to four nitrogen atoms of **L** and one bridging cyanide C/N atom. The τ parameters for the geometries^[10] of both five-coordinate Zn^{II} ions are 1.0, where $\tau = 1.0$ for trigonal bipyramidal (TBP) and 0.0 for square pyramidal (SP), that is, the geometries of both Zn^{II} ions are ideal TBPs. In **4**, the two bridgehead nitrogen atoms, two Zn^{II} ions, and cyanide anion are almost collinear. The C–N distance of 1.141(5) Å in **4** is not significantly different to that of 1.155(6) Å in **3**, whereas the $\text{Zn}1 \cdots \text{Zn}2$ separation of 5.230(1) Å is slightly longer than the $\text{Cu}1 \cdots \text{Cu}2$ separation

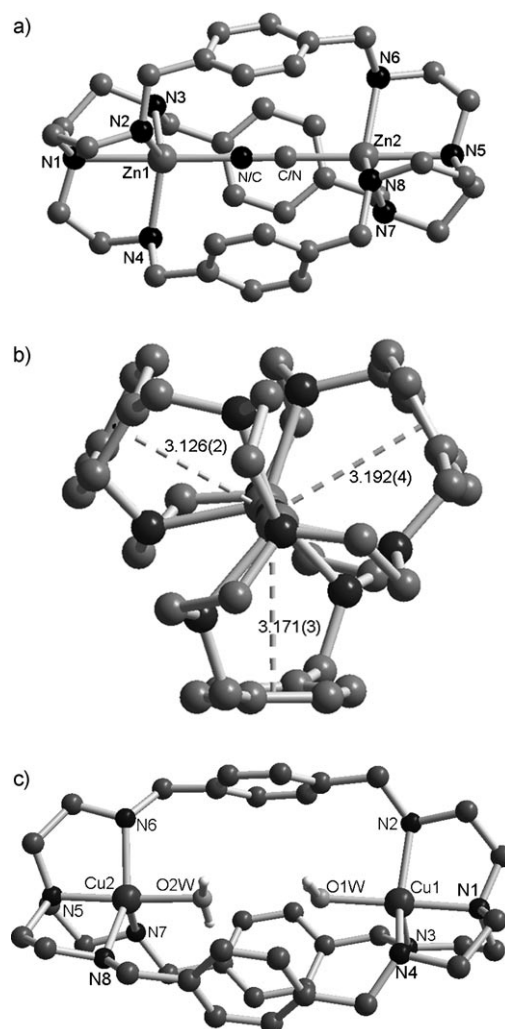


Figure 1. a) Structure of $[\text{Zn}_2\text{L}(\text{CN})]^{3+}$ in **4**. b) Centroid–centroid distances between cyano bridge and the three phenyl rings. c) Structure of $[\text{Cu}_2\text{L}(\text{H}_2\text{O})_2]^{4+}$ in **5**.

of 5.163(1) Å in **3**; the longer Zn1...Zn2 distance is probably due to the larger size of a five-coordinate Zn^{II} ion (0.82 Å for Zn^{II} and 0.79 Å for Cu^{II}). The average centroid...centroid distance from the cyano bridge to the three phenyl rings is only 3.16(3) Å (Figure 1b). This distance is less than the van der Waals radii of two carbon atoms (3.40 Å) or "C+N" atoms (3.25 Å), and indicates the existence of interactions between the p_z orbitals of the phenyl rings and the p orbitals of the cyano bridge. This is confirmed by DFT calculations on [Zn₂L(CN)]³⁺ in **4**.

In **5**, the axial positions of two five-coordinate Cu^{II} ions are occupied by two water molecules (Figure 1c), and the geometries of the two Cu^{II} ions are TBPs. The Cu–N (bridgehead) distances (1.991(5) and 1.999(5) Å) are close to the Cu–O distances (1.996(4) and 1.998(4) Å), which are shorter than the other Cu–N distances (2.098(5)–2.205(5) Å). The O1W...O2W distance of 3.032 Å is longer than the O1...O1' separation of 2.665(6) Å in [Co₂L(OH)(OH₂)]³⁺,^[9a] and much longer than the O1...O1' separation of 2.325(9) Å in [Cu₂L(OH)(OH₂)](ClO₄)₃ (**6**), in which the axial positions of the two Cu^{II} ions are occupied by OH[−] and H₂O, respectively.^[8a] The short O...O separation in [Cu₂L(OH)(OH₂)]³⁺ was attributed to cryptate encapsulation squeezing the bridge.^[8a] The structures of **5** and [Co₂L(OH)(OH₂)]³⁺^[9a] illustrate the axial flexibility of the cryptate ligand. The Cu...Cu and Co...Co distances of 7.013(1) Å in **5** and 6.482(2) Å in [Co₂L(OH)(OH₂)]³⁺ are substantially longer than the Cu...Cu separation in [Cu₂L(OH)(OH₂)]³⁺ (6.121(1) Å),^[8a] that is, the Cu...Cu separation in [Cu₂L]⁴⁺ can be expanded to encapsulate different sizes of guest molecules within its cavity, and a squeezing effect does not exist in [Cu₂L]⁴⁺.

DFT calculations: The frontier orbitals and H-28 bonding orbital of [Zn₂L(CN)]³⁺ are shown in Figure 2, which illustrates that the LUMO and HOMO are mainly based on the ligand L (88% for the LUMO and 93% for the HOMO, see Table S2 in the Supporting Information). Figure 2 also depicts some orbital overlap between the cyano bridge and the phenyl rings in the H-28 bonding orbital, and the contribution of the cyano bridge to the orbitals increases from 4% in the HOMO to 13% in the H-28 bonding orbital (Table S2, Supporting Information), that is, it is favorable to form a stable receptor ([Zn₂L]⁴⁺)–substrate (CN[−]) complex of [Zn₂L(CN)]³⁺. To our knowledge, this may be the first report of orbital overlap between a cyano group and a phenyl ring. The natural electron charges on the free CN[−] ion are −0.246 for the C atom and −0.754 for the N atom. In [Zn₂L(CN)]³⁺, these are reduced to values of −0.081 and −0.723 for the C and N atoms, respectively, which indicate significant donation from the μ-CN[−] group to Zn^{II} after formation of cyano-bridged cryptate **4**.

Reactivity of [Cu₂L]⁴⁺: We previously communicated that dinuclear copper(II) cryptate **1** could be prepared by the reaction of L and Cu(ClO₄)₂·6H₂O in anhydrous methanol (method I), and that **1** cleaves the C–C bond of acetonitrile

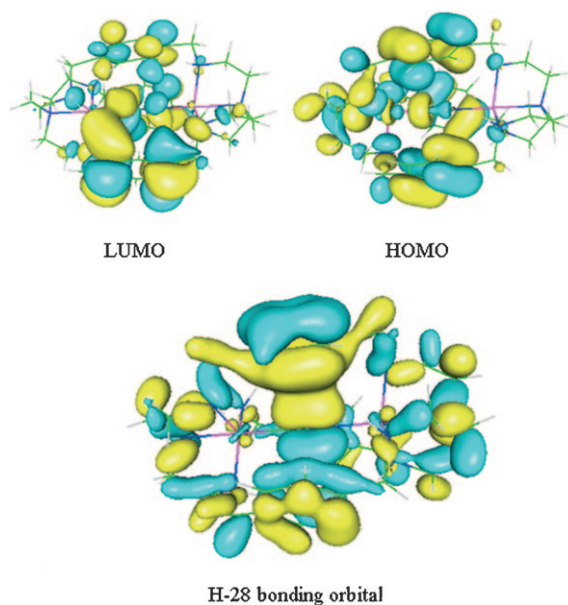


Figure 2. Schematic diagrams of the frontier orbitals and H-28 bonding orbital of [Zn₂L(CN)]³⁺ in **4**.

at room temperature to produce **3** and methanol.^[6] Reported difficulties^[8] in replicating this reaction may be related to moisture sensitivity, as the axial positions of [Cu₂L]⁴⁺ are easily occupied by water or OH[−] groups to give cryptate **5** or **6**. In fact complex **5** was obtained serendipitously (see Experimental Section). Despite repeated attempts employing different solvent combinations, we have not been successful in obtaining crystals of **1** and **2**. These attempts result in unidentified powders, oil-like precipitates, or crystals of **5** or [Cu₂L(OH)(OH₂)](ClO₄)₃ (**6**).^[8a] We discovered that cryptates **5** and **6** are incapable of cleaving the C–C bond of nitriles. Indeed, there is competition between water and nitrile molecules for the inner axial positions of [Cu₂L]⁴⁺. Water molecules can either easily enter the cavity of [Cu₂L]⁴⁺, perhaps assisted by H-bonding to sites on ligand L, or by already being bonded to Cu²⁺ before cryptation. Essentially, once these inner axial positions of [Cu₂L]⁴⁺ are occupied by water or OH[−] groups, the complex is incapable of cleaving the C–C bond of nitriles. This suggests that scrupulously dry conditions must be employed to afford complex **1** and **2** with empty axial positions on both Cu^{II} and Zn^{II} atoms, respectively, in order to demonstrate C–C bond cleavage of nitriles.

We found that using nitrate as the starting material in anhydrous methanol (method II, see Experimental Section for the preparations of **1** and **2**) more reliably results in cryptate **1** than method I, and axially deficient cryptates **1** and **2** prepared by method II always display reactivity towards C–C bond cleavage of nitriles. Therefore, we used **1** and **2** prepared by method II to investigate the cleavage reactions in this report. Our previous study^[6] showed that the ESI-MS spectrum of **1** in acetonitrile contains three peaks assigned as [Cu₂L]³⁺, [Cu₂L]²⁺, and [Cu₂L(ClO₄)]⁺, which are no longer observed after heating the solution at 50 °C for one

day, and new signals attributed to $[\text{Cu}_2\text{L}(\text{CN})]^{3+}$ and $[\text{Cu}_2(\text{L-2H})(\text{CN})]^+$ are observed. Further investigations indicated that anhydrous **1** can also cleave the C–C bond of other nitriles at room temperature, and the cleavage reaction appears to be instantaneous on mixing **1** with propionitrile (Figure 3a) or benzonitrile (Figure S1a, Supporting Information). Additionally, cryptate $[\text{Zn}_2\text{L}](\text{ClO}_4)_4$ (**2**) shows similar cleavage capability to cryptate **1** for the C–C bond in acetonitrile, benzonitrile, and propionitrile, as evidenced by ESI-MS spectra.

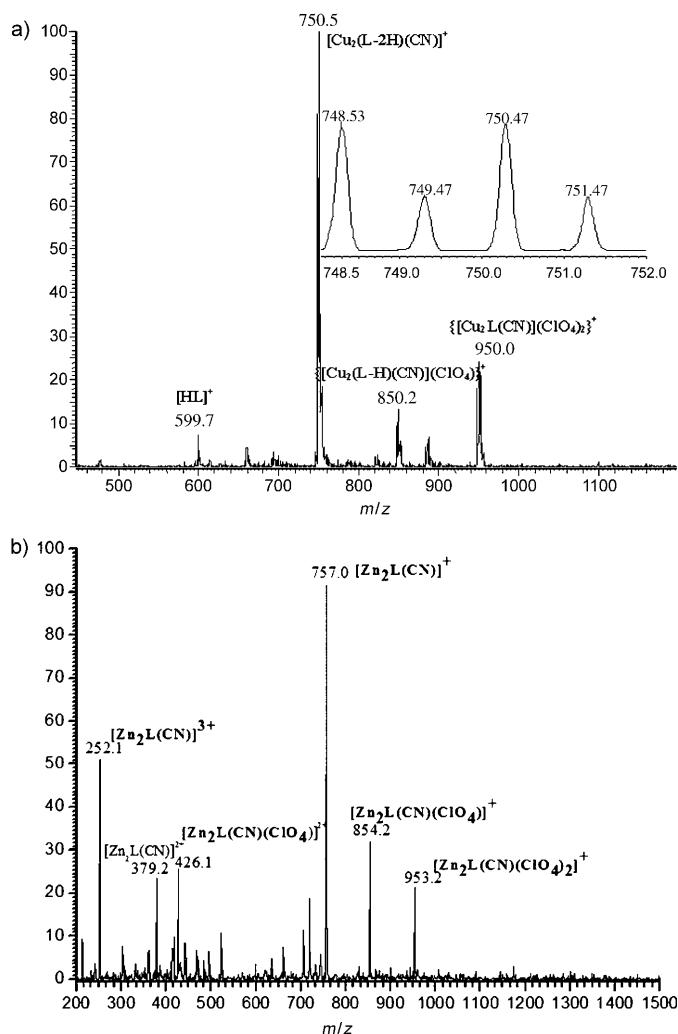


Figure 3. ESI mass spectra of a) **1** and b) **2** in propionitrile; the absence of species corresponding to $[\text{Cu}_2\text{L}]^{4+}$ and $[\text{Zn}_2\text{L}]^{4+}$ indicates that the cleavage reaction appears to be instantaneous on mixing **1** or **2** with propionitrile

Spectra and cleavage rate constant: The IR spectra of **3** and **4** exhibit weak absorptions due to the bridging cyano group^[8b] at 2134 and 2157 cm^{-1} , respectively, which indicate that cyano-bridged cryptates of **3** and **4** were formed. The electronic absorption spectrum of cryptate **1** in HPLC-grade acetonitrile is similar to that obtained for **1** in AR-grade acetonitrile,^[6] that is, the initial maximum peak around

700 nm slowly changes to 890 nm over one day on standing at room temperature. However, if **1** is dissolved in benzonitrile or propionitrile, the electronic absorption spectrum obtained is similar to that for **3** (Figure 4), with a maximum around 890 nm for benzonitrile and 880 nm for propionitrile. This confirms that the cleavage reaction is instantaneous on mixing **1** with benzonitrile or propionitrile.

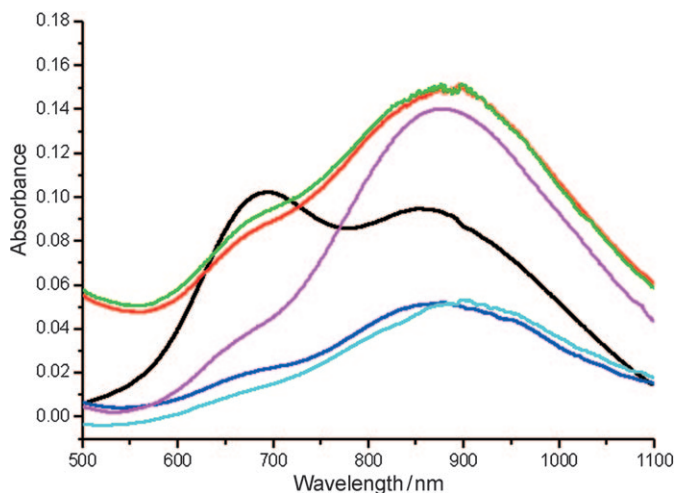


Figure 4. Electronic spectra of **1** in acetonitrile (black line, immediately measured; pink line, after one day), benzonitrile (green line, immediately measured; red line, after one day), and propionitrile (deep blue line, immediately measured; light blue line, after one day).

Measurements by GC (see Figure 5) indicate that methanol, ethanol, and phenol are produced when solutions of **1** in acetonitrile (HPLC grade), propionitrile (99 %), and benzonitrile (HPLC grade) were left at room temperature. This suggests that methanol, ethanol, and phenol are produced during the cleavage reactions of **1** with acetonitrile, propionitrile, and benzonitrile, respectively. Dissolution of **2** in acetonitrile, propionitrile, and benzonitrile also results in the formation of methanol, ethanol, and phenol, as evidenced by GC.

The cleavage rate constant of **1** with acetonitrile was previously determined by measurements of the electronic absorption spectra at $\lambda=890$ nm for the appearance of **3** at 20 °C,^[6] with $k_{\text{obsd}}=1.52 \times 10^{-4} \text{ s}^{-1}$ ($t_{1/2}=76$ min). As complexes **2** and **4** do not display absorptions in the visible region, the cleavage rate constant of acetonitrile by **2** was determined by measuring the concentration of methanol in solution at 20 °C by GC (Supporting Information, Figure S2). In the presence of an excess of acetonitrile, the reaction exhibits ideal pseudo-first-order kinetics. The rate law can be described as $dC_A/dt = -k_{\text{obsd}}C_A$, where C_A is the concentration of **2** at time t . Plotting $-\ln C_A$ versus time gives a line in the 0–60 min time range whose slope k is 0.018(2) min^{-1} ($t_{1/2}=39(3)$ min). The smaller k value and shorter $t_{1/2}$ for **2** indicate that the cleavage rate for **2** is faster than that of **1**.

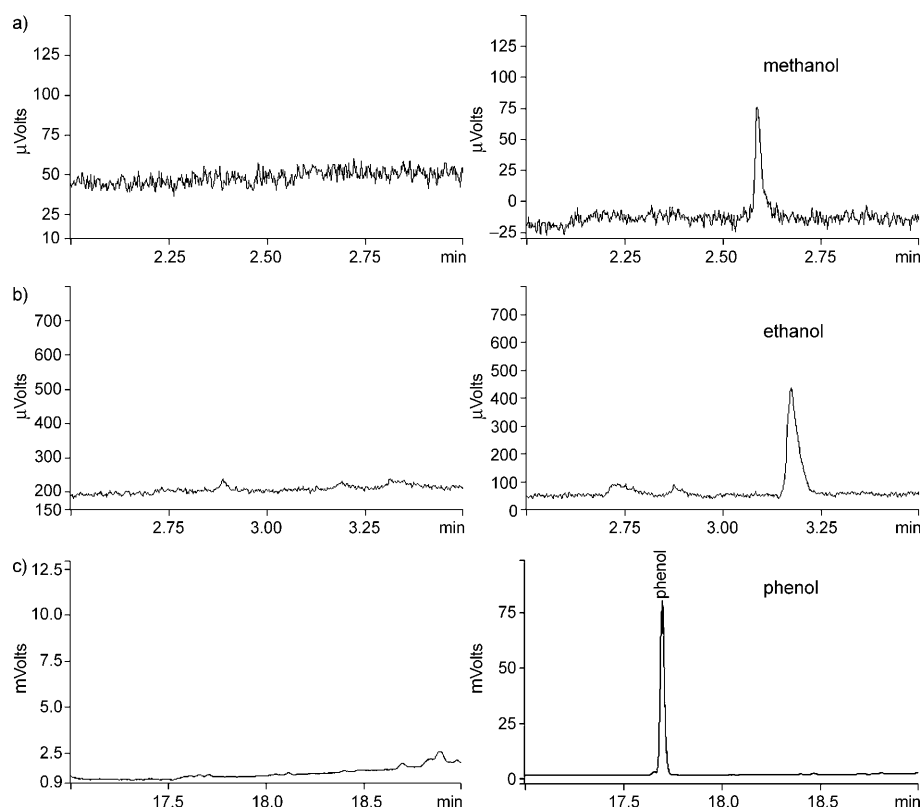
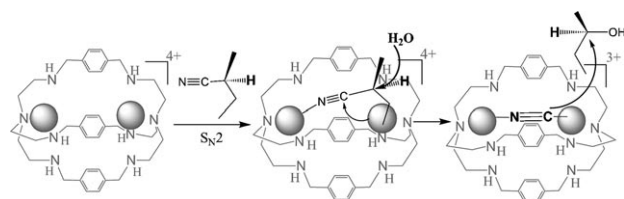


Figure 5. Gas chromatograms of a) acetonitrile and b) propionitrile before (left) and after (right) adding **1**; c) GC spectra of benzonitrile before (left) and after (right) adding **2** (standing at room temperature for 24 h before measuring). This clearly indicates that methanol, ethanol, and phenol are produced during the reactions of **1** with acetonitrile and propionitrile, and **2** with benzonitrile.

Mechanistic studies: To distinguish between Equations (3) and (4) in Scheme 1 for C–C bond cleavage by $[M^2L]^{4+}$ ($M = Cu^{II}, Zn^{II}$), the chiral nitrile, (*S*)-(+)-2-methylbutyronitrile, was allowed to react with **2**. If the cleavage reaction proceeds through the S_N1 pathway of Equation (3), the 2-butanol product should be racemic, as the reaction proceeds through the intermediate $[CH(CH_3)(C_2H_5)]^+$. If the cleavage reaction proceeds through the S_N2 pathway of Equation (4), 2-butanol of inverted chirality should be obtained, as the cleavage of the C–C bond in (*S*)-(+)-2-methylbutyronitrile by $[M^2L]^{4+}$ and water through an S_N2 type process would result in an inversion of the configuration producing (*R*)-(–)-2-butanol (Walden inversion, Scheme 2).

The HPLC measurements indicate that *rac*-*s*-butyl benzoate shows two separate peaks with retention times at



Scheme 2.

13.381 and 13.972 min (see Figure 6a). Under similar conditions, chiral (*R*)- and (*S*)-*s*-butyl benzoate display retention times of 13.354 and 13.967 min, respectively (Figure 6b and c), that is, the peak around 13.354 min belongs to (*R*)-*s*-butyl benzoate, and that around 13.967 min to (*S*)-*s*-butyl benzoate.

In a typical reaction, (*S*)-(+)-2-methylbutyronitrile and **2** (10:1) were mixed in nitromethane and left at room temperature for ten days, and then benzoyl chloride was added. The resulting mixture was stirred at room temperature for 24 h before measurement. The HPLC measurement clearly indicated that only (*R*)-*s*-butyl benzoate was formed, with a retention time of 13.353 min (Figure 6d), that is, only (*R*)-(–)-2-butanol was produced in the C–C bond cleavage of (*S*)-(+)-2-methylbutyronitrile. This reversal of chirality from (*S*)-(+)-2-methylbutyronitrile to (*R*)-(–)-2-butanol clearly demonstrates that the cleavage reaction

proceeds by an S_N2 -type process [Eq. (4)]. To our knowledge, this is the first example of using (*R*)-*s*-butyl benzoate for a mechanistic study on C–C bond cleavage. In this process (Scheme 2), the nitrogen atom of RCN binds to one M^{II} atom in the $[M^2L]^{4+}$ receptor through its electron pair, and the other M^{II} atom possibly interacts with the filled π orbital of the *sp*-hybridized RCN carbon atom. This should result in electron flow from the π bond to the M^{II} atom and increase the “leaving ability” of cyanide and the electrophilicity of the alkyl or aryl carbon atom, resulting in cleavage by adventitious water to form alcohol and a receptor–substrate complex of $[ML(CN)]^{3+}$. This unique mechanism of C–C bond cleavage by an S_N2 -type process is different from those reported previously,^[3,7] and, to our knowledge, has not been reported before.

Formation of alcohol requires participation of water molecules. Our earlier synthetic strategies to produce **1** and **2** employed nitriles to exclude water molecules. However, once the nitrogen atom of a nitrile binds to the inner axial position of one Cu^{II} or Zn^{II} atom, a water molecule is required to attack the carbon atom adjacent to the CN group to cleave the C–C bond. In our location, atmospheric moisture suffices for the cleavage reaction, and no extra water needs to be added to the reaction mixture.

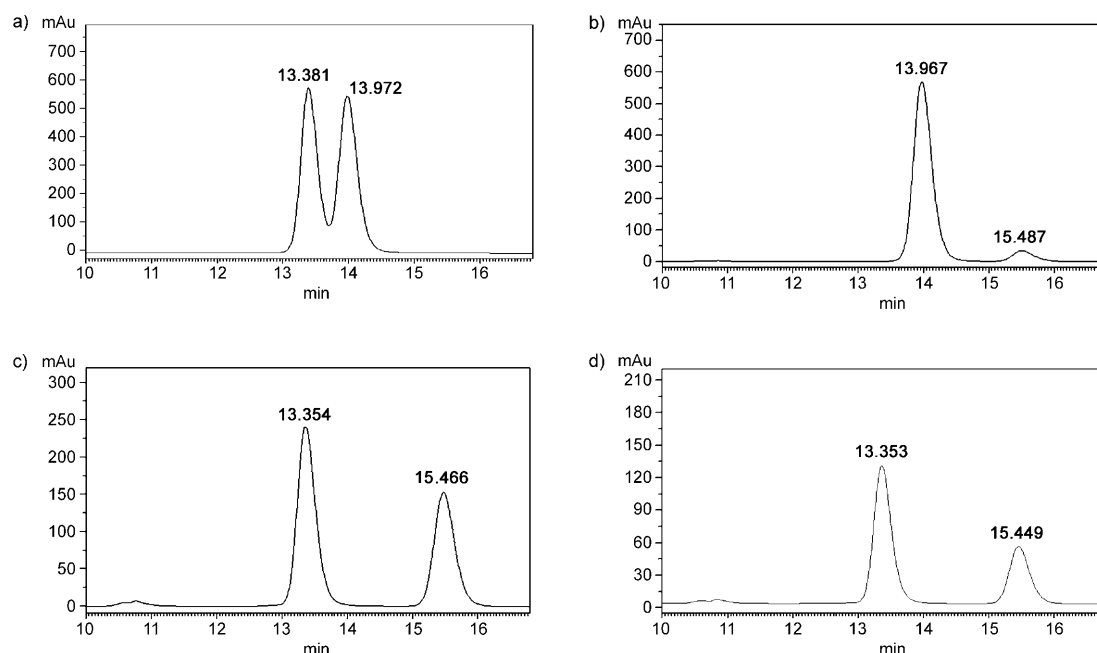


Figure 6. HPLC spectra of a) *rac*-*s*-butyl benzoate, b) (*S*)-*s*-butyl benzoate, c) (*R*)-*s*-butyl benzoate; and d) the reaction mixture of (*S*)-(+)-2-methylbutyronitrile, **2**, and benzoyl chloride (see text) in nitromethane on an OB-H 250×4.6 mm 3 μm chiral column. This clearly indicates that (*R*)-(-)-2-butanol was produced during the reaction of **2** with (*S*)-(+)-2-methylbutyronitrile. The peaks around 15.4 min correspond to benzoyl chloride (all of the benzoyl chloride was used up during the reaction of benzoyl chloride with *rac*-2-butanol; thus, no peak corresponding to benzoyl chloride appears in Figure 6a).

Conclusions

Receptors **1** and **2** can cleave the C–C bonds of nitriles in an S_N2 -type process to produce the corresponding alcohols and receptor–substrate complexes of **3** and **4**, due to the strong recognition between the receptors and the substrate (cyanide anion). A key point in the cleavage reaction is to obtain complexes **1** and **2** with empty axial positions. Cryptates **5** and **6**, in which the axial positions are occupied by H_2O or OH^- , do not cleave the C–C bond of acetonitrile at room temperature.

Experimental Section

Materials and measurements: Ligand **L** was prepared as previously described.^[11,9b] $Cu(NO_3)_2 \cdot 3H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and **L** were dried under vacuum over P_2O_5 before use. (*S*)-(+)-2-methylbutyronitrile, (*R*)-(-)-2-butanol, (*S*)-(+)-2-butanol, and *rac*-2-butanol were purchased from Aldrich. Acetonitrile and benzonitrile solvents were of HPLC grade and the purity of propionitrile was 99%. Anhydrous methanol was refluxed and distilled over magnesium methoxide under nitrogen. Other solvents and chemicals were obtained commercially and used without further purification. Elemental analyses were determined by using an Elementar Vario EL elemental analyzer. The IR spectra were recorded in the 4000–400 cm^{-1} region at room temperature in the form of KBr pellets on a Bruker EQUINOX 55 spectrometer. UV/Vis spectra were obtained on a Shimadzu UV-3150 spectrophotometer. ESIMS was performed on a Thermo Finnigan LCQDECA XP HPLC-MSn mass spectrometer. GC-MS was performed on a Thermo Finnigan Voyager mass spectrometer. The concentration of methanol and ethanol produced was determined with a Varian CP3800 GC instrument, with a HP-INNOWax polar column.

HPLC analyses were carried out on a Shimadzu LC-20A system with a quaternary pump.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care.

[Cu₂L](ClO₄)₄ (1**):** A solution of **L** (60 mg, 0.1 mmol) in anhydrous methanol (5 mL) was added to a solution of $Cu(NO_3)_2 \cdot xH_2O$ (58 mg, 0.24 mmol) in anhydrous methanol (5 mL). The resulting solution was stirred at room temperature for 15 min, and then a solution of anhydrous $NaClO_4$ (650 mg, 5.3 mmol) in anhydrous methanol (6 mL) was added to result in a large amount of blue precipitate. The precipitate was separated by centrifugation, washed with anhydrous methanol, and dried under vacuum. Yield: 86 mg, 76%. Elemental analysis (%) calcd for $C_{36}H_{54}N_8Cu_2Cl_4O_{16}$ (**1**): C 38.48, H 4.84, N 9.97; found: C 38.87, H 5.13, N 10.23; IR (KBr): $\tilde{\nu}$ = 3471 (s), 2925 (m), 2877 (m), 1623 (m), 1445 (m), 1095 (s), 809 (m), 624 cm^{-1} (m); ESIMS (MeCN): m/z : 242 $[Cu_2L]^3+$, 361 $[Cu_2L]^2+$.

[Zn₂L](ClO₄)₄ (2**):** This complex was prepared by a similar procedure to that for **1** from $Zn(NO_3)_2 \cdot xH_2O$ and **L** in 54% yield. Elemental analysis (%) calcd for $C_{36}H_{54}N_8Zn_2Cl_4O_{16}$ (**2**): C 38.35, H 4.83, N 9.94; found: C 37.93, H 5.18, N 10.18; IR (KBr): $\tilde{\nu}$ = 3506 (m), 3276 (m), 2946 (m), 2883 (m), 1622 (w), 1474 (m), 1441 (m), 1389 (w), 1360 (m), 1287 (m), 1214 (w), 1098 (s), 1023 (m), 991 (m), 932 (m), 886 (m), 814 (m), 624 (m), 570 cm^{-1} (m); ESIMS (MeCN): m/z : 364 $[Zn_2L]^2+$, 414 $[Zn_2L(ClO_4)]^2+$. We tried our best to get crystals of **1** or **2** by crystallizing from different anhydrous solvents, but failed. Every time only unidentified powder (sometimes oil-like precipitate) was obtained.

[Cu₂L(CN)](ClO₄)₃ (3**):** $[Cu_2L](ClO_4)_4$ (50 mg) was dissolved in AR-grade acetonitrile (10 mL) and the solution filtered. The resulting solution was evaporated slowly at room temperature in the open air to give emerald green crystals of **3**·2CH₃CN·4H₂O. Yield: 33 mg, 62%. Elemental analysis (%) calcd for $C_{41}H_{68}N_{11}Cu_2Cl_3O_{16}$ (**3**·2CH₃CN·4H₂O): C 40.85, H 5.65, N 12.79; found: C 41.12, H 5.37, N 12.96; IR (KBr): $\tilde{\nu}$ = 3422 (s), 3295 (s), 2927 (s), 2878 (m), 2249 (w), 2194 (w), 2143 (w), 2024 (w), 1626 (m), 1446 (s), 1388 (m), 1278 (m), 1093 (s), 1009 (s), 924 (s), 897 (m), 814 (s), 625 cm^{-1} (s); ESIMS (MeCN): m/z : 251 $[Cu_2L(CN)]^3+$, 599

[HL]⁺, 750 [Cu₂L(CN)]⁺. Crystals of **3**·2CH₃CN·4H₂O were also obtained by dissolving **1** in HPLC-grade acetonitrile.

[Zn₂L(CN)](ClO₄)₃ (4): [Zn₂L](ClO₄)₄ (50 mg) was dissolved in HPLC-grade acetonitrile (10 mL) and the solution filtered. The resulting solution was allowed to evaporate slowly in the open air at room temperature to give colorless crystals of **4**·4CH₃CN. Yield: 43 mg, 80%. Elemental analysis (%) calcd for C₃₇H₃₈N₉Zn₂Cl₃O₁₄ (4·2H₂O): C 40.77, H 5.36, N 11.56; found: C 40.53, H 5.47, N 11.39; IR (KBr): $\tilde{\nu}$ = 3429 (s), 3282 (s), 2932 (m), 2881 (m), 2157 (w), 2020 (w), 1624 (w), 1520 (s), 1445 (s) 1390 (m), 1286 (m), 1214 (m), 1093 (s), 1025 (s), 936 (s), 860 (m), 814 (s), 626 (s), 567 cm⁻¹ (w); ESIMS (MeCN): *m/z*: 378 [Zn₂L(CN)]²⁺, 854 [Zn₂L(CN)(ClO₄)]⁺, 954 [Zn₂L(CN)(ClO₄)₂]⁺.

[Cu₂L(H₂O)₂](CF₃SO₃)₄ (5): A solution of **L** (120 mg, 0.20 mmol) in acetonitrile (5 mL) was added dropwise to a solution of Cu(CF₃SO₃)₂ (150 mg, 0.41 mmol) in acetonitrile (5 mL). The resulting blue solution was stirred at room temperature for 1 h. Blue crystals of **5**·3CH₃CN (presumably formed on this occasion due to adventitious water in the solvent) were obtained by diffusion of diethyl ether into the resulting solution. Yield: 192 mg, 65%. Elemental analysis (%) calcd for Cu₂C₄₆H₆₇N₁₁O₁₄S₄F₁₂ (5·3CH₃CN): C 37.29, H 4.56, N 10.40; found: C 36.94, H 4.58, N 9.98; IR (KBr): $\tilde{\nu}$ = 3484 (s), 3225 (m), 2887 (m), 1630 (m), 1449 (s), 1250 (m), 1167 (s), 1068 (m), 1030 (s), 812 (m), 759 (m), 639 (m), 575 cm⁻¹ (m); ESIMS (MeCN): *m/z*: 361 [Cu₂L]²⁺, 659 [Cu₂L(CF₃SO₃)₂]⁺, 723 [Cu₂L]⁺, 871 [Cu₂L(CF₃SO₃)₃]⁺.

[Cu₂L(OH)(OH)](ClO₄)₃ (6): A solution of **L** (600 mg, 1 mmol) and NaOH (82 mg, 2.05 mmol) in methanol (4 mL) was added dropwise to a solution of Cu(ClO₄)₂·6H₂O (741 mg, 2 mmol) in methanol (4 mL). The blue-green precipitate obtained was filtered off, washed with methanol, and dried under vacuum over P₄O₁₀. Yield: 710 mg, 67%. Elemental analysis (%) calcd for C₃₆H₅₇N₈Cu₂Cl₃O₁₄(6): C 40.82, H 5.42, N 10.58; found: C 40.52, H 5.57, N 10.44; IR (KBr): $\tilde{\nu}$ = 3592 (s), 3269 (s), 2916 (m), 2859 (s), 1632 (w), 1445 (s), 1366 (w), 1308 (m), 1092 (s), 924 (m), 807 (s), 623 (s), 578 (w), 556 (w), 495 (w), 442 cm⁻¹ (w); ESIMS (MeCN): *m/z*: 599 [HL]⁺, 662 [CuL]⁺, 823 [Cu₂L(OH)(MeCN)₂]⁺. The above preparation method is different from the reported method,^[8a] in which crystals of **6** were obtained by diffusion of diethyl ether into an acetonitrile solution of [Cu₂L](ClO₄)₄·4H₂O, that is, the axial positions of Cu^{II} are easily occupied by H₂O/OH⁻ groups.

X-ray crystallography: Single-crystal data for **4**·4CH₃CN and **5**·3CH₃CN were collected at 293(2) K on a Bruker Smart 1000 CCD diffractometer with MoK α radiation (λ = 0.71073 Å). All empirical absorption corrections were applied by using the SADABS program.^[12] The structures were solved by direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically to convergence. The cyano bridge in **4** and one CF₃SO₃⁻ in **5** were disordered, and free-variable refinements gave occupancy factors for each disordered CN group of about 0.5. All hydrogen atoms (except those bound to water molecules) were placed in calculated positions with fixed isotropic thermal parameters and included in structure-factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed with the SHELXTL-97 suite of computer programs.^[13] The crystallographic data are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

DFT calculations: DFT calculations and geometry optimization were performed with the Gaussian 03 package.^[14] Based on the crystal structure of **4**, the cation [Zn₂L(CN)]²⁺ was fully optimized as an isolated entity in vacuum without any symmetry constraints. Atomic charges were calculated by Mulliken^[15] and natural^[16] population analyses as implemented in Gaussian 03. GaussSum^[17] was used to calculate the contributions from the groups of atoms to each molecular orbital. Graphical representations of the orbital were produced by gOpenMol^[18] graphics program. The optimized Cartesian coordinates are given in Table S1 in the Supporting Information. The orbital energies ϵ and compositions for the frontier molecular orbitals are listed in Table S2 in the Supporting Information.

Determination of the absolute configuration of 2-butanol: Formation of 2-butanol in the reaction of [Zn₂L]²⁺ with (S)-(+)-2-methylbutyronitrile in nitromethane was evident in the chromatogram obtained in a GC-MS measurement. As 2-butanol is not amenable to HPLC detection due to

Table 1. Crystallographic data and refinement parameters for **4** and **5**.

| | 4 ·4CH ₃ CN | 5 ·3CH ₃ CN |
|--|---|--|
| formula | C ₄₅ H ₆₆ N ₁₃ Zn ₂ Cl ₃ O ₁₂ | C ₄₆ H ₆₇ N ₁₁ Cu ₂ F ₁₂ O ₁₄ S ₄ |
| fw | 1218.20 | 1481.43 |
| crystal size [mm] | 0.52 × 0.48 × 0.47 | 0.32 × 0.28 × 0.26 |
| crystal system | triclinic | monoclinic |
| space group | <i>P</i> $\bar{1}$ | <i>C</i> 2/ <i>c</i> |
| <i>a</i> [Å] | 13.456(2) | 35.342(4) |
| <i>b</i> [Å] | 13.822(2) | 14.2953(15) |
| <i>c</i> [Å] | 15.815(3) | 25.688(3) |
| α [°] | 85.713(3) | 90 |
| β [°] | 65.575(3) | 107.748(2) |
| γ [°] | 82.141(3) | 90 |
| <i>V</i> [Å ³] | 2652.4(7) | 12361(2) |
| <i>Z</i> | 2 | 8 |
| ρ_{calcd} [g cm ⁻³] | 1.525 | 1.592 |
| μ [mm ⁻¹] | 1.128 | 0.929 |
| reflns collected | 15008 | 31305 |
| GO on <i>F</i> ² | 1.024 | 1.036 |
| <i>R</i> ₁ ^[a] , <i>wR</i> ₂ ^[b] [<i>I</i> > 2 σ (<i>I</i>)] | 0.0554, 0.1525 | 0.0726, 0.1982 |
| <i>R</i> ₁ ^[a] , <i>wR</i> ₂ ^[b] (all data) | 0.0846, 0.1770 | 0.1620, 0.2482 |

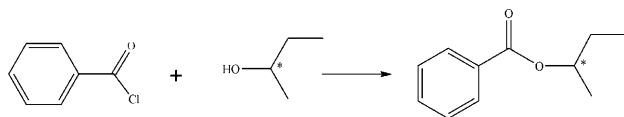
[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)]^{1/2}$. Weighting: **4**, $w = 1/[\sigma^2(F_o)^2 + (0.1099P)^2 + 0.7448P]$; **5**, $w = 1/[\sigma^2(F_o)^2 + (0.1457P)^2 + 7.6353P]$; where $P = [(F_o^2) + 2F_c^2]/3$.

Table 2. Selected distances [Å] and angles [°] for **4** and **5**.

| 4 | | | |
|------------|------------|------------|------------|
| Zn1–C/N | 2.041(4) | Zn2–N/C | 2.048(4) |
| Zn1–N1 | 2.273(4) | Zn2–N5 | 2.279(4) |
| Zn1–N2 | 2.129(4) | Zn2–N6 | 2.131(3) |
| Zn1–N3 | 2.141(3) | Zn2–N7 | 2.125(3) |
| Zn1–N4 | 2.120(4) | Zn2–N8 | 2.125(4) |
| C/N–N/C | 1.141(5) | Zn1...Zn2 | 5.230 |
| C/N–Zn1–N4 | 99.64(14) | C/N–Zn1–N2 | 99.66(14) |
| N4–Zn1–N2 | 116.79(15) | C/N–Zn1–N3 | 98.96(14) |
| N4–Zn1–N3 | 117.68(14) | N2–Zn1–N3 | 117.66(15) |
| C/N–Zn1–N1 | 178.88(14) | N4–Zn1–N1 | 81.18(15) |
| N2–Zn1–N1 | 80.61(15) | N3–Zn1–N1 | 79.96(13) |
| N/C–Zn2–N8 | 98.80(14) | N/C–Zn2–N7 | 100.50(13) |
| N8–Zn2–N7 | 117.37(14) | N/C–Zn2–N6 | 98.90(14) |
| N8–Zn2–N6 | 117.59(14) | N7–Zn2–N6 | 117.21(14) |
| N/C–Zn2–N5 | 179.04(14) | N8–Zn2–N5 | 80.87(14) |
| N7–Zn2–N5 | 80.45(14) | N6–Zn2–N5 | 80.49(14) |

| 5 | | | |
|------------|------------|------------|------------|
| Cu1–O1W | 1.996(4) | Cu2–O2W | 1.998(4) |
| Cu1–N1 | 1.999(5) | Cu1–N2 | 2.103(5) |
| Cu1–N3 | 2.204(5) | Cu1–N4 | 2.098(5) |
| Cu2–N5 | 1.991(5) | Cu2–N6 | 2.100(5) |
| Cu2–N7 | 2.205(5) | Cu2–N8 | 2.104(5) |
| Cu1...Cu2 | 7.013 | | |
| O1W–Cu1–N1 | 176.6(2) | O1W–Cu1–N4 | 91.70(17) |
| N1–Cu1–N4 | 85.23(19) | O1W–Cu1–N2 | 95.11(16) |
| N1–Cu1–N2 | 86.16(19) | N4–Cu1–N2 | 136.9(2) |
| O1W–Cu1–N3 | 98.24(19) | N1–Cu1–N3 | 84.3(2) |
| N4–Cu1–N3 | 111.51(19) | N2–Cu1–N3 | 109.49(19) |
| N5–Cu2–O2W | 176.2(2) | N5–Cu2–N6 | 85.66(19) |
| O2W–Cu2–N6 | 91.52(16) | N5–Cu2–N8 | 85.6(2) |
| O2W–Cu2–N8 | 94.88(17) | N6–Cu2–N8 | 138.3(2) |
| N5–Cu2–N7 | 84.5(2) | O2W–Cu2–N7 | 98.88(19) |
| N6–Cu2–N7 | 109.8(2) | N8–Cu2–N7 | 109.8(2) |

the lack of fluorescent or UV/Vis-adsorbing groups, pre-column derivatization^[19] is required to facilitate its detection. Benzoyl chloride was used as the derivatization reagent, as it reacts with 2-butanol at room tempera-



Scheme 3. Reaction of 2-butanol with benzoyl chloride for pre-column derivatization.

ture to produce butyl benzoate (Scheme 3). In a typical reaction, 2-butanol and benzoyl chloride in 1:0.6 ratio were mixed in nitromethane and stirred at room temperature for 48 h before measurement. Additionally, treating benzoyl chloride with (*R*)-(-)-2-butanol, (*S*)-(+)-2-butanol, and racemic-2-butanol produced (*R*)-, (*S*)-, and *rac-s*-butyl benzoate, respectively. *rac-s*-Butyl benzoate can be separated by using hexane/isopropyl alcohol (95/5 v/v) as mobile phase with a flow rate of 0.3 mL min⁻¹ on an OB-H 250 × 4.6 mm 3 μm Chiral column, resulting in two separate peaks with retention times of 13.381 and 13.972 min (see Figure 6a). Under similar conditions, chiral (*R*)- and (*S*)-s-butyl benzoate display retention times of 13.354 and 13.967 min, respectively (Figure 6b and c), that is, the peak around 13.354 min belongs to (*R*)-s-butylbenzoate, and that around 13.967 min to (*S*)-s-butyl benzoate (the peak around 15.4 min is due to benzoyl chloride).

Acknowledgements

This work was supported by the NSFC (20625103, 20831005, 20821001) and 973 Program of China (2007CB815305).

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Received: June 13, 2009

Revised: August 8, 2009

Published online: October 6, 2009