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Cleavage of C−S Bonds with the Formation of a Tetranuclear Cu(I) Cluster

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The treatment of a ligand, 2,6-bis((4-(pyridin-2-yl)pyrimidin-2-ylthio)methyl)-4-chlorophenol (**ClPPT2**), with cuprous chloride under a weak base condition led to the formation of a neutral Cu^{I}_4-centered cluster [Cu_4(**PPT2**)$_4$], whose X-ray diffraction analysis indicated that C−S bonds of the ligand were cleaved in the course of the reaction. To explain the C−S bond cleavage, a reasonable mechanism has been proposed. In support of it, four additional ligands, 2,6-bis((4-(pyridin-2-yl)pyrimidin-2-ylthio)methyl)-4-methylphenol (**MePPT2**), 2,6-bis((4-(pyridin-3-yl)pyrimidin-2-ylthio)methyl)-4-methylphenol (**MePPT3**), 2,6-bis((4-(pyridin-3-yl)pyrimidin-2-ylthio)methyl)-4-chlorophenol (**ClPPT3**), and 5-((4-(pyridin-3-yl)pyrimidin-2-ylthio)methyl)-2-hydroxybenzaldehyde (**HBPPT2**) were further tested to undertake the analogous reaction, and the cleaved products in these experiments were detected by electrospray ionization mass spectrometry techniques to clarify the process.

Introduction

Supramolecular chemistry, connecting inorganic and organic chemistry as a whole, has been an important area of modern chemistry for more than a decade. Upon its concepts, scientists have been trying to produce materials with multiple functions, such as electronic, optical, magnetic, and catalytic properties, far beyond their purely inorganic or organic building-block compounds.[1,2] The metal−ligand interaction in the course of spontaneous self-assembly may lead to interesting chemical and physical phenomena,[3] which intrigue researchers to design organic ligands with specific structures and versatile potential donors. The interest in the activation (or cleavage) of chemical bonds via transition-metal complexation is justified by its potential application of organic synthesis, since the formation of new bonds is based upon the breaking of old ones. To our knowledge, it has been widely investigated in activation of single or multiple bonds of C−H, C−C, C−N, C−X, and so forth.[4] As far as the activation of C−S bonds is concerned, it is of fundamental value in both organic synthesis[5] and the bioorganic chemistry

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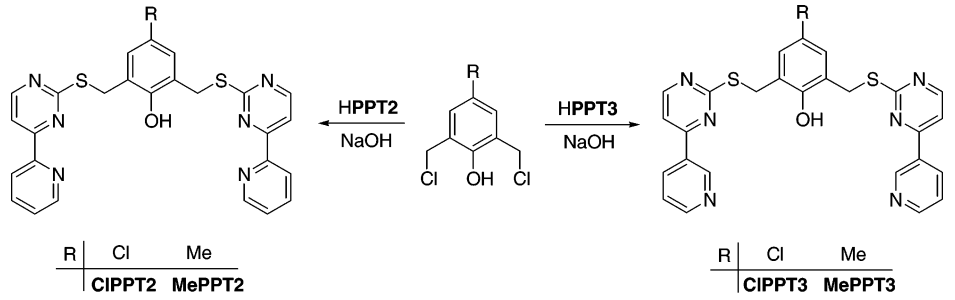
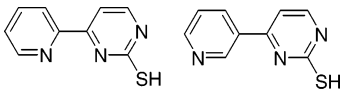
Scheme 1. Synthetic Methods for Thioether Ligands



of C−S lyase,[6] also of importance in removing the organosulfur compounds present in petroleum-based feedstock.[7] Several kinds of C−S bond cleavage within ligands mediated by metals (e.g., Cu, Co, Pd, Re, Zr, and Nb) were reported;[8] however, its mechanism was poorly studied.[8e,9] In our previous efforts, we reported a series of ligands, containing arms of 1*H*-imidazole, 1,2,4-triazole, or 1*H*-tetrazole,[10,11] to explore the activation of C−C bonds in the course of studying their supramolecular self-assembly. For further study, 4-(pyridin-2-yl)pyrimidine-2-thiol (H**PPT2**) and 4-(pyridin-3-yl)pyrimidine-2-thiol (H**PPT3**) have been introduced to the ligand system to extend our research on the above aspects.



HPPT2 HPPT3

A number of thioether ligands have been designed and synthesized in our laboratory, including **ClPPT2**, **ClPPT3**, **MePPT2**, and **MePPT3**, that can be abbreviated as **RPPT*n*** (R = Cl or Me; n = 2 or 3) (Scheme 1). Each ligand bears a potential N_6OS_2 donor site consisting of substituted phenol, thioether, pyridine, and pyrimidine functionalities. Herein, we report the preparation of these new thioether ligands and the generation of the cuprous cluster, Cu_4(**PPT2**)$_4$, whose structure was determined by X-ray crystallography. In contrast with that of the original thioether ligands, the molecular structure of the cluster strongly indicated the rupture of C(benzylic)−S(thioether) bonds. To learn more about the nature of C−S bond cleavage in our compounds, a reasonable mechanism is proposed.

Experimental Section

Materials and Measurements. All solvents and reagents were of analytical reagent grade and used as purchased without further purification unless otherwise stated. H**PPT2**,[12] H**PPT3**,[12] 4-chloro-2,6-bis(chloromethyl)phenol,[13] 2,6-bis(chloromethyl)-4-methylphenol,[14] and 5-(chloromethyl)-2-hydroxybenzaldehyde[15] were synthesized according to literature methods. NMR spectra were recorded on a Bruker DRX500 spectroscopy instrument in $CDCl_3$ or $(CD_3)_2SO$ using $SiMe_4$ as the interior standard. Elemental analyses for C, H, N, and S were performed on a CHN-O-Rapid analyzer and an Elementar Vario MICRO analyzer. Electrospray ionization mass spectrometry (ESI-MS) spectra were carried on a Mariner mass spectrometer. Thermal analysis (TA) data were collected on a Perkin-Elmer Pyris 1 TGA analyzer. Infrared spectra were performed on a Bruker Vector 22 spectrophotometer with KBr pellets in the 400−4000 cm^{-1} region.

Preparation of 4-Chloro-2,6-bis(chloromethyl)phenol. A portion of 37% formaldehyde (18 mL, 0.25 mol) was slowly added to a mixture of 4-chlorophenol (16.1 g, 0.125 mol) and 20% aqueous NaOH solution (25 mL, 0.125 mol) under vigorous stirring. It was heated to 55 °C for 3 h and was then cooled to room temperature. The mixture was then filtered and washed with saturated brine three times to give the crude product as a reddish solid. The solid was added to water (100 mL), and the resulting mixture was acidified to pH 3 with acetic acid. It was then filtered to give 4-chloro-2,6-bis(hydroxymethyl)phenol (11.80 g, yield 50%) as a pink solid, which was washed with water and dried under vacuum. The resulting 4-chloro-2,6-bis(hydroxymethyl)phenol (8.20 g, 0.04 mol) was dissolved in diethyl ether (100 mL), and then $SOCl_2$ (20.0 mL, 0.27 mol) was carefully added. The mixture was stirred at room temperature for 24 h, filtered, and concentrated under reduced pressure to give 4-chloro-2,6-bis(chloromethyl)phenol as an oil, which afforded a white solid (7.22 g, yield 80%) by adding *n*-hexane (30 mL). Mp: 89−91° (lit.[13] 91.0−91.6°)

2,6-Bis(chloromethyl)-4-methylphenol. Reaction of *p*-cresol (10.8 g, 0.10 mol) with 37% formaldehyde (18 mL, 0.25 mol) and

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20% aqueous NaOH solution (25 mL, 0.125 mol) as described above gave 2,6-bis(hydroxymethyl)-4-methylphenol (15.9 g, yield 95%) as a white solid. The resulting phenol (15.0 g, 0.073 mol) was treated with $SOCl_2$ (26.8 mL, 0.36 mol) in an analogous way that the preparation of 4-chloro-2,6-bis(chloromethyl)phenol gave 2,6-bis(chloromethyl)-4-methylphenol (4.32 g, yield 32%) as a white solid. Mp: 79−80° (lit.[14] 80°).

2,6-Bis((4-(pyridin-2-yl)pyrimidin-2-ylthio)methyl)-4-chlorophenol (ClPPT2). NaOH (0.88 g, 22 mmol) was added to acetone (30 mL) with vigorous stirring for 10 min, then a solution of H**PPT2** (3.78 g, 20 mmol) in acetone (70 mL) was added to the above. After the mixture was refluxed for 1 h, another solution of 4-chloro-2,6-bis(chloromethyl)phenol (2.03 g, 9.0 mmol) in acetone (40 mL) was added dropwise. Then the resulting solution was refluxed for 24 h. In the course of refluxing, an extra 130 mL of acetone was added. Finally, the solution was cooled to room temperature and filtered. The resulting solid was washed with acetone several times and dried under vacuum (4.35 g, yield 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.3 (br, 1H, OH), 8.74 (d, 2H), 8.70 (d, 2H), 8.48 (d, 2H), 8.11 (d, 2H), 7.88 (t, 2H), 7.44 (t, 2H), 7.29 (s, 2H, PhH), 4.45 (s, 4H, CH_2). Anal. Calcd for $C_{26}H_{19}ClN_6OS_2$: C, 58.80; H, 3.61; N, 15.83. Found: C, 58.76; H, 3.59; N, 16.10. IR (KBr, cm^{-1}): ν = 3431w, 1572s, 1537s, 1420m, 1346s, 1202m, 830w, 766m.

MePPT2, **MePPT3**, and **ClPPT3**, prepared via an analogous way to the above method, were characterized as follows:

2,6-Bis((4-(pyridin-2-yl)pyrimidin-2-ylthio)methyl)-4-methylphenol (MePPT2). Yield: 93%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.19 (s, 1H, OH), 8.72 (d, 2H), 8.70 (d, 2H), 8.49 (d, 2H), 8.06 (d, 2H), 7.86 (t, 2H), 7.42 (t, 2H), 7.12 (s, 2H, PhH), 4.48 (s, 4H, CH_2), 2.23 (s, 3H, CH_3). Anal. Calcd for $C_{27}H_{22}N_6OS_2$: C, 63.51; H, 4.34; N, 16.46. Found: C, 63.50; H, 4.46; N, 16.31. IR (KBr, cm^{-1}): ν = 3417vs, 1557s, 1537s, 1417m, 1344m, 1200m, 830w, 764m.

2,6-Bis((4-(pyridin-3-yl)pyrimidin-2-ylthio)methyl)-4-methylphenol (MePPT3). Yield: 85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.04 (s, 1H, OH), 9.29 (s, 2H), 8.76 (d, 2H), 8.67 (d, 2H), 8.45 (d, 2H), 7.51 (t, 2H), 7.45 (d, 2H), 7.11 (s, 2H, PhH), 4.45 (s, 4H, CH_2), 2.22 (s, 3H, CH_3). Anal. Calcd for $C_{27}H_{22}N_6OS_2$: C, 63.51; H, 4.34; N, 16.46; S, 12.56. Found: C, 63.50; H, 4.25; N, 16.43; S, 12.59. IR (KBr, cm^{-1}): ν = 3422w, 1559s, 1537s, 1402m, 1344m, 1204m, 829w, 775w.

2,6-Bis((4-(pyridin-3-yl)pyrimidin-2-ylthio)methyl)-4-chlorophenol (ClPPT3). Yield: 71%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.40 (s, 1H, OH), 9.26 (d, 2H), 8.76 (t, 2H), 8.66 (d, 2H), 8.41 (d, 2H), 7.48 (d, 2H), 7.46 (d, 2H), 7.28 (s, 2H, PhH), 4.42 (s, 4H, CH_2). Anal. Calcd for $C_{26}H_{19}ClN_6OS_2$: C, 58.80; H, 3.61; N, 15.83; S, 12.08. Found: C, 58.23; H, 3.33; N, 16.02; S, 12.76. IR (KBr, cm^{-1}): ν = 3418m, 1560s, 1537m, 1422m, 1345m, 1203m, 828w, 774w.

5-(Chloromethyl)-2-hydroxybenzaldehyde. A mixture of 2-hydroxybenzaldehyde (9.30 g, 0.076 mol), polyformaldehyde (5.05 g, 0.168 mol), and concentrated hydrochloric acid (50 mL, 0.6 mol) was stirred at room temperature for 20 h to give a large quantity of pink solids. The solids were washed with water until the pH was close to 7 and then dried under vacuum. They were further recrystallized from petroleum ether to give white needle crystals (5.83 g, yield 45%). Mp: 84−85° (lit.[15] 88°).

5-((4-(Pyridin-3-yl)pyrimidin-2-ylthio)methyl)-2-hydroxybenzaldehyde (HBPPT2). A suspension of H**PPT2** (0.39 g, 2.05 mmol) and dry Na_2CO_3 (3 g, 28 mmol) in acetone (90 mL) was refluxed for 1 h, then a solution of 5-(chloromethyl)-2-hydroxybenzaldehyde (0.34 g, 2.0 mmol) in acetone (25 mL) was added dropwise. The mixture was kept refluxing overnight, then cooled to room temperature, filtered, and washed with acetone. The filtrate was concentrated under reduced pressure to near dryness, then water (50 mL) was added to give **HBPPT2** as a white solid (0.43 g, yield 67%). ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ = 10.68 (s, 1H, OH), 10.23 (s, 1H, CHO), 8.78 (d, 1H), 8.75 (d, 1H), 8.44 (d, 1H), 8.05−8.01 (m, 2H), 7.79 (s, 1H), 7.64 (m, 1H), 7.59 (m, 1H), 6.95 (d, 1H), 4.49 (s, 2H, CH_2). Anal. Calcd for $C_{17}H_{13}N_3O_2S$: C, 63.14; H, 4.05; N, 12.99. Found: C, 63.05; H, 4.12; N, 13.68. IR (KBr, cm^{-1}): ν = 3440w, 1659vs, 1570vs, 1535s, 1486m, 1427s, 1342s, 1218s, 799w, 767m.

The General Procedure of C−S Bond Cleavage and Formation of Cu_4(PPT2)$_4$ (described by an example treatment of **ClPPT2** with commercially available CuCl, ≥99%). To a suspension of **ClPPT2** (0.051 g, 0.10 mmol) in methanol (20 mL) was added Et_3N (0.1 mL, 0.7 mmol). Under an N_2 atmosphere, the resulting solution was heated to 60 °C, and then a solution of CuCl (0.020 g, 0.20 mmol) in CH_3CN (20 mL) was added. The mixture was kept at 60 °C for 2 h to give dark red crystallites, which were washed with methanol and dried under vacuum (0.097 g, yield 48%). Crystals suitable for X-ray crystallography were obtained from the filtrate by slow evaporation over several days. The characterizations of the resulting crystallites and crystals showed that they were identical in composition. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ = 8.74 (br, 4H), 8.33 (br, 8H), 8.07 (br, 4H), 7.74 (br, 8H). Anal. Calcd for $C_{36}H_{24}Cu_4N_{12}S_4$: C, 42.94; H, 2.40; N, 16.69. Found: C, 42.65; H, 2.59; N, 16.58. IR (KBr, cm^{-1}): ν = 3433s, 1626w, 1557m, 1535m, 1397m, 1326m, 1193m, 760w. The compound exhibits remarkable thermal stability. TA analysis indicated that it had an onset temperature for decomposition at ca. 370 °C.

The reaction of **MePPT2**, **MePPT3**, **ClPPT3**, or **HBPPT2** with CuCl (or CuI) was the same as the above sample procedure involving C−S bond cleavage.

Cu_4(**PPT2**)$_4$ can also be easily obtained by simply mixing H**PPT2** with CuCl. To a solution of H**PPT2** (0.189 g, 1.00 mmol) in MeOH (100 mL) was added Et_3N (0.3 mL, 2.0 mmol). The mixture was vigorously stirred until H**PPT2** was fully dissolved, then a solution of CuCl (0.100 g, 1.00 mmol) in CH_3CN (100 mL) was added at room temperature. The resulting dark red solution was stirred for 1 min and left for 3 days. Dark red crystals were obtained (0.210 g, yield 83%). Further experiments showed that the addition of NaN_3 or KSCN to the above reactants did not help to yield other kinds of products containing counteranions. Characterizations of ^{1}H NMR and IR spectra showed almost identical signals, with identified crystals within experimental errors.

Crystallographic Studies. The single-crystal data were collected on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. The θ range for data collection was 2.0−25.0°. Of the 21 371 reflections, 7701 were unique (R_{int} = 0.098). The absorption correction was applied by a multiscan. The space group was determined from the systematic absences and further verified by the refinement results and *PLATON*.[16] The structures were solved by direct methods and refined using a full-matrix least-squares technique with *SHELXL-97*.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas the hydrogen atoms of the ligands were placed at idealized positions. Experi-

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Table 1. Crystal Data and Structure Refinement for Cu_4(**PPT2**)$_4$

formula	$C_{36}H_{24}Cu_4N_{12}S_4$
fw	1007.15
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	12.870(9)
b, Å	20.912(15)
c, Å	16.469(11)
α, deg	90
β, deg	97.562(13)
γ, deg	90
V, Å^3	4394(5)
Z	4
ρ_{cald}, g cm^{-3}	1.522
μ (Mo Kα), mm^{-1}	2.140
T, K	291(2)
F(000)	2016
cryst dimens, mm	0.20 × 0.10 × 0.10
θ range, deg	2.0−25.0
index ranges	$-15 \le h \le 12$ $-24 \le k \le 21$ $-19 \le l \le 19$
no. reflns collcd	21 371
no. of indep reflns/R_{int}	7701/0.098
no. of indep reflns with $I > 2\sigma(I)$	5128
GOF (F^2)	1.027
R_1 (F) ($I > 2\sigma(I)$)	0.0590
R_1 (all data)	0.0829
R_2 ($I > 2\sigma(I)$)	0.1761
R_2 (all data)	0.1864
largest diff peak/hole e/Å^3	1.373/−0.528

Table 2. Selected Distances (Å) and Angles (deg) for Cu_4(**PPT2**)$_4$

	Interatomic Distances (Å)		
Cu1−S2	2.267(2)	Cu1−S4	2.291(3)
Cu1−N1	2.050(6)	Cu1−N3	2.187(7)
Cu2−S1	2.231(2)	Cu2−S3	2.254(3)
Cu2−N5	2.022(5)	Cu3−S2	2.304(2)
Cu3−S3	2.297(3)	Cu3−N10	2.070(5)
Cu3−N12	2.165(6)	Cu4−S1	2.344(3)
Cu4−S4	2.280(3)	Cu4−N7	2.065(5)
Cu4−N9	2.173(7)	Cu1−Cu2	2.827(2)
Cu1−Cu3	2.949(2)	Cu1−Cu4	2.852(2)
Cu2−Cu3	2.642(2)	Cu2−Cu4	2.637(2)
Cu3···Cu4	3.193(2)		
	Bond Angles (deg)		
S2−Cu1−S4	122.31(7)	S2−Cu1−N1	126.86(17)
S2−Cu1−N3	100.06(17)	S4−Cu1−N1	109.10(17)
S4−Cu1−N3	104.68(18)	N1−Cu1−N3	77.7(2)
S1−Cu2−S3	125.39(8)	S1−Cu2−N5	121.61(15)
S3−Cu2−N5	108.61(15)	S2−Cu3−S3	119.20(7)
S2−Cu3−N10	107.91(15)	S2−Cu3−N12	108.53(17)
S3−Cu3−N10	130.35(15)	S3−Cu3−N12	100.82(18)
N10−Cu3−N12	76.9(2)	S1−Cu4−S4	124.39(7)
S1−Cu4−N7	104.53(15)	S1−Cu4−N9	107.48(18)
S4−Cu4−N7	129.57(15)	S4−Cu4−N9	97.6(2)
N7−Cu4−N9	76.8(3)		

mental details of the X-ray analyses are given in Table 1. Selected interatomic distances and angles are listed in Table 2.

Results and Discussion

Crystal Structure. The reaction of **ClPPT2** and CuCl afforded an electron-neutral cluster of Cu_4(**PPT2**)$_4$ in moderate yield. X-ray crystallographic analysis revealed that the cluster was composed of thiolate species (**PPT2**), which were apparently derived from **ClPPT2** by breaking its C(benzylic)−S(thioether) bonds. As shown in Figure 1, the resulting Cu^I_4-center of the cluster adopts a V-shaped structure via Cu−Cu interactions with dihedral angle 84.59(5)°. Five copper−copper contacts are classified into two categories: Cu1 and Cu2 interact with three copper atoms, whereas Cu3 and Cu4 interact with two copper atoms. The intermetallic distances of Cu1−Cu2 (2.827(2) Å), Cu1−Cu3 (2.949(2) Å), Cu1−Cu4 (2.852(2) Å), Cu2−Cu3 (2.642(2) Å), and Cu2−Cu4 (2.637(2) Å) are close to the sum of the van der Waals radii of Cu^I−Cu^I (2.80 Å);[17] however, direct Cu−Cu bonding is not thought to be present.[8i,18] The relatively longer distance of Cu3···Cu4 (3.193(2) Å) suggests that the intermetallic interaction is rather weak. It is noted that Cu1, Cu3, and Cu4 exhibit similar distorted-tetrahedral coordination environments with N_2S_2 donors from three different ligands. For example, as illustrated in Figure 1b, Cu1 is coordinated by two nitrogen atoms of the ligand (orange colored) and two sulfur atoms from two other different ligands (marked with red and blue colors). However, Cu2 lies in a triangular geometry with NS_2 donors that are also from three different ligands, among which the nitrogen atom is from the "red" ligand and the two sulfur atoms are from the "green" and "orange" ligands. It is found that Cu2 is deviated slightly from the N5S1S3 triangular plane (0.2624(10) Å).

As for the thiolate ligands, two kinds of coordination modes are present: one serves as a chelating ligand bonding three copper atoms with one μ_2-S bridge and a N,N-chelating site (Figure 2a, corresponding to the orange, green and blue ligands in Figure 1b), and the other serves as to connect three copper atoms via an exo-N donor and one μ_2-S bridge (Figure 2b, corresponding to the red ligand in Figure 1b). Such coordination modes in this cluster are quite different from those in $[Cu_3(pymt)_3]_n$[19] and $[Ag_6(pymt)_6]_n$[20] (pymt = pyrimidine-2-thiolate). The average Cu−S and Cu−N bond lengths are 2.284(3) and 2.104(6) Å, respectively, similar to those found in Cu^I complexes and proteins containing Cu−S and Cu−N bonds.[19,21]

Interestingly, such nonequivalent Cu−Cu interactions are not common in synthetic multinuclear complexes[22] but occur in natural compounds like nitrous oxide reductase (N_2OR).[21c,23] It is of much significance to note that the Cu^I_4 core of our cluster is quite similar to the Cu_Z active site of N_2OR

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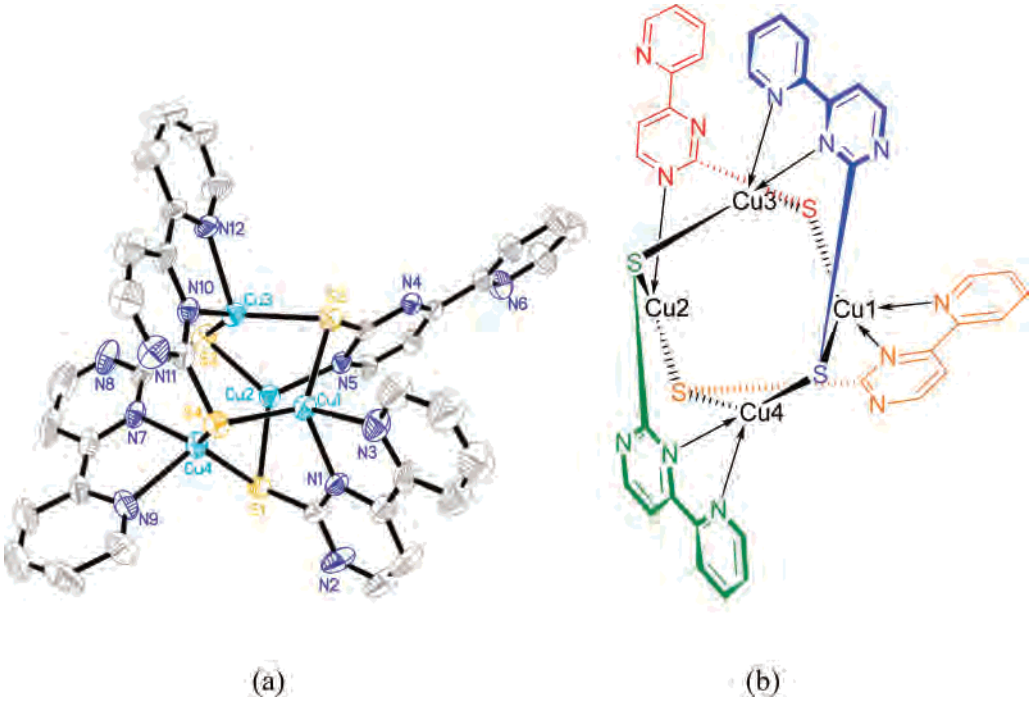

Figure 1. (a) ORTEP drawing (291 K, 30% probability thermal ellipsoids) of Cu_4(**PPT2**)$_4$. All hydrogen atoms are omitted, and only heteroatoms are labeled for clarity. (b) A ChemDraw view of Cu_4(**PPT2**)$_4$, in which the ligands are marked with different colors.

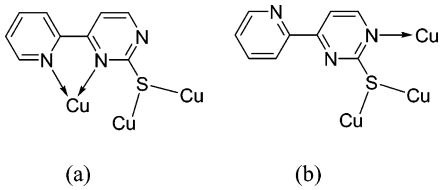

Figure 2. Two coordination modes of the ligand in the cluster.

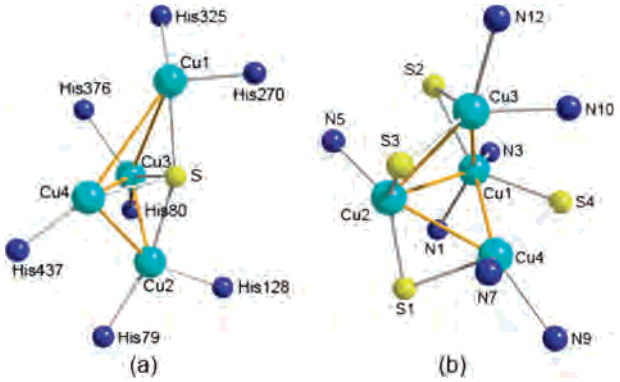

Figure 3. (a) Cu_Z site of N_2OR (ref 21b, pdb 1FWX, with the uncertain O donor omitted). Selected interatomic distances (Å): Cu1−Cu3(Cu4), 3.36; Cu2−Cu3(Cu4), 2.56; Cu3−Cu4, 2.98; Cu1−S, 2.28; Cu2(Cu3, Cu4)−S, 2.23; Cu−N(avg.), 2.06. (b) Core of Cu_4(**PPT2**)$_4$. Interatomic distances are given in Table 2.

except for the S donors (Figure 3). As a possible model compound for the enzyme in the structure, Cu_4(**PPT2**)$_4$ will be further investigated in the future.

C−S Bond Cleavage. As observed from the structure in Figure 1, an unexpected phenomenon of the C−S bond cleavage within **ClPPT2** happened during metal complexation. This is quite different from other analogous d^{10}-metal−thioether complexations in which the ligands did not offer cleaved products or byproducts when reacting with Cu^I [24] or Ag^I [25] ions. In addition, it is found that S donors of heterocycle-based thioether ligands are not often coordinated with Cu^I ions due, in part, to the geometrical effects.[24b,d,26] This kind of cleavage is also fundamentally dissimilar to the sulfur elimination from thiourea in the treatment of CuCl with naphthalene that served as an electron-transfer agent.[27] According to the difference between **ClPPT2** and previously reported ligands, it is proposed that the pathway of the C−S bond cleavage might be induced by a strong coordination effect between the cuprous ions and NS donors so that the electrons could be transferred from the oxygen to sulfur atoms. (Scheme 2).

It has been noticed that the treatment of **RPPT3** (R = Me or Cl) with CuCl in MeOH/CH_3CN in the absence of Et_3N under the same condition did not lead to cleavage. However, the addition of Et_3N led to the formation of red deposits immediately, and the filtrate turned out to be colorless after the reaction. Moreover, if one overlooks groups other than OH that could be deprotonated like NH in other similar thioether ligands,[18d] the Cu^I−S coordination

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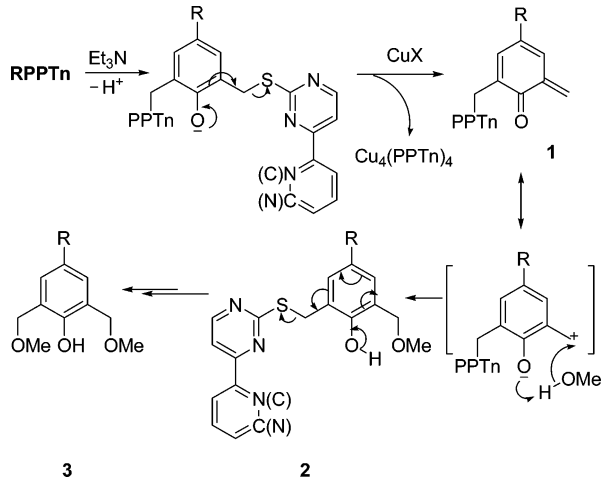
Scheme 2. Proposed Mechanism for the C−S Bond Cleavage Reaction[a]



[a] Mw: 321 (**1a**), 341 (**1b**), 353 (**2a**), 373 (**2b**), 196 (**3a**), 216 (**3b**); **a**, R = Me; **b**: R = Cl.

scarcely happened without the opportunity of charge transfer in either the OH-absent[24b−d] or OH-blocked way.[28] So, it is concluded that Et_3N serves as a deprotonation agent, and the occurrence of the cleavage is accompanied by the strong coordination and charge transfer from oxygen to sulfur atoms. Accordingly, **1** should be a cleaved byproduct, in which no extra electrons could be further transferred to another sulfur atom to induce the cleavage of the remaining C−S bond. Nevertheless, **1** was not supposed to be inert enough in the presence of the nucleophilic solvent of methanol. Once **2** formed, the remaining C−S bond could be cut off by the residual CuX in the same way to finally develop **3**.

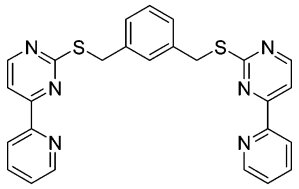
ESI-MS Spectra Studies. To support the mechanism shown in Scheme 2, five ligands, **RPPT*n*** (R = Me or Cl; *n* = 2 or 3) and **HBPPT2**, were reacted with CuCl or CuI to give parallel solutions by filtering out the precipitated cuprous clusters. Possible byproducts in the solutions were examined by means of ESI-MS spectra. The results, listed in Table 3, were found to be quite consistent with the proposed mechanism. When **ClPPT*n*** reacted with CuCl in a mixed solvent of MeOH/CH_3CN, they only gave *m*/*z* 239 and 241 peaks, suggesting that the byproducts were **3b**. However, these two signals were still observed when **ClPPT*n*** was replaced by **MePPT*n***. Apart from *m*/*z* 239 and 241 peaks in the **MePPT*n*** system, the peak at *m*/*z* 219 proved that **3a** was the byproduct. Why did **MePPT*n*** also exhibit signals at *m*/*z* 239 and 241? It could be attributable to the ion peak of $[(Et_3NH)_2Cl]^+$, whose molecular formula weight is equivalent to that of [**3b** + Na^+]. That is to say, we believe there were

Table 3. ESI-MS Analyses of Byproducts Derived from C−S Bond Cleavage under Different Conditions (Base = Et_3N)

	m/*z* (%)			
ligand[a]	**1**	**2**	**3**	$[(Et_3NH)_2X]^+$
ClPPT2	[b]		239.1(100) 241.1(42)[c] [**3b** + Na^+]	239.1(100) 241.1(42)
ClPPT2[d]			239.4(100) 241.4(20) [**3b** + Na^+]	331.4(23)
MePPT2		376.1(95) [**2a** + Na^+] 729.7(22) [2(**2a**) + Na^+]	219.1(50) [**3a** + Na^+]	239.2(100) 241.2(36)
MePPT2[e]	322.1(100) [**1a** + H^+]			239.2(60) 241.2(18)
MePPT2[f]	344.1(100) [**1a** + Na^+]			239.2(30) 241.2(8)
ClPPT3			239.2(100) 241.2(24) [**3b** + Na^+]	239.2(100) 241.2(24)
MePPT3		376.1(100) [**2a** + Na^+] 730.1(10) [2(**2a**) + Na^+]	219.1(34) [**3a** + Na^+]	239.2(62) 241.2(21)
HBPPT2		165.6(100)[g] [**4** − H^+]		239.4(100)[h] 241.4(20)

[a] All ligands were treated with CuCl in MeOH/CH_3CN mixture except those italicized. [b] Not detected by ESI-MS. [c] A ^{37}Cl isotopic peak. [d] Treated with CuI in MeOH/CH_3CN. [e] Treated with CuCl in pure CH_3CN. [f] Treated with CuCl in EtOH/CH_3CN. [g] Detected by a negative source. [h] Detected by a positive source.

both **3b** and $[(Et_3NH)_2Cl]^+$ species present in the **ClPPT*n*** system, and mass signals of them were overlapped in the spectra. To confirm this point, the substitution of CuI for CuCl in the **ClPPT*n*** system gave spectral data in which the peaks at *m*/*z* 239 and 241 attributed to **3b** did not vanish, and a peak at *m*/*z* 331 corresponding to the $[(Et_3NH)_2I]^+$ species appeared as expected. When **MePPT*n*** interacted with CuCl, another kind of byproduct, **2a**, appeared with peaks at *m*/*z* 376 and 730, which are consistent with [**2a** + Na^+] and [2(**2a**) + Na^+], respectively. According to the proposed mechanism, methanol is prone to react with possible intermediate **1** to give **2** and/or **3**, upon the ratio of **RPPT*n*** and CuX. Therefore, methanol was removed or replaced by ethanol so as to capture **1** in an example system of **MePPT2**. Mass spectral results indicated that **1a** was detected at *m*/*z* 322 and 344, ascribed to [**1a** + H^+] and [**1a** + Na^+], respectively. But neither **2a** nor **3a** were detected, demonstrating that the absence of methanol can terminate the reaction process as expected.



L

As pointed out previously, the phenolic hydroxyl group in these ligands, affording electrons to transfer, was necessary for the C−S cleaving reaction. To prove this point, a relevant

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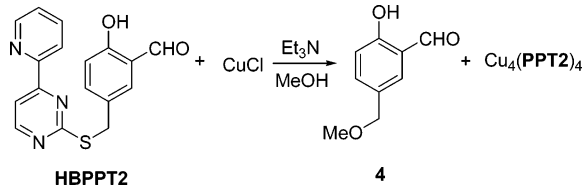
Scheme 3. Reaction of **HBPPT2** with CuCl



ligand **L**, without the hydroxyl and R groups compared with **RPPT2**, was also investigated to interact with CuCl. The result indicated that $Cu_2\mathbf{L}Cl_2$ was obtained instead of Cu_4-(**PPT2**)$_4$ after the reaction (*m*/*z* 711, 713, 715 [$Cu_2\mathbf{L}Cl_2$ + MeOH $+H^+$]). This further demonstrated that the cleavage of thioether by CuX was not initiated in the absence of electron transfer within the ligand.

Moreover, it can be deduced that the cleavage would also occur if the hydroxyl group of the ligand was on the para position of the thio-substituted group. In this case, **HBPPT2** was deliberately designed to demonstrate its feasibility (Scheme 3). As expected, **4** was apparently detected at *m*/*z* 165 [**4** $- H^+$] in a negative-ion mass spectrum (Table 3).

Conclusions

We have synthesized several thioether compounds that perform novel cleavage of C−S bonds when treated with CuX under a weak base condition. By tuning variables such as solvents, thio-substituted moieties, ligand/metal ratios, etc., our next efforts will pursue the questions of how to control the cleavage reaction to stop at the desired steps effectively and how to utilize the reaction to synthesize new compounds. On the other hand, the similar V-shaped geometry and identical all-reduced states between our cluster, Cu_4(**PPT2**)$_4$, and the catalytic Cu_Z core found in N_2OR give promising clues to how to mimic the reaction of the reduction of N_2O to N_2 with Cu_4(**PPT2**)$_4$.

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Supporting Information Available: An X-ray crystallographic file in CIF format; copies of ^{1}H NMR, ESI-MS, and TA spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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