

Synthesis of Copper Halide Coordination Polymers with Ligands Formed by In Situ Cyclization of 2-Aminopyrimidine and Ethanol

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The design and synthesis of coordination polymers from transition metals and organic ligands have been extensively studied for their crystallographic diversity and potential applications. Recently, the synthesis of coordination polymers by hydro(solvo)thermal in situ metal/ligand reactions has drawn great interest because of its potential to generate novel coordination architectures and new organic reactions. As described in our manuscript, the nitrogen heterocyclic

2,3-dihydroimidazo[1,2-*a*]pyrimidine ($C_6H_7N_3$) ligand was synthesized by an in situ reaction starting from 2-aminopyrimidine and ethanol. At the same time, two luminescent copper halide coordination polymers, $(CuCl)_3C_6H_7N_3$ and $(CuI)_2C_6H_7N_3$, were assembled under solvothermal conditions.

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Introduction

Hydro(solvo)thermal in situ metal/ligand reactions, as a new bridge between coordination chemistry and organic synthetic chemistry,^[1] are of great interest for the discovery of novel coordination architectures – especially those that are inaccessible by direct preparation – and organic reactions.^[2] Although in situ metal/ligand reactions have been extensively investigated for many decades, only a few kinds of organic ligand in situ reactions have been found under hydro(solvo)thermal conditions, such as the transformation of inorganic and organic sulfur,^[3c] dehydrogenative carbon–carbon coupling,^[3b] hydroxylation of aromatic rings,^[3a] and cycloaddition of organic nitriles with azide and ammonia.^[3d] The exploration of new in situ metal/ligand reactions has remained a challenge for researchers in both coordination and organic chemistry.

A few kinds of ligand in situ reaction have been found in copper halides system,^[4] but the use of the reduction of Cu^{2+} to Cu^+ is rare relative to the efforts directed towards CuX (X = halide).^[5] Because the oxidation ability of XO_4^{1-} is much stronger than that of Cu^{2+} , we used not only the reduction of Cu^{2+} to Cu^+ , but also the reduction of XO_4^{1-} to X^- in order to discover novel structures. In this communication, we report two examples of the simultaneous redox of Cu^{2+} to Cu^+ and XO_4^{1-} to X^- (X = Cl, I) and

their self-assembly under solvothermal conditions to afford luminescent a copper(I) layer and a chain polymer, $(CuCl)_3C_6H_7N_3$ (**1**) and $(CuI)_2C_6H_7N_3$ (**2**) ($C_6H_7N_3$ = 2,3-dihydroimidazo[1,2-*a*]pyrimidine), respectively. We found an in situ cycloaddition of 2-aminopyrimidine and EtOH.

Results and Discussion

Single-crystal X-ray structure analysis of the two compounds showed that compound **1** is a two-dimensional inorganic–organic $CuCl$ coordination polymer and that compound **2** is a one-dimensional hybrid CuI chain. The structure of compound **1** can be decomposed into two parts of crystallographically independent metal atom centers (Figure 1). The Cu center, a Cl atom, and the ligand make up a metal–ligand chain, and the Cu center adopts a distorted tetrahedral geometry coordinated to two Cl atoms and two N atoms from the ligand. The other part of the structure is a $(CuCl)_6$ chain, which is constructed by combination of two chair-shaped trinuclear Cu_3Cl_3 units that are joined through six Cl anions. The unit structure feature of the chain is similar to the double six-membered (D6R, hexagonal prism) rings found in zeolites, and this structure is an important and attractive unit in zeolites.^[6] As shown in Figure 1, each metal–ligand chain connects two double six-membered rings through the Cl atoms to form the 2D grid of compound **1**. The structure of compound **2** is a zigzag ladder chain; each copper cation serves as a tetrahedral coordination site where each iodine anion is coordinated to three copper cations (Figure 2). This structure can be attributed to the ligand, and it is different from other ladder

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chains reported so far. The distance of the two coordination nodes of the ligand is 2.4 Å, which is shorter than twice the bond length of CuI making the ladder zigzag.

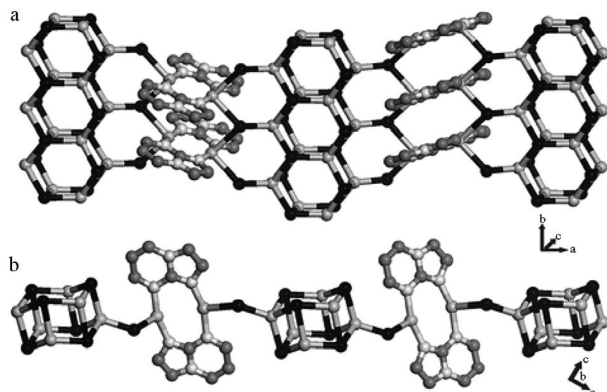


Figure 1. Two-dimension net of compound **1** (a) and connection between the six-membered rings (b).

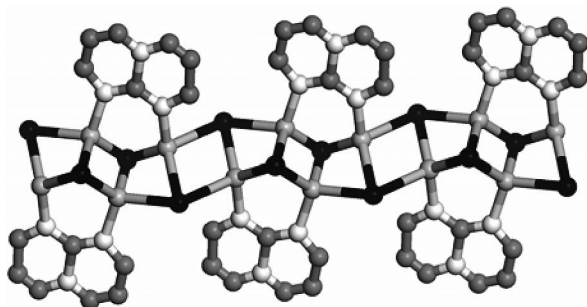
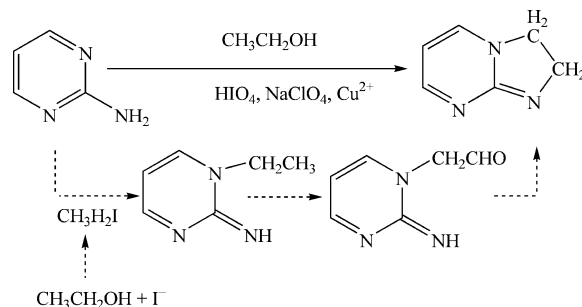


Figure 2. Single zigzag ladder chain of compound **2**.

Like most crystals synthesized by solvothermal reactions, the two compounds are stable in air and water but soluble in aqueous HCl. Copper halides are easily dissolved in CH_3CN but the ligand is indiscernible, which facilitates the isolation of the pure ligand. After characterizing its structure by X-ray single-crystal structure analysis, we also carried out ^1H NMR spectroscopic measurements of the ligand to ensure its structure. The ^1H NMR spectrum of the ligand [(500 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): δ = 3.9 (t, J = 10 Hz, 2 H), 4.6 (t, J = 10 Hz, 2 H), 6.9 (t, J = 5 Hz, 1 H), 8.4 (d, J = 5 Hz, 1 H), 8.6 (d, J = 2.5, 1 H) ppm] is consistent with the assigned structure, which indicates that our determination of the crystal structure is correct (see Figure S1, Supporting Information). Nitrogen heterocyclic complexes, as key units in medicinal chemistry and versatile intermediates in organic synthesis, have been extensively studied in organic synthetic chemistry for the past years.^[7] Continuous efforts have been focused on the search for simpler but more efficient synthetic procedures for heterocycles. Relative to conventional routes, metal/ligand in situ reactions are simple and convenient synthetic procedures for nitrogen-containing heterocycles; thus they represent attractive and interesting methods in synthetic organic and medicinal chemistry.

One of the interesting features in the synthesis of the two compounds is that during the hydrothermal reaction, the nitrogen heterocyclic 2,3-dihydroimidazo[1,2-*a*]pyrimidine ligand was formed in situ, as illustrated in Scheme 1. Among the solvothermal in situ reactions reported, cycloaddition reactions are rare. The synthesis of 3,5-dimethyl-1,2,4-triazole under solvothermal conditions is the only cycloaddition reaction that has been reported,^[8] and the formation of a ligand by ethanol reactions has never been reported. So, this is the first example of a nitrogen heterocycle synthesized by an ethanol in situ reaction. The synthesis of 2,3-dihydroimidazo[1,2-*a*]pyrimidine was reported by Kochergin and coworkers in a routine organic reaction by using 1,2-dibromoethane and 2-aminopyrimidine,^[9] but the generation of 1,2-diiodoethane was impossible under our reaction conditions. According to the mechanism proposed by Kochergin, we speculate that the mechanism for the formation of 2,3-dihydroimidazo[1,2-*a*]pyrimidine in our system involves four steps. The first step is the conversion of some ethanol into iodoethane, which is an easy reaction because there are some I^- anions in our system (we checked the liquid after the reaction and found the I^- anions). The second step is the alkylation of 2-aminopyrimidine, in which iodoethane attacks the N atom of the 2-aminopyrimidine ring to destroy aromaticity (this step is similar to the Kochergin routine^[9]). The third step, which is the most important one, is HIO_4 oxidation of $-\text{CH}_3$ to $-\text{CHO}$. The fourth step is the formation of the five-membered ring. Each $-\text{CHO}$ and each $-\text{NH}_2$ dehydrate to generate 2,3-dihydroimidazo[1,2-*a*]pyrimidine. To test our mechanism, we used trapping agents such as hydrazine and 1,2,4-triazole to capture the aldehyde intermediates. Unfortunately, our reaction system involves oxidative and high-temperature conditions, in which the trapping agent is not stable. So, we had to choose an indirect method to prove our hypothesis. By using 2-aminopyrimidine and 2-bromoacetaldehyde as starting chemicals, we obtained 2,3-dihydroimidazo[1,2-*a*]pyrimidine, which is a good attestation to our hypothesis (see Figure S2, Supporting Information).



Scheme 1. The in situ reaction of 2-aminopyrimidine and EtOH.

Similar to other in situ reactions, pressure also proved to be effective for the dehydrogenation of methyl when a suitable transition-metal salt was present. We speculate that the oxidation of Cu^{2+} to Cu^+ is very important, because when we changed Cu to other metals such as Zn, Mn, or Co this reaction did not proceed.

Similar to other copper halide complexes, the two compounds exhibit photoluminescent properties (see Figures S3 and S4, Supporting Information). Intense emission occurred at 585 nm for compound **1** and at 582 nm for compound **2** ($\lambda_{\text{ex}} = 390$ nm) in the solid state at room temperature. According to the photoluminescent properties of other copper halide clusters, the origin of the emission of the two compounds is likely to involve the cluster-centered triplet excited state mixed with some halide-to-metal charge transfer (3LMCT) character. The existence of a “metal-cluster-centered” excited state is supported by a Cu...Cu nonbonding interaction.^[10]

Conclusions

In summary, we prepared two copper halide compounds by a solvothermal redox reaction and in situ ligand synthesis, which provides a new strategy for the preparation of coordination polymers and nitrogen heterocycles. As we know, nitrogen-containing heterocycles are structural constituents of many bioactive natural products, medicinally important compounds, and organic materials. The nitrogen heterocyclic compound 2,3-dihydroimidazo[1,2-*a*]pyrimidine, which contains two activated nitrogen atoms, can act as a template for solid frameworks or as a starting material for the conversion of other ring systems, as it contains unsaturated C–N bonds. We will continue to work in this area, and we expect that more progress will be made on the present reaction, for example, by using other alcohols, such as propanol and butanol.

Experimental Section

1: The solvothermal reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.20 mmol, 0.200 g), $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ (0.44 mmol, 0.100 g), $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (1.42 mmol, 0.200 g), NaHCO_3 (2.40 mmol, 0.200 g), $\text{C}_4\text{H}_5\text{N}_3$ (0.315 mmol, 0.300 g), and EtOH (5 mL) at 180 °C for 3 d produced red-block crystals of **1**. Yield: 25% (based on copper).

2: The solvothermal reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.20 mmol, 0.200 g), $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ (1.32 mmol, 0.300 g), $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (2.13 mmol, 0.300 g), NaHCO_3 (2.40 mmol, 0.200 g), $\text{C}_4\text{H}_5\text{N}_3$ (0.210 mmol, 0.200 g), and EtOH (5 mL) at 160 °C for 3 d produced red-block crystals of **2**. Yield: 60% (based on copper).

Single-Crystal Structure Determination: Measurements were carried out with a Rigaku RAXIS-RAPID diffractometer equipped with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. The intensity data sets were collected with an ω -scan technique and reduced by CrystalClear software. The structures were solved by direct methods and refined with the full-matrix least-squares technique by using the program SHELXTL. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Crystal data for **1**: $M_r = 418.12$, crystal size $0.24 \times 0.20 \times 0.18$ mm, monoclinic, space group $C2/c$, $a = 28.127(6)$ Å, $b = 3.8140(8)$ Å, $c = 19.595(4)$ Å, $\beta = 98.61(3)^\circ$, $V = 2078.5(7)$ Å³, $Z = 8$, $\rho_{\text{calcd.}} = 2.672$ g cm^{−3}, $R_1 = 0.0697$ [2238 $I > 2\sigma(I)$] and $wR2 = 0.1968$ (all 5548 unique data) for 132 variables, GOF = 0.990. Crystal data for **2**: $M_r = 502.03$, crystal size $0.24 \times 0.22 \times 0.16$ mm, triclinic, space group $P\bar{1}$, $a = 7.781(5)$ Å, $b = 8.648(6)$ Å, $c = 9.163(7)$ Å, $a =$

$109.91(2)^\circ$, $\beta = 100.64(3)^\circ$, $\gamma = 109.24(2)^\circ$, $V = 515.8(6)$ Å³, $Z = 2$, $\rho_{\text{calcd.}} = 3.232$ g cm^{−3}, $R_1 = 0.0400$ [2336 $I > 2\sigma(I)$] and $wR2 = 0.0924$ (all 5095 unique data) for 116 variables, GOF = 1.077. CCDC-655716 and -655717 (for **1** and **2**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystal data and structural refinement data, selected bond lengths and angles, selected synthetic procedures, X-ray diffraction patterns, and solid-state emission spectra of compounds **1** and **2**.

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