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Unprecedented copper(I)-catalyzed *in situ* double cycloaddition reaction based on 2-cyanopyrimidine†

Tian Wen, Mian Li, Xiao-Ping Zhou and Dan Li*

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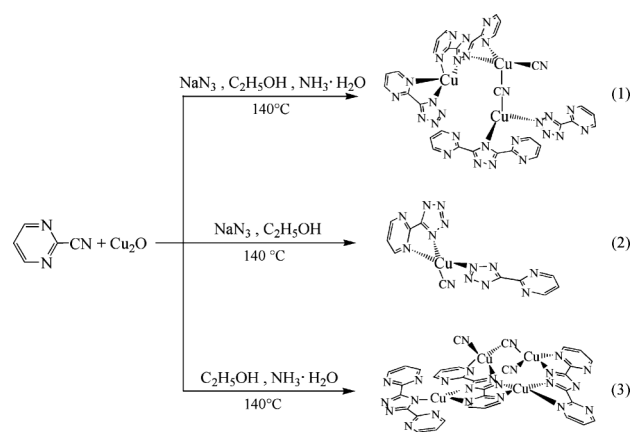
The solvothermal *in situ* double cycloaddition reaction of 2-cyanopyrimidine, Cu₂O and NaN₃ with aqueous ammonia additive generated a two dimensional copper(I) coordination polymer with 5-pyrimidyl-tetrazolate, 3,5-bispyrimidyl-1,2,4-triazolate and the cyano group as the ligands. This reaction can be tuned to yield two dimensional coordination polymers solely based on tetrazolate or 1,2,4-triazolate ligands.

Dating back to 2001, Sharpless and colleagues proposed that synthetic targets should be restricted to molecules that are easy to make, and termed “click chemistry” for organic reactions that are modular, wide in scope, give very high yields, and generate only inoffensive byproducts that can be easily removed.¹ Resonantly, the past decade has witnessed the vast development of the click reactions and their widespread applications in the sectors of materials and biology.² Compared with the most renowned click reaction of the alkyne-azide cycloaddition, the analogous [2 + 3] click reaction of the nitrile-azide cycloaddition, also developed by Sharpless *et al.*,³ received less attention.

Nevertheless, the nitrile-azide cycloaddition is a powerful tool for *in situ* reactions producing tetrazole coordination polymers with various interesting physical properties.⁴ Our group extensively explored the click formation of tetrazole coordination polymers by introducing an acetonitrile reagent, which was catalyzed by copper or silver salts to form a 5-methyl tetrazolate ligand.^{5,6} Subsequently, our researches were extended into heteroaromatic nitrile reagents and the possibility of various metal salts as the click catalysts was attempted.⁷ In this work, the reagent 2-cyanopyrimidine⁸ is involved, aiming to produce functional materials of the tetrazole coordination polymer *via* solvothermal *in situ* ligand synthesis.⁹ We unexpectedly identified a rare solvothermal reaction simultaneously incorporating the cycloadditions of both tetrazole and 1,2,4-triazole catalyzed by copper(I) salts, namely, an *in situ* double cycloaddition reaction.¹⁰ Herein, we wish to report the solvothermal synthesis of the targeted compound, and the control experiments exclusively yielding related tetrazole or 1,2,4-

triazole coordination polymers, along with their crystal structures and preliminary physical properties.

The title reaction was carried out by reacting the 2-cyanopyrimidine reagent with Cu₂O and NaN₃ in ethanol as the solvent under solvothermal condition (Scheme 1, see ESI for experimental details†). Into the reactant mixture, a few drops of aqueous ammonia were added, with the original intent of facilitating the nitrile-azide cycloaddition process undergoing the recently suspected nitrile activation mechanism.^{3b} Unexpectedly, the major product, namely [Cu₃(L1)(L2)(CN)]_n (**1**), of this reaction was found to be a copper(I) coordination compound incorporating three different *in situ* generated ligands, namely 5-pyrimidyl-tetrazolate (**L1**), 3,5-bispyrimidyl-1,2,4-triazolate (**L2**) and the cyano group, which was revealed by single-crystal X-ray crystallography.‡



Scheme 1 Reaction conditions of the double cycloaddition reaction and related control experiments, showing the coordination environments of the resulting complexes **1**, **2** and **3**.

To be noted, the *in situ* cycloadditions of organic nitriles with ammonia to yield 1,2,4-triazoles were extensively investigated by Chen and coworkers, and a convincing reaction mechanism was proposed therein.^{9b,11} However, the simultaneous occurrence of tetrazole and 1,2,4-triazole within a coordination compound is unprecedented, according to a survey in the latest version of the Cambridge Structural Database. The precedent coexistence of the tetrazole and 1,2,4-triazole components in a crystal refers to a series of organic energetic azolium azolate salts.¹² The nitrile-ammonia-nitrile cycloaddition, though undergoing a more

Department of Chemistry, Shantou University, Guangdong 515063, P. R. China. E-mail: dli@stu.edu.cn

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complicated reaction pathway, is extremely facile and versatile for producing 1,2,4-triazoles with various functional groups,^{9b} which is similar to the above mentioned click reactions yielding 1,2,3-triazoles and tetrazoles. Hence, evoking *in situ* double cycloaddition to describe the solvothermal reaction that gave complex **1** should be warranted.

The previous mechanism suggested the presence of copper(II) cations is a key factor for the oxidative cycloaddition of 1,2,4-triazoles.^{9b,11} In this work, though the copper cations in both the reactant and resultant (complex **1**) were monovalent, we noticed the mother liquid (and those in all subsequent control and repeat experiments) showed typical blue colour of copper(II) cations, indicating that an *in situ* metal redox reaction^{9b} was involved. Moreover, the cyano ligand was also *in situ* generated, and was suspected to come from the carbon–carbon bond cleavage of 2-cyanopyrimidine, yielding cyano and pyrimidine groups. The carbon–carbon bond cleavage of nitriles to cyanide mediated by metal complexes was previously documented,¹³ and we also identified a new complex composed of copper(I) iodide and pyrimidine in one set of our control experiments based on 2-cyanopyrimidine (See Fig. S4 in ESI,† the crystal structure of this complex is not reported in this work).

Single-crystal X-ray structural analysis reveals that complex **1** crystallizes in the triclinic space group of $P\bar{1}$ and its asymmetric unit is composed of three crystallographically independent copper(I) atoms, one **L1** ligand, one **L2** ligand and one cyano linker (Fig. S1a in ESI†). The coordination spheres of the three copper(I) ions are shown in Fig. 1a: Cu1 is trigonal-planar coordinated, with the coordination sphere filled by N5 from the triazololate ring, N9 from the triazololate ring and C/N from the cyano linker. Cu2 and Cu3 both exhibit distorted tetrahedral coordination geometry, with the former surrounded by the chelating N8 and N10 in the **L2** ligand and two C/N sites in two cyano linkers, while the latter is bis-chelated by the **L1** (N2 and N6) and **L2** (N11 and N13) ligands. The overall structure of complex **1** is extended *via* the cyano linkers and stabilized by various weak interactions, such as $\pi \cdots \pi$ stacking (3.68 Å, Fig. S1c in ESI†) and a Cu \cdots Cu close contact (2.58 Å, Fig. S1d in ESI†), constructing a 2D layer. Since the pyrimidine groups only show a chelating coordination mode, they can be neglected when considering the extended structure of the coordination polymer. In this regard, the overall structure shows a grid layer with alternating hexagonal and tetragonal arrangement shown in Fig. 1b, which can be topologically viewed as a trinodal

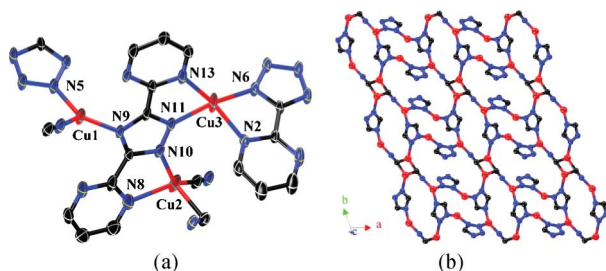


Fig. 1 (a) The coordination environments of the copper(I) atoms in complex **1**, shown with thermal ellipsoids of 50% probability. (b) View of the 2D layer of complex **1**, with all pyrimidine rings and hydrogen atoms omitted for clarity. Colour codes: red for Cu, blue for N, black for C.

(3,3,4)-connected network (Fig. S1d in ESI†) with the Schläfli symbol of $(4.6^2)(4.6^2)(6^4.10^2)$.

In order to examine the exact role of the azide and the ammonia in the above double cycloaddition reaction, we performed sets of control experiments with subtle variations of the reactants, *i.e.* only adding azide or ammonia in two separate experiments while all other reaction conditions remained the same (Scheme 1, see ESI for experimental details†). The results showed the double cycloaddition reaction could be fine-tuned to yield copper(I) complexes solely based on the **L1** or **L2** ligands, along with *in situ* generated cyano ligands, and interestingly, the resulting complexes **2** and **3** also exhibited 2D framework structures.

Complex **2**, namely $[\text{Cu}_2(\text{L1})(\text{CN})]_n$, crystallizes in the monoclinic space group of $C2/c$, and contains only one crystallographically independent copper(I) atom in its asymmetric unit, which also includes one **L1** ligand and one half of a cyano linker (Fig. S2a in ESI†). Cu1 adopts a distorted tetrahedral coordination geometry, surrounded by the chelating N4 and N6 in the **L1** ligand, N2 in another triazololate ring and C/N in the cyano linker (Fig. 2a). As shown in Fig. 2b, four **L1** ligands and two cyano groups construct a six-membered copper(I) ring, which is further extended *via* six adjacent such rings to form a 2D honeycomb-like 6^3 network (Fig. S2f in ESI†). The 2D layers of complex **2** are parallel to the *ab* plane, and stack in a face-to-face fashion along the *c* axis, allowing 1D hexagonal channels (with the diagonal distances of 10.145(4), 10.396(2), and 12.693(6) Å) to be present across the overall porous framework with no solvent molecule embedded. The calculation using PLATON suggests a 27.2% void space of the total crystal volume.

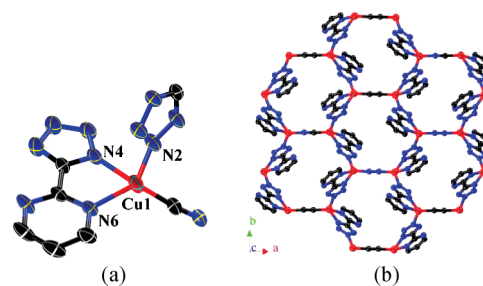


Fig. 2 (a) The coordination environments of the copper(I) atom in complex **2**, shown with thermal ellipsoids of 50% probability. (b) View of the 2D layer of complex **2**, with all hydrogen atoms omitted for clarity. Colour codes: red for Cu, blue for N, black for C.

Complex **3**, namely $[\text{Cu}_4(\text{L2})_2(\text{CN})_2]_n$, crystallizes in the triclinic space group of $P\bar{1}$. There exist up to four crystallographically independent copper(I) centres in its asymmetric unit (Fig. S3a in ESI†). Their coordination environments are illustrated in Fig. 3a: Cu1 and Cu4, co-bridged *via* a cyano linker, both show highly distorted tetrahedral spheres, and each is coordinated with another cyano group and one chelating site (N2 and N3, or N11 and N13, respectively) in the **L2** ligand. In contrast, Cu2 adopts a regular tetrahedral coordination, defined by two pairs of chelating sites (N4 and N6, N8 and N10) from two **L2** ligands. Cu3 is trigonal-planar coordinated, formed by two 1-position N (N5 and N12) in two triazololate rings and N8 in the pyrimidine ring. Similar to the structure of complex **2** (Fig. 2b), the overall 2D layer of complex **3** can be viewed as a series of 1D propagation of the copper(I)-azoles linkages connected *via* the cyano linkers (Fig. 3b),

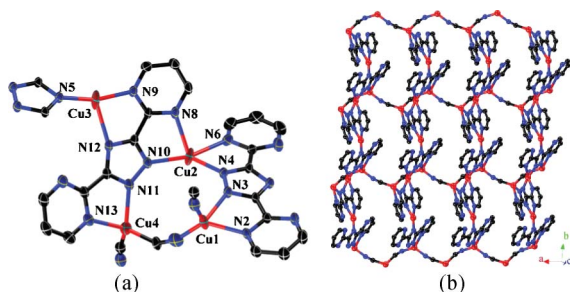


Fig. 3 (a) The coordination environments of the copper(I) atoms in complex **3**, shown with thermal ellipsoids of 50% probability. (b) View of the 2D layer of complex **3**, with all hydrogen atoms omitted for clarity. Colour codes: red for Cu, blue for N, black for C.

but the topology of the 2D layer of complex **3** is different from that of complex **2**, showing a 2D lattice-like 4^4 network (Fig. S3b in ESI[†]). The neighbouring layers are interconnected via C–H... π weak interactions (Fig. S3d in ESI[†]).

Thermogravimetric analysis was performed to assess the thermal stability of these materials; the results (Fig. S5 in ESI[†]) indicate that complexes **1**, **2** and **3** are all thermally robust, stable up to 300–400 °C. The solid-state luminescent spectra of complex **1** at room temperature shows the solid sample produces strong emission with the maximum at 370 nm when excited at 300 nm wavelength (Fig. S6 in ESI[†]). Given the high-energy profile of the emission, the luminescent origin is probably the excited states of the organic azolate ligands.

In summary, we have identified in this work an unprecedented copper(I)-catalyzed solvothermal *in situ* double cycloaddition reaction simultaneously yielding tetrazolate and 1,2,4-triazolate ligands based on an organic nitrile reagent. This reaction utilizes a facile and efficient synthetic procedure with readily available sources such as azide and ammonia to fabricate coordination polymers, and for the first time unites tetrazole and 1,2,4-triazole functionalities in a coordination compound, which will find applications similar to, or even better than, the organic energetic azolium azolate salts.¹² Though the mechanism of this double cycloaddition reaction may be complicated and thus is unclear at this stage, the reaction can be finely tuned to separately yield tetrazolate or 1,2,4-triazolate based coordination polymers, both of which feature 2D framework topology. This finding will shed light on and facilitate our further researches on *in situ* ligand synthesis and the click formation of functional coordination materials.

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Notes and references

† Crystal data for **1**: triclinic, space group $P\bar{1}$, $M_r = 587.99$, $a = 9.7029(6)$ Å, $b = 10.1842(6)$ Å, $c = 11.1003(7)$ Å, $\alpha = 107.2920(10)^\circ$, $\beta = 91.1910(10)^\circ$,

$\gamma = 109.5120(10)^\circ$, $V = 987.99$ Å³, $Z = 2$, $\rho_c = 1.996$ g cm⁻³, $T = 293(2)$ K, 12 414 reflections collected, 2368 unique with $R_{\text{int}} = 0.0222$, $R_1 [I > 2\sigma(I)] = 0.0466$, $R_2 = 0.0689$, $wR_2 = 0.1135$, GOF = 1.106 for all data. Crystal data for **2**: monoclinic, space group $C2/c$, $M_r = 447.37$, $a = 16.039(2)$ Å, $b = 9.0345(12)$ Å, $c = 14.6031(19)$ Å, $\beta = 111.974(2)^\circ$, $V = 1962.3(4)$ Å³, $Z = 4$, $\rho_c = 1.514$ g cm⁻³, $T = 293(2)$ K, 4572 reflections collected, 1570 unique with $R_{\text{int}} = 0.0430$, $R_1 [I > 2\sigma(I)] = 0.0716$, $R_2 = 0.0815$, $wR_2 = 0.2287$, GOF = 1.075 for all data. Crystal data for **3**: triclinic, space group $P\bar{1}$, $M_r = 754.68$, $a = 8.3754(15)$ Å, $b = 10.891(2)$ Å, $c = 14.418(3)$ Å, $\alpha = 101.866(3)^\circ$, $\beta = 101.866(3)^\circ$, $\gamma = 1266.2(4)^\circ$, $V = 1266.2(4)$ Å³, $Z = 2$, $\rho_c = 1.979$ g cm⁻³, $T = 293(2)$ K, 8878 reflections collected, 4375 unique with $R_{\text{int}} = 0.0206$, $R_1 [I > 2\sigma(I)] = 0.0436$, $R_2 = 0.0528$, $wR_2 = 0.1111$, GOF = 1.058 for all data. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo-K α , $\lambda = 0.71073$ Å).

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