

# Solvothermal in Situ Metal/Ligand Reactions: A New Bridge between Coordination Chemistry and Organic Synthetic Chemistry

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## ABSTRACT

Several important solvothermal (including hydrothermal) in situ metal/ligand reactions and their mechanisms, including dehydrogenative carbon–carbon coupling, hydroxylation of aromatic rings, cycloaddition of organic nitriles with azide and ammonia, transformation of inorganic and organic sulfur, as well as the Cu<sup>II</sup> to Cu<sup>I</sup> reduction, are outlined in this Account. The current progress clearly demonstrates the important potential of such reactions in the crystal engineering of functional coordination compounds and one-pot synthesis of some unusual organic ligands that are inaccessible or not easily obtainable via conventional methods, thereby substantiating our expectation that a new bridge has been created between coordination chemistry and synthetic organic chemistry.

## 1. Introduction

As a very important research field in both coordination chemistry and organic chemistry, in situ metal/ligand reactions have been extensively investigated for many decades for the discovery of new organic reactions, elucidation of reaction mechanisms, as well as generation of novel coordination compounds, especially those that are inaccessible in direct preparation from the ligands.<sup>1,2</sup> Conventionally, in situ metal/ligand reactions are conducted in open air and under mild conditions. In contrast, solvothermal (including hydrothermal hereafter) method, featuring chemical reactions in a sealed solution at elevated temperature and pressure, began to involve this kind of reactions only several years ago, although this method has been a well-known and powerful technique for synthesis of inorganic solid materials for many decades and have also been widely adopted in the preparations

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of new metal–organic frameworks (MOFs) that exhibit intriguing structural diversity and promising physical/chemical properties for potential applications in the past decade.<sup>3–6</sup>

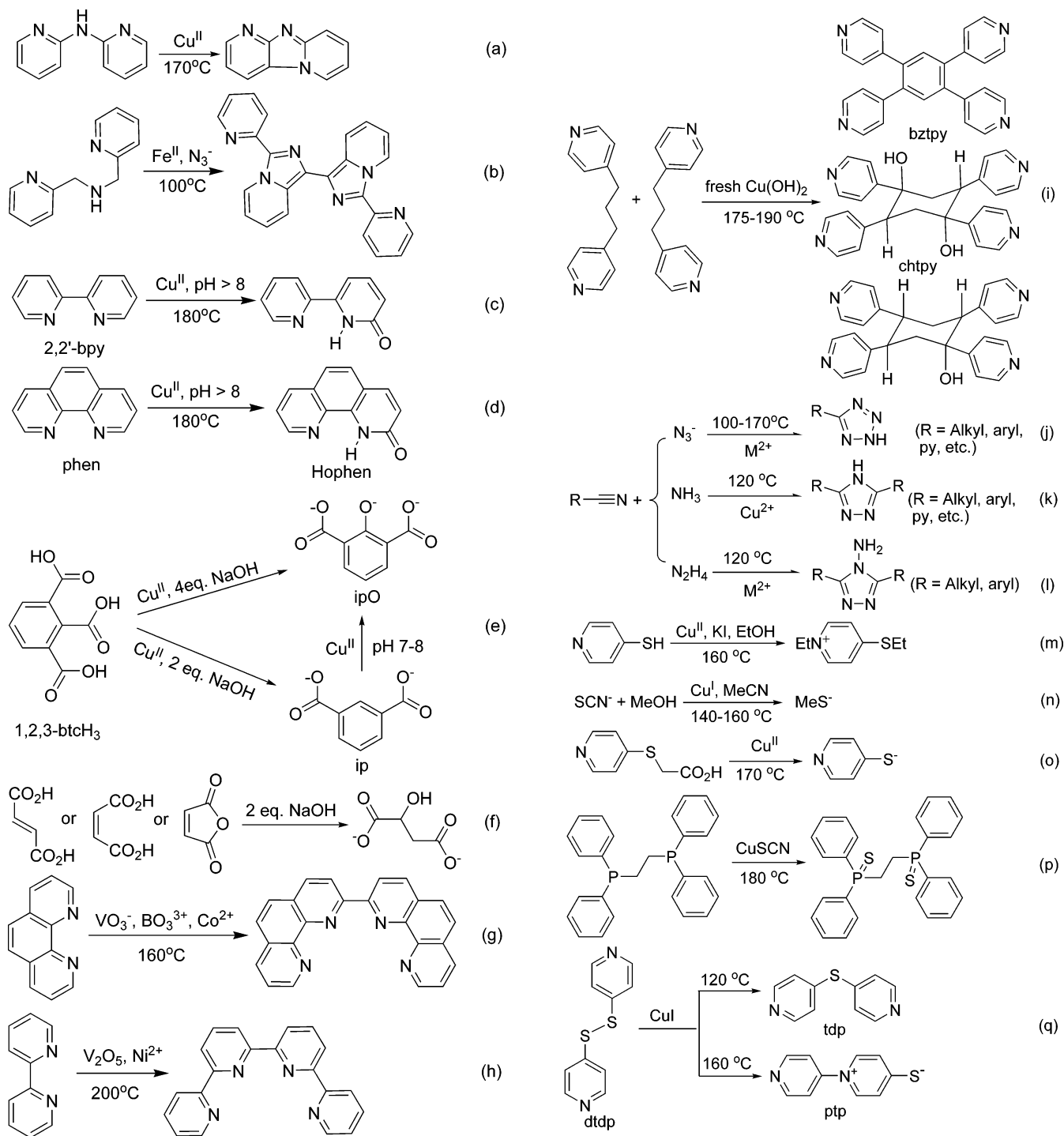
As a nonconventional method, solvothermal in situ ligand reactions were first reported by Li et al. in 1998 on the rearrangement of 2,2'-dipyridylamine into dipyrido-[1,2-*a*:2',3'-*d*]imidazole (Scheme 1a) in the synthesis of one-dimensional (1D) coordination metal halides.<sup>7</sup> Almost at the same time, Lin et al. applied such in situ ligand reactions into the synthesis of acentric MOFs of metal carboxylates with second-order nonlinear optic properties, which may not be accessible from their corresponding acids.<sup>8</sup> Such reactions usually include hydrolysis of carboxylate esters, organic nitriles, and aldehydes into the corresponding carboxylates,<sup>3</sup> cleavage of acetonitrile/ethylene carbon–carbon bonds and 1,3,4-oxadiazole carbon–nitrogen/oxygen bonds,<sup>5,9</sup> cleavage and formation of disulfide bonds,<sup>10</sup> substitution of aromatic groups,<sup>11</sup> as well as decarboxylation of aromatic carboxylates.<sup>12</sup> Notably, these kinds of ligand reactions, being relatively straightforward in the context of reaction chemistry, have also become an important approach in the crystal engineering of MOFs exhibiting porosity, photoluminescence, and other physical properties.<sup>3–6</sup>

Since solvothermal in situ metal/ligand reactions are usually performed under relatively high temperature and pressure in the presence of transition-metal ions, they may provide not only very stable materials for potential applications, such as functional coordination polymers via crystal engineering, but also products that are inaccessible or not easily obtainable by conventional methods. In fact, several unusual solvothermal, one-pot, in situ ligand reactions that are important in synthetic chemistry, including dehydrogenative carbon–carbon coupling, hydroxylation of aromatic rings, cycloaddition of organic nitriles with azide and ammonia, and transformation of inorganic and organic sulfur, have been documented very recently. Meanwhile, as another aspect of solvothermal metal/ligand reactions, the metal reactions are usually simple redox ones and are very important in promoting the ligand reactions as well as controlling the final supramolecular structures of specific MOFs.<sup>4,6</sup>

Our interest in solvothermal metal/ligand reactions has been primarily concerned with the discovery of new ligand reactions and their application in the crystal engineering of functional coordination polymers.<sup>6</sup> Subsequently, we realized that understanding the mechanism is particularly necessary for the application to specific syntheses, the development of novel synthetic methods, and the preparations of new materials with desired structures and properties. However, the complexities involved in the organic reactions or supramolecular assemblies could hardly be “seen” in the one-pot, black-box-like solvothermal metal/ligand reactions, and hence, in depth investi-

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Scheme 1

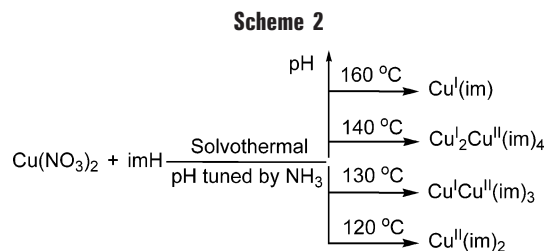


gation on the mechanism of a multistep organic ligand reaction under solvothermal condition encounters great difficulty. Therefore, besides the exploitation of these reactions in assembly of molecular architectures with desired properties, we have also directed our major effort to the study of several types of solvothermal in situ metal/ligand reactions with an anticipation to answering two challenging questions: (i) can we rationalize the reaction mechanisms through experiments, and (ii) can we exploit these reactions in synthesis of new and useful organic compounds?

In the present Account, we wish to describe the recent advances in the in situ ligand reactions, along with  $\text{Cu}^{\text{II}}$  reduction, particularly our effort to answer the above questions mainly through the crystal engineering approach. The solvothermal in situ ligand reactions to be discussed are illustrated in Scheme 1.

## 2. Metal Redox Reaction

The primary role of metal ions in an in situ metal/ligand reaction is to activate the ligand precursors. In addition,

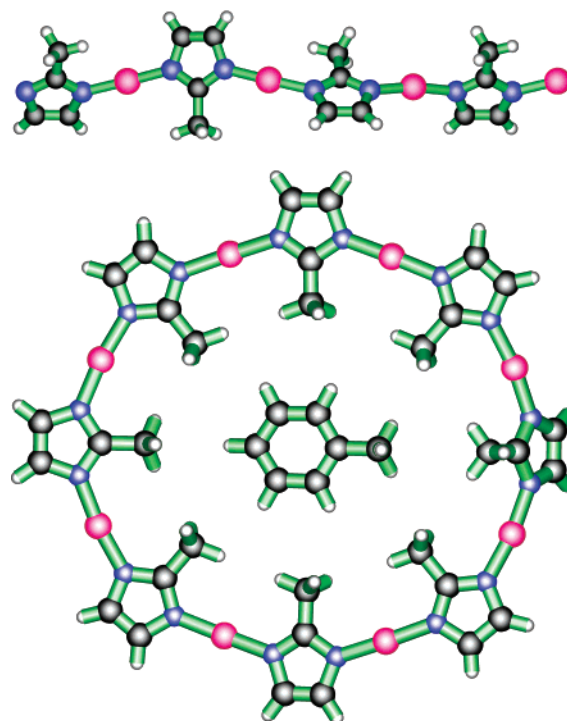


when the ligand involves a redox (typically oxidative so far) reaction in this process, the oxidant is usually  $\text{Cu}^{\text{II}}$ .<sup>5–7</sup> In contrast, only very limited examples of  $\text{Cu}^{\text{I}}$  to  $\text{Cu}^{\text{II}}$  oxidation have been found so far.<sup>5</sup>

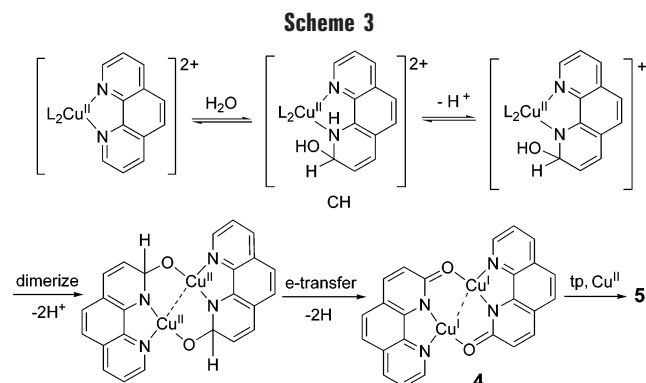
The first example of in situ reduction of  $\text{Cu}^{\text{II}}$  occurred in the generation of a  $\text{Cu}^{\text{I}}$  coordination polymer, in which 4,4'-bipyridine (4,4'-bpy) was suggested to mediate such metal reduction.<sup>13</sup> By stepwise increase of the reaction temperature and pH, we have successfully synthesized a series of polymeric  $\text{Cu}^{\text{II}}$ , mixed-valent  $\text{Cu}^{\text{I,II}}$  and  $\text{Cu}^{\text{I}}$  imidazolates (Scheme 2) exhibiting intriguing structures.<sup>14</sup> This fact demonstrates that the reduction of  $\text{Cu}^{\text{II}}$  into  $\text{Cu}^{\text{I}}$  in the presence of imidazole (imH) is sensitive to the reaction temperature and pH, and that higher temperature (usually >140 °C) and pH (usually >7) is in favor of the reduction.

Actually,  $\text{Cu}^{\text{II}}$  can be easily solvothermally converted into  $\text{Cu}^{\text{I}}$  in the presence of different types of aromatic species,<sup>4</sup> and such conversion is the most convenient approach for solvothermal preparations of  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{I,II}}$  coordination polymers.<sup>5,7</sup> For example, imidazolates are very strong, curved, exo-bidentate ligands, and binary univalent metal imidazolates strongly tend to form the kinetic products of 1D chainlike polymers for their very low solubility in common solvents. In conventional synthetic approach, such reactions usually yield microcrystals that are not suitable for X-ray single-crystal diffraction.<sup>6</sup> By taking advantage of solvothermal in situ generation of  $\text{Cu}^{\text{I}}$  ions, we have established an approach by addition of ammonia and guest templates to generate polygonal isomers of the 1D chainlike  $[\text{Cu}(\text{mim})]_{\infty}$  (**1**) (mim = 2-methylimidazole).<sup>15</sup> In such an approach, ammonia functions not only as a base but also as a coordination buffering agent to reduce the crystallization speed and increase the solubility of some intermediate  $\text{M}^{\text{I}}$ -mim species, while the guest templates, such as toluene and *p*-xylene, are helpful for inducing the formation of discrete polygonal species and offering additional supramolecular stabilization energy for the crystallization of the polygonal  $[\text{Cu}(\text{mim})]_n$  species, leading to the formation of the predesigned, uniform molecular octagon  $[\text{Cu}_8(\text{mim})_8]$ -toluene (**2**) (Figure 1) and decagon  $[\text{Cu}_{10}(\text{mim})_{10}]$ (*p*-xylene)<sub>2</sub> (**3**). Similar approaches have also been applied to the controlled assembly of other supramolecular isomers of  $\text{Cu}^{\text{I}}$  imidazolates<sup>16</sup> and  $\text{Cu}^{\text{I}}$  1,2,4-triazolates,<sup>17</sup> which are not easily reachable by other methods.<sup>6</sup> These facts clearly illustrate the significance of the in situ approach for the crystal engineering of  $\text{Cu}^{\text{I}}$  coordination polymers.

Besides  $\text{Cu}^{\text{II}}$  ion, only a few other metal or inorganic ions (e.g.,  $\text{V}^{\text{V}}$ ,  $\text{SeO}_2$  and possibly  $\text{Fe}^{\text{III}}$ )<sup>18,19</sup> seem to be



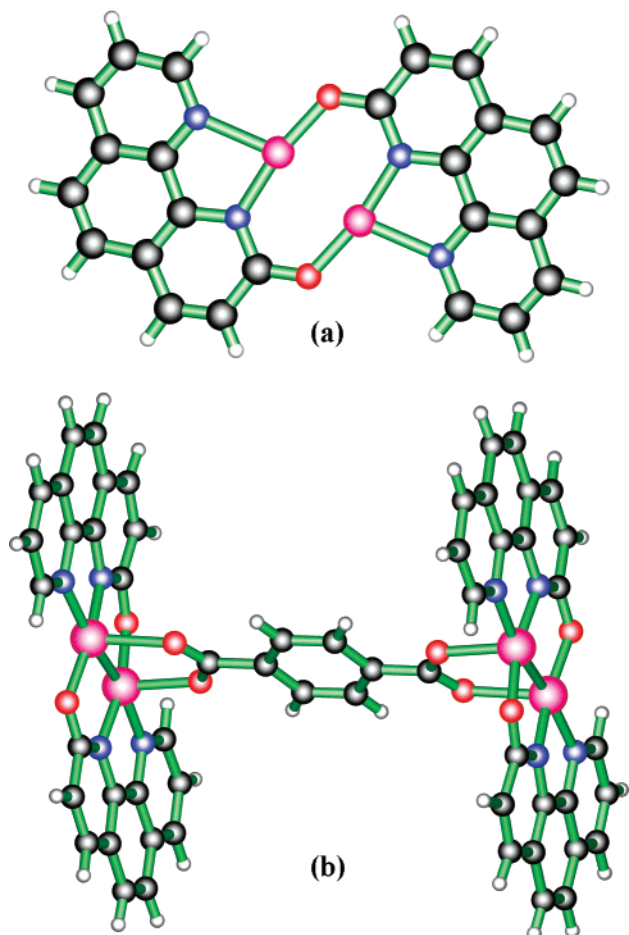
**FIGURE 1.** Crystal structures of **1** (upper) and **2** (lower). Color code: Cu, purple; C, black; H, gray; N, blue.



involved in the redox reactions. We will further demonstrate that  $\text{Cu}^{\text{II}}$  ion is a versatile oxidant under solvothermal conditions in the following sections.

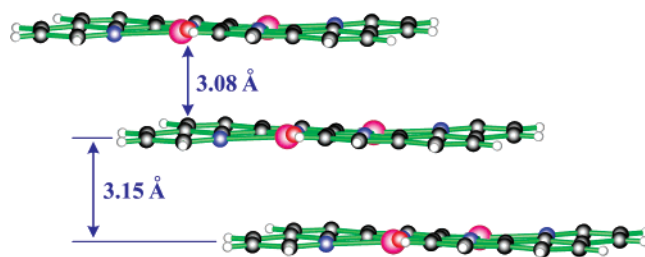
### 3. Oxidative Hydroxylation of Aromatic Rings

Metal complexes of 2,2'-bipyridine-like ligands, such as 2,2'-bipyridine (2,2'-bpy) and 1,10-phenanthroline (phen), have been most investigated in coordination chemistry and were well-known for their so-called anomalous behaviors in the aqueous medium.<sup>1,20</sup> In 1975, Gillard postulated an important covalent hydrate (CH) mechanism to rationalize the “anomalies” in the reactions of this kind of metal complexes, and the core of which is that the metal ligation to a pyridyl or 2,2'-bpy-like ligand leads to electronic changes in the pyridyl ring, thus enhancing nucleophilic attack of a hydroxide ion on the 2-position of a pyridine or phen (or the 6-position of 2,2'-bpy) ligand to form a CH (see Scheme 3) before further intramolecular shift of  $\text{OH}^-$  or  $\text{H}_2\text{O}$  onto the metal to form the final hydrolyzed or other related products.<sup>20</sup> Unfortunately, this



**FIGURE 2.** Structures of **4** (a) and **5** (b). Color code: Cu, purple; O, red; C, black; H, gray; N, blue.

important mechanism became a long-term debate due to the lack of structural evidence for the CH intermediate.<sup>1</sup> In 2002, we provided the key structural evidence for the Gillard mechanism by the isolation of 2-hydroxylated phen (and 6-hydroxylated 2,2'-bpy) ligands (see Scheme 1c,d) in their dinuclear Cu<sup>I</sup> and tetranuclear Cu<sup>I</sup>–Cu<sup>II</sup> complexes, such as [Cu<sub>2</sub>(ophen)<sub>2</sub>] (**4**) and [Cu<sub>4</sub>(ophen)<sub>2</sub>(tp)] (**5**) [ophen = 1,10-phenanthroline-2(1*H*)-one; tp = terephthalate] (Figure 2), from the solvothermal reactions of Cu<sup>II</sup> salt with phen or 2,2'-bpy.<sup>21</sup> The formation of **4** can be proposed with the aid of the CH mechanism to be via the formation of CH and related intermediates (Scheme 3), followed by dimerization, intramolecular electron transfer, and dehydrogenation, while one-electron oxidization of **4** and bridging of a tp furnishes **5**. In this procedure, Cu<sup>II</sup> serves not only as a metal ion to activate the 2-position of phen for the hydroxyl attack but also as an oxidant for trapping the unstable CH into a stable hydroxyl group that becomes a ketone group after tautomerization; the solution basicity (usually pH ≥ 8) is important not only for enhancing the hydroxyl attack, but also for the oxidizability of Cu<sup>II</sup>. To observe any other possible hydroxylated forms generated in these reactions, we also conducted a careful search and only found the dihydroxylation reactions of 2,2'-bpy to 3,3'-dihydroxy-2,2'-bipyridine and phen to 2,9-dihydroxy-1,10-phenanthroline as very minor



**FIGURE 3.** The molecular packing in **6**. Color code: Ag, purple; C, black; H, gray; N, blue.

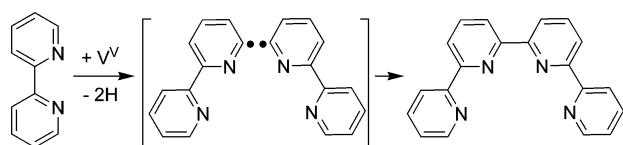
products.<sup>22</sup> We can therefore conclude that the hydroxyl attack occurs mainly at the 2- or 6-position of phen or 2,2'-bpy, respectively, in accord with the CH mechanism.

Note that the hydroxylated bpy/phen ligands can be isolated from their metal complexes by demetallization and used to prepare a series of photoluminescent d<sup>10</sup> complexes,<sup>23</sup> as well as a highly electrical conducting single-component molecular material, [Ag<sub>2</sub>(ophen)<sub>2</sub>] (**6**) ( $\sigma = 14 \text{ S cm}^{-1}$  at room temperature),<sup>24</sup> which is isostructural to **4** and very closely packed in the solid via intermolecular strong Ag<sup>I</sup>– $\pi$  (3.08 Å) and very strong  $\pi$ – $\pi$  stacking (ca. 3.15 Å) interactions (Figure 3), leading to the presence of excited species with a sharp ESR signal and a high conductivity in its powder form at room temperature.

Another in situ oxidative hydroxylation of aromatic rings has also been documented for isophthalate (ip). A hydrothermal reaction of ip and 4,4'-bpy with Cu(NO<sub>3</sub>)<sub>2</sub> at 180 °C (Scheme 1e) yielded a mixed-valence Cu<sup>I</sup>–Cu<sup>II</sup> coordination polymer, [Cu<sub>2</sub>(ipO)(4,4'-bpy)] (ipOH = 2-hydroxyisophthalate) (**7**), which is composed of an in situ generated ipO ligand and exhibits a 3D structure having a very strong antiferromagnetic interaction admixture with a weak ferromagnetic interaction.<sup>25</sup> Interestingly, ipO can also be hydrothermally generated by replacement of the 2-carboxyl group of 1,2,3-benzenetricarboxylic acid (1,2,3-btcH<sub>3</sub>) with a hydroxy group upon addition of 4 equiv of NaOH (Scheme 1e), furnishing **7** in very high yield (95%).<sup>12a</sup> When reducing the amount of NaOH to 2 equiv, the 2-carboxylate group was removed without the formation of a hydroxy group, furnishing a mixed-valence Cu<sup>I</sup>–Cu<sup>II</sup> compound [Cu<sub>2</sub>(ip)(ipH)(4,4'-bpy)<sub>1.5</sub>] (**8**). However, without addition of NaOH, the 2-carboxylate group was retained, resulting in a 3D porous framework, [Cu<sub>2</sub>(1,2,3-btc)(4,4'-bpy)(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>) (**9**). The observation indicates that the in situ reaction of 1,2,3-btc is highly pH-dependent, giving ip at lower pH, which can be further mediated by Cu<sup>II</sup> into ipO at higher pH (Scheme 1e).

Aside from the hydroxylation that occurs on the aromatic groups of bpy-like ligands and polycarboxylates, a hydroxylation of the ethylene group of fumaric acid (and maleic acid or anhydride) into malate (ma) (Scheme 1f) has been utilized by us to prepare a microporous MOF [Co<sub>2</sub>(ma)(ina)<sub>n</sub>·2*n*H<sub>2</sub>O (ina = isonicotinate), which exhibits complicated magnetic properties tunable by guest water removal and exchange of it with methanol and formamide.<sup>26</sup>

Scheme 4



#### 4. Dehydrogenative Coupling of Carbon–Carbon Bonds

Carbon–carbon (C–C) bond formation is a very important type of reaction in modern organic syntheses and is the essence of organic synthesis that provides a basis for generating more complicated organic compounds from simpler ones.<sup>27</sup> The main drawback to current synthesis methods is the general use of highly reactive, expensive organometallic reagents of late transition metals for catalyzing the reactions. So far, a few examples of solvothermal C–C bond formation have been documented, in which the first example was the unexpected oxidative coupling of methanol to oxalate (ox) in the reaction of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and pyridine in methanol at 140 °C that yielded 2D (methylpyridinium)<sub>2</sub>[Zn<sub>2</sub>(ox)<sub>3</sub>] (**10**).<sup>28</sup> The nitrate groups were suggested to be the oxidant for the oxidative coupling of methanol into ox. Later, ox. has also been found to be generated by decarboxylative couplings of isonicotinates or acetates.<sup>29</sup>

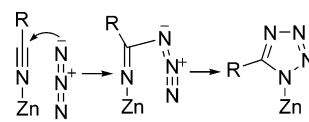
An unprecedented dehydrogenative coupling of phen into 2,2'-biphenanthroline (Scheme 1g) was observed by Gao et al. in a hydrothermal reaction of  $\text{NH}_4\text{VO}_3$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{Co}(\text{NO}_3)_2$ , and phen, which generates a layered coordination polymer, [Co(2,2'-biphenanthroline)]V<sub>3</sub>O<sub>8.5</sub> (**11**).<sup>18</sup> An analogous dehydrogenative coupling of 2,2'-bpy was also reported in a hydrothermal reaction of  $\text{NiCl}_2$ ,  $\text{V}_2\text{O}_5$ , and 2,2'-bpy (Scheme 1h).<sup>30</sup> Presumably, the reactions may involve radical processes, and the V<sup>V</sup> ions act as the oxidants in both cases (Scheme 4).<sup>30</sup>

A more unusual dehydrogenative coupling of 1,3-bis-(4-pyridyl)propane (bpp) into 1,2,4,5-tetra(4-pyridyl)benzene (bztpy) (Scheme 1i) was recently observed in a hydrothermal reaction of  $\text{Cd}_{10}\text{S}_4(\text{SPh})_{12}$ , bpp, and  $\text{Na}_2\text{SO}_4$  at 190 °C,<sup>31</sup> giving rise to a 3D photoluminescent framework [Cd<sub>8</sub>(SPh)<sub>12</sub>(bztpy)<sub>2</sub>SO<sub>4</sub>](HSO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (**12**). However, no oxidant was mentioned in the report.

Later, we carried out hydrothermal treatments of fresh  $\text{Cu}(\text{OH})_2$  with bpp, 1,4-cyclohexanedicarboxylic acid, and water in dilute HCl media at 175–190 °C, from which we observed a dehydrogenative coupling and hydroxylation of bpp into a dihydroxylcyclohexane ligand *a,a*-1,4-dihydroxy-*e,e,e,e*-1,2,4,5-tetra(4-pyridyl)cyclohexane (chtpy) (Scheme 1i) in its Cu<sup>I</sup> coordination polymers, which could be isolated by demetallization with  $\text{Na}_2(\text{H}_2\text{edta})$ .<sup>32</sup> The formation of Cu<sup>I</sup> indicates clearly Cu<sup>II</sup> is the oxidant.

We then envisioned that the monohydroxyl and even other polyhydroxyl cyclohexane ligands as the intermediates or other relevant species may also be present in the final products. Fortunately, the monohydroxyl cyclohexane ligand and the bztpy ligand (Scheme 1i) have also been successfully isolated from the powder product of the above hydrothermal systems, which can be applied to

Scheme 5



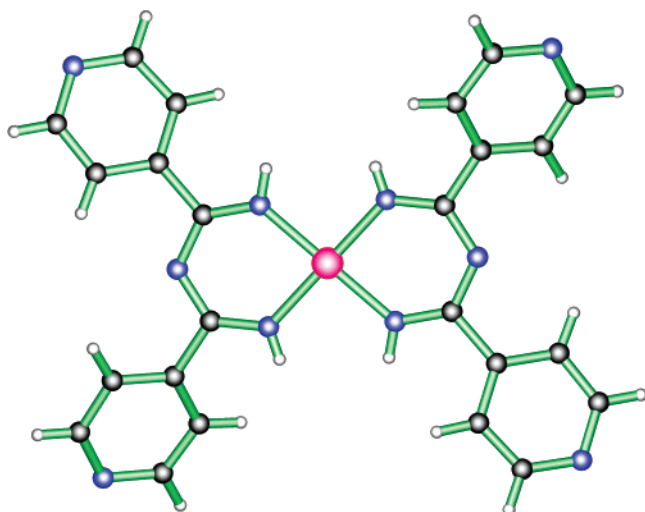
construct a series of novel 2D and 3D microporous MOFs with zeolite topologies.<sup>33</sup> More importantly, the isolation of the three different ligands implies that the Cu<sup>II</sup>-mediated in situ ligand reaction from bpp may involve complicated radical reactions, which simultaneously furnishes the bztpy and hydroxyl cyclohexane ligands.

#### 5. Cycloaddition of Organic Nitriles with Azide or Ammonia

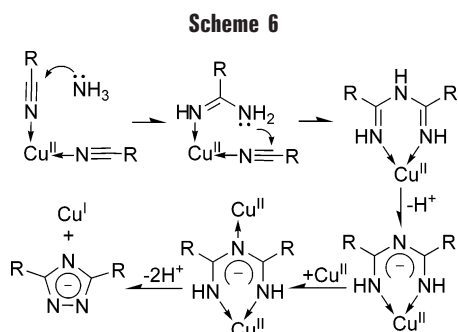
As important kinds of heterocyclic organic compounds, both 1,2,4-triazoles and tetrazoles have been extensively investigated in organic synthetic chemistry for several decades due to the fact that they have wide ranging applications in pharmaceuticals, specialty explosives, photography, information recording systems, agriculture, and as precursors to a variety of heterocycles.<sup>34,35</sup> Continuous efforts have been focused in the search for more efficient and simple synthetic procedures of these kinds of heterocycles.<sup>35,36</sup> In particular, a few one-pot, solvothermal in situ synthetic approaches have been recently established (Scheme 1j–l).

Recently, Sharpless et al. reported several simple synthetic approaches for 5-substituted 1*H*-tetrazoles via [2 + 3]-cycloadditions of organonitriles with organic and inorganic azides in water.<sup>36</sup> They found that the reaction rate is dependent on the electron deficiency of the nitrile, and unactivated alkylnitriles and some electron-rich aromatic nitriles can only react at higher temperatures under hydrothermal conditions, while Zn<sup>II</sup> salts can significantly promote the reactions of organonitriles with inorganic azide ions in water, where the coordination of nitrile rather than azide to Zn<sup>II</sup> is the key step in reducing the energy barrier and enhancing the azide attack on the nitrile carbon atom before an intramolecular cyclization (Scheme 5).<sup>34</sup> This safe, convenient, and environmentally friendly procedure of the in situ generation of 1*H*-tetrazoles has been utilized by Xiong et al. to construct functional coordination polymers exhibiting interesting structural diversity, as well as nonlinear optical and other properties.<sup>37</sup>

Many 1,2,4-triazoles were prepared with multistep procedures, which usually involve hydrazine derivatives as starting agents or conversion of other ring systems. Recently, we accidentally discovered a one-pot, solvothermal synthetic approach for 1,2,4-triazoles from reactions of aqueous ammonia and a variety of alkyl-, phenyl-, pyridylnitriles in the presence of Cu<sup>II</sup> (Scheme 1k),<sup>38</sup> leading to the generation of a series of structurally interesting MOFs of Cu<sup>I</sup> 3,5-disubstituted-1,2,4-triazolates.<sup>39</sup> Therefore, such an in situ generation approach of the ligands represents not only a widely applicable non-hydrazine-based synthetic route to triazolates but also a successful crystal engineering approach for microporous



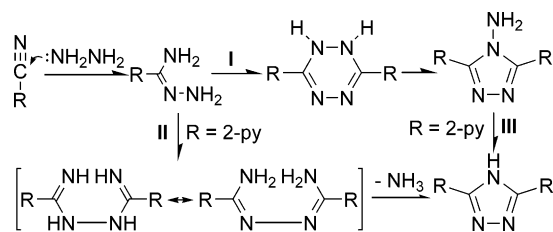
**FIGURE 4.** Structure of **13**. Color code: Cu, purple; C, black; H, gray; N, blue.



MOFs and different supramolecular isomers of  $\text{Cu}^{\text{I}}$  triazoles through tuning the local coordination structures and orientations of the triazolate ligands by changing the reaction conditions and addition of different coordination buffering agents.<sup>6,17,38,39</sup>

Obviously, such 1,2,4-triazole formation may involve complicated courses. To gain insight into the mechanism,<sup>39</sup> we conducted a systematic investigation by proper selection and control over the reaction temperature, time, and medium for trapping the proposed intermediates that may be stabilized by complexation with metal ions or supramolecular interactions in crystalline state. Initially, we found that the cyclization of organonitriles with ammonia should be performed at temperature higher than 100 °C, and the  $\text{Cu}^{\text{II}}$  ions should act as an oxidant during the multistep formation of the triazolate ring. Similar to the formation of tetrazoles, the ligation of  $\text{Cu}^{\text{II}}$  and other metal ions can promote the attack of ammonia on the nitrile carbon atom. Among the several possible reaction paths, the one involving the formation of amidine and 1,3,5-triazapentadiene (tap) seems to be most likely (Scheme 6), in which tap may further undergo a two-electron oxidative cyclization into the triazole. Indeed, we have then isolated the proposed tap intermediate by controlling the solvothermal reaction. The reaction of  $\text{Cu}(\text{OH})_2$ ,  $(\text{NH}_4)_2\text{CO}_3$ , and 4-cyanopyridine in THF at 90 °C afforded the intermediate in its complex  $[\text{Cu}^{\text{II}}(4\text{-pytap})_2]$  (**13**, 4-Hpytap = 2,4-di(4-pyridyl)-1,3,5-triazapentadiene) (Figure 4). The important conditions for this isolation are

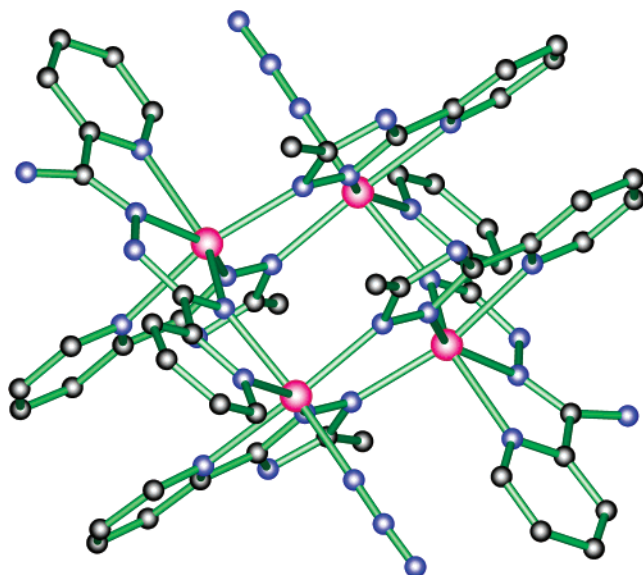
**Scheme 7**



the use of  $(\text{NH}_4)_2\text{CO}_3$  as a source of ammonia to slow down the reaction rate and avoid hydrolysis the intermediate (together with THF as solvent), 4-cyanopyridine as the starting nitrile to increase the crystallization rate of product (**13**), since it is virtually insoluble in THF, and the lower reaction temperature to avoid further conversion of 4-pytpap into the final triazolate. Isostructural  $[\text{Ni}(4\text{-pytpap})_2]$  was also obtained by using  $\text{Ni}^{\text{II}}$  in the place of  $\text{Cu}^{\text{II}}$  under a similar reaction condition, while no similar metal complex was obtained by using  $\text{Zn}^{\text{II}}$  or  $\text{Co}^{\text{II}}$  in place of  $\text{Cu}^{\text{II}}$ , suggesting that the square-planar coordination behaviors of  $\text{Cu}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  are critical in stabilizing 4-pytpap while no oxidative ability is required in this step. Subsequently, we also confirmed that 4-pytpap was really the intermediate by a further conversion into the final triazolate with the aid of extra  $\text{Cu}^{\text{II}}$  ions at a higher temperature. For example, with the addition of excessive  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , **13** could be converted at 120 °C in THF into  $[\text{Cu}_6\text{Cl}_3(4\text{-pytz})_3]$  (**14**) in high yield (80%).<sup>39</sup>

Later, we have further explored other solvothermal approaches for the in situ generations of triazoles by using hydrazine as a nucleophile to attack various organonitriles (Scheme 11) in the presence of metal salts. Actually, alkyl-, phenyl-, and 4-pyridylnitriles can react with hydrazine hydrate in the presence of a  $\text{Cu}^{\text{II}}$  or  $\text{Mn}^{\text{II}}$  salt to form the corresponding 4-amino-3,5-disubstituted-1,2,4-triazolates in the crystalline form free of metal coordination in good yields (50–80%).<sup>40</sup> We found that path I via the formation of the tetrazine should be dominant in this case (Scheme 7), being similar to the synthesis of aryl- or pyridyl-4-amino-1,2,4-triazoles by acid catalysis.<sup>33</sup> Note that alkylnitriles are inactive in the case of acid catalysis but are active in our case.

However, when 2-cyanopyridine (2-cpy) or 2-pyridylamidrazone (2-pya) derived from 2-cpy and hydrazine hydrate was used as the starting agent,  $[\text{Mn}_2(\text{bpt})_2\text{X}_2 \cdot (\text{H}_2\text{O})_2]$  (**15**,  $\text{X} = \text{Cl}^-$  or  $\text{SCN}^-$ ) with the deaminated bpt rather than 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole (abpt) was isolated, which suggests that the pathway involving 2-cpy as a starting reactant is different from those involving other organonitriles in the presence of metal salts, which should be via path II (Scheme 7). In fact, the deamination (path III) occurred to abpt but not to other 4-amino-3,5-disubstituted-1,2,4-triazoles when solvothermally treated in the presence of metal ions.<sup>40</sup> By controlling the solvothermal conditions and addition of appropriate counteranions, an intermediate  $N,N'$ -bis(picolinamide)azine ( $\text{H}_4\text{bpa}$ ) was trapped in crystalline  $[\text{Mn}_4(\text{H}_3\text{bpa})_4(\text{SCN})_4] \cdot 2\text{C}_2\text{H}_5\text{OH}$  (**16**), while a reaction of  $\text{H}_4\text{bpa}$  with  $\text{Mn}^{\text{II}}$  furnished **15**. This fact demonstrates that path II is



**FIGURE 5.** Structure of **17**. Color code: Mn, purple; C, black; N, blue.

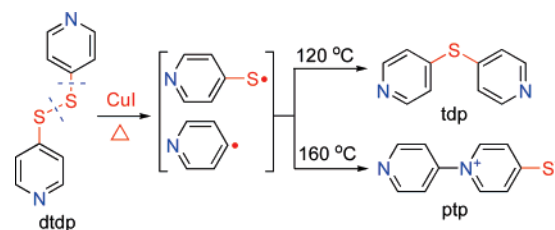
dominant in the formation of bpt in the presence of metal ions, in which the metal ligation can stabilize the tautomers of H<sub>4</sub>bpa and enhance the nucleophilic reactivity of the imino carbon atom and deamination, hence leading the formation of the deaminated bpt or H<sub>4</sub>bpa in the complexation. Note that we also observed the solvothral in situ cycloaddition of 2-pya with formate or acetate into the corresponding asymmetric 3,5-disubstituted-1,2,4-triazolates, e.g., [Mn<sub>4</sub>(H<sub>3</sub>bpa)<sub>2</sub>(mpt)<sub>4</sub>(N<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (**17**) (Hmpt = 3-methyl-5-(2-pyridyl)-1H-1,2,4-triazole) containing both H<sub>3</sub>bpa and asymmetric mpt (Figure 5).<sup>40</sup>

## 6. Transformation of Inorganic and Organic Sulfur

Organosulfides are important ligands exhibiting versatile binding modes. A simultaneous redox-alkylation was found by Yao et al. in the solvothral self-assembly of CuCl<sub>2</sub>, KI, HS-4-C<sub>5</sub>H<sub>4</sub>N, and ethanol, which afforded a photoluminescent chainlike Cu<sup>I</sup> polymer, [(Cu<sub>3</sub>I<sub>4</sub>)(EtS-4-C<sub>5</sub>H<sub>4</sub>NEt)]<sub>n</sub> (**18**) (Scheme 1m).<sup>41</sup> An in situ generated organosulfide ligand from inorganic sulfur or thiocyanate was later observed by Li et al.<sup>42</sup> through a solvothral reaction of CuSCN with acetonitrile and methanol, which yielded a photoluminescent, 3D polymer, {[Cu(μ<sub>3</sub>-SCH<sub>3</sub>)<sub>2</sub>(CN)]<sub>2</sub>[Cu<sub>10</sub>(μ<sub>3</sub>-SCH<sub>3</sub>)<sub>4</sub>(μ<sub>4</sub>-SCH<sub>3</sub>)<sub>2</sub>]}<sub>n</sub> (**19**) (Scheme 1n). On the basis of their examination, the sulfur atom in methyl mercaptide comes from thiocyanate while the methyl group comes from methanol rather than acetonitrile. Meanwhile, the presence of acetonitrile and Cu<sup>I</sup> is essential, while using other salts M(SCN)<sub>n</sub> (M = Ag, Ni, Co, Zn; n = 1, 2) in the place of CuSCN did not yield similar products.

Relevant in situ generations of organosulfides have also been applied to prepare interesting cluster-based, twelve-connected face-centered cubic topological networks [Cu<sub>12</sub>-(μ<sub>4</sub>-SCH<sub>3</sub>)<sub>6</sub>(CN)<sub>6</sub>]<sub>n</sub>·2H<sub>2</sub>O (**20**)<sup>43</sup> and [Cu<sub>3</sub>(pdt)<sub>2</sub>(CN)] (**21**, pdt = 4-pyridinethiolate),<sup>44</sup> which are possibly inaccessible by

**Scheme 8**



direct reactions using the organosulfides. The methyl mercaptide was derived by simultaneous redox and transformation of thiocyanate sulfur (Scheme 1n) similar to that found for **19**, while pdt in **21** and cyanide ligands in **20** and **21** were in situ generated from the cleavages of S–C bonds of (4-pyridylthio)acetic acid (Scheme 1o) and thiocyanate, respectively.

More interestingly, the sulfur atom in thiocyanate can be transferred onto 1,2-bis(diphenylphosphino)ethane (dppe) in a solvothral reaction of CuSCN with dppe, giving rise to 1,2-bis(diphenylthiophosphinyl)ethane (dppeS<sub>2</sub>) (Scheme 1p) in a 3D coordination polymer [(CuCN)<sub>2</sub>(dppeS<sub>2</sub>)]<sub>n</sub> (**22**).<sup>45</sup> Two other unusual in situ transformations of organosulfides were observed in solvothral reactions of Cu<sup>I</sup> with 4,4'-dithiodipyridine (dtdp) in acetonitrile in different ratios at 120 and 160 °C, giving a 2D coordination network, [Cu<sub>4</sub>I<sub>4</sub>(tdp)<sub>2</sub>] (**23**) (tdp = 4,4'-thiodipyridine), and two 3D coordination networks, [Cu<sub>5</sub>I<sub>5</sub>(ptp)<sub>2</sub>] (**24**) and [Cu<sub>6</sub>I<sub>6</sub>(ptp)<sub>2</sub>] (**25**) (ptp = 1-(4-pyridyl)-4-thiopyridine), respectively (Scheme 1q).<sup>46</sup> Surprisingly, dtdp was unprecedentedly converted into two isomeric tdp and ptp ligands, rather than into a pdt ligand.<sup>10a</sup> Considering the structure of dtdp as well as the formation of S<sub>8</sub> as byproducts of **23**–**25**, we believe that two free-radical [4-pyS•] and [4-py•] intermediates resulted from cleavages of the S–S and S–C(sp<sup>2</sup>) bonds, respectively (Scheme 8).<sup>10a</sup> The tdp ligand should result from the recombination of both free-radical intermediates at 120 °C, whereas ptp was formed at a higher temperature of 160 °C, which suggests that the energy barrier in the formation of ptp is larger and the temperature plays a critical role in the formation of final products.

## 7. Concluding Remarks

As solvothral in situ metal/ligand reactions have only recently been aroused in the lately very active research of the crystal engineering of coordination polymers via solvothral treatments, we are now only at the earlier stage of investigations on solvothral metal/ligand reactions; hence, many of such ligand reactions were accidentally uncovered rather than designed. However, as outlined in this Account, several important types of solvothral, one-pot in situ metal/ligand reactions that are very attractive in view of organic synthetic chemistry have been established to generate products usually inaccessible or not easily obtainable by conventional methods. These unusual reactions include dehydrogenative carbon–carbon coupling, hydroxylation of aromatic rings, cycloaddition of organic nitriles with ammonia, as well as

transformation of inorganic and organic sulfur, which involve the metal-mediated procedures of the nucleophilic attack of hydroxide on aromatic and ethylene groups, the nucleophilic attack of ammonia on organonitriles, or the generation of organic radicals of aromatic derivatives.

More importantly, the current progress strongly indicates that it is possible to rationalize some complicated solvothelmal in situ metal/ligand reactions, as well as to exploit these reactions in the synthesis of new and useful organic compounds and the assembly of coordination molecular architectures with desired properties. We are therefore optimistic that such reactions not only can play a critical role in crystal engineering of functional coordination compounds but also may serve as a new bridge between coordination chemistry and synthetic organic chemistry.

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