DOI: 10.1002/ejic.201001061

Two Coordination Polymers with Rare Topologies Based on Copper(II) and Ligands Generated by In Situ Reactions

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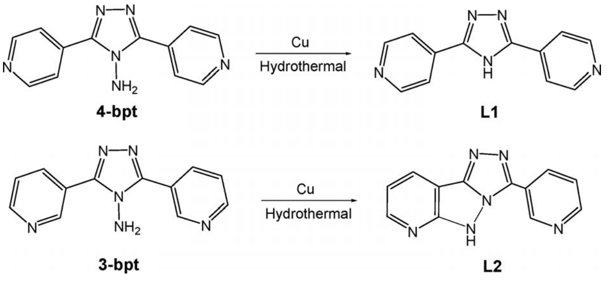
Keywords: Copper / Coordination polymers / Magnetic properties / Topology / Structure elucidation

Hydro(solvo)thermal in situ reactions provide an important strategy for the construction of coordination polymers with interesting structures and topologies. In our study, two interesting coordination polymers $[Cu(C_2O_4)(L1)_{0.5}(H_2O)_{2.5}]_n$ (**1**) (L1 = 3,5-bipyridyl-1,2,4-triazole) and $[Cu_3O_2(NO_3)_2(L2)_2(H_2O)_2]_n$ (**2**) {L2 = 5-(3-pyridyl)-1,2,4-triazolo[3,2-*c*](7-aza-1-H-indazole)} were prepared through an in situ ligand deaminization reaction and an in situ ligand intramolecular amination cyclization reaction, respectively. To the best of our knowledge, the formation of an indazole cycle through an in situ intramolecular amination cyclization reaction is reported for the first time. The two coordination polymers present a rare NiP_2 topology and kgd topology. Their magnetic properties have also been studied.

Introduction

In recent years, hydro(solvo)thermal in situ metal/ligand reactions have attracted extensive research interest in coordination and organic chemistry.[1] This is not only because this method facilitates the synthesis of complexes with beautiful topology and excellent properties, which is not easy for the direct reaction of metal ions and organic ligands, but also because it can be an effective method for preparing organic compounds that are difficult to obtain by the usual routes.[2] To date, more than ten types of ligand in situ reactions under the hydro(solvo) thermal conditions are known, including hydroxylation,[3] carbon–carbon bond formation,[4] ether bond formation,[5] decarboxylation,[6] hydrolysis,[7] alkylation,[8] transformation between inorganic sulfur and organic sulfur,[9] acylation,[10] cycloaddition,[1f,11] and isomerization.[12] However, it is still difficult to anticipate the target organic compounds and the structural topologies of coordination polymers generated by in situ reactions.

In situ deaminization reaction of 4-amino-3,5-disubstituted-1,2,4-triazole has been reported by Lu et al..[13] They adopted 4-amino-3,5-bis(hydromethyl)-1,2,4-triazole and 4-amino-3,5-diethyl-1,2,4-triazole ligands to synthesize three compounds, two with jph topologies and one with a (4,4) grid. The substituent groups of the two ligands do not coordinate to metal center because of the weak coordination ability of the hydro groups. In our work, we attempt to introduce coordination groups at the 3 and 5 sites of triazole and to construct coordination polymers with an attractive topology. The ligands 4-amino-3,5-bis(4-pyridine)-1,2,4-triazole (4-bpt) and 4-amino-3,5-bis(3-pyridine)-1,2,4-triazole (3-bpt) were chosen because there are two pyridyl groups at positions 3 and 5, which can provide further linkage to the metal centers. However, beyond our expectations, in addition to the in situ deaminization reaction of the ligands, we also found an in situ intramolecular amination cyclization reaction (Scheme 1). The magnetic properties of the two coordination polymers $[Cu(C_2O_4)(L1)_{0.5}(H_2O)_{2.5}]_n$ (**1**, L1 = 3,5-bipyridyl-1,2,4-triazole) and $[Cu_3O_2(NO_3)_2(L2)_2(H_2O)_2]_n$ {**2**, L2 = 5-(3-pyridyl)-1,2,4-triazolo[3,2-*c*](7-aza-1-H-indazole)} were studied.



Scheme 1. The in situ reaction of 3-bpt and 4-bpt.

Results and Discussion

Single-crystal X-ray structure analysis shows that crystal **1** is a three-dimensional coordination polymer, in which 4-bpt loses an amino group to form L1 (Scheme 1).

Each Cu^{II} atom is in an octahedral sphere coordinated by one nitrogen atom of L1 and five oxygen atoms from three different oxalic acid molecules. There are two types of

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$(C_2O_4)^{2-}$ ions in crystal **1**, mode A and mode B (Figure 1a), which are formed by the oxidation of glycol. Each oxalic acid of mode A links four Cu^{II} atoms around it to form a 2D-wave layer. The $(C_2O_4)^{2-}$ group of mode B fills the 2D layer by linking two Cu^{II} atoms to construct an interesting 2D layer (Figure 1). L1 acts as a rod by linking two $N_{pyridyl}$ atoms to the Cu^{II} atoms in adjacent 2D layers to construct a 3D structure (Figure 1b).

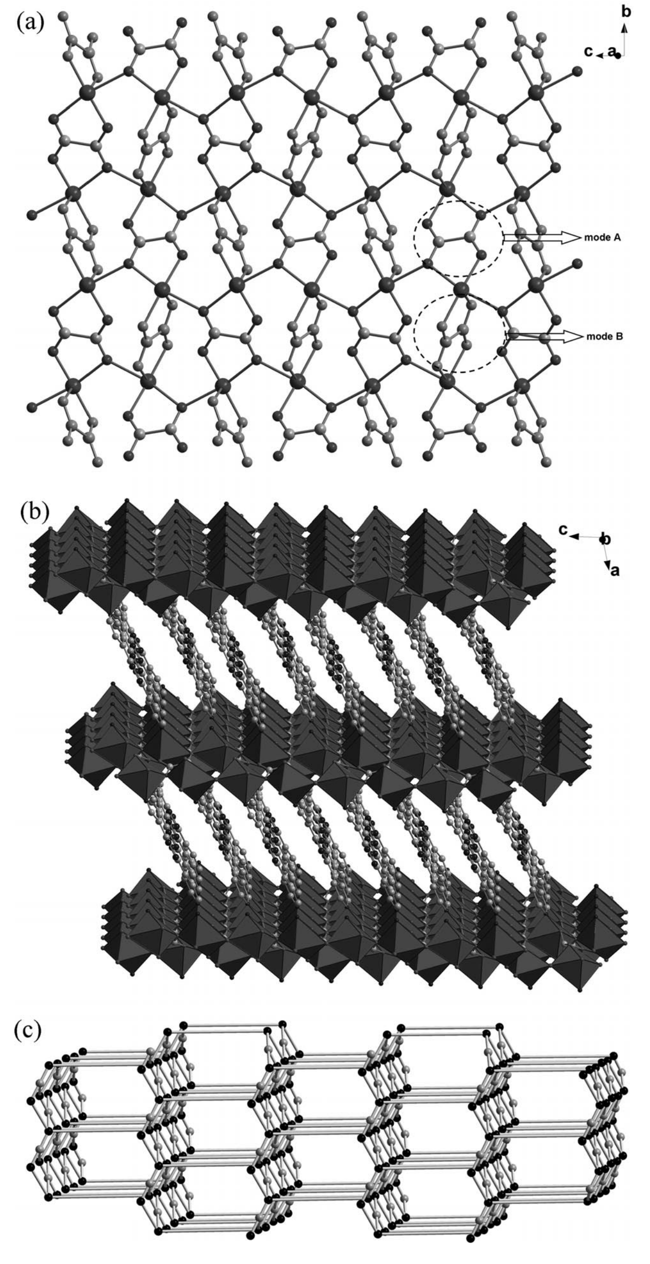

Figure 1. (a) The 2D layer structure of compound **1**; (b) the 3D structure of compound **1**; (c) the NiP_2 topology of compound **1**.

As a result, crystal **1** presents a NiP_2 topology with the point (Schläfli) symbol for a net $(5^3.6^2.7)_2(5^4.8^2)$ (Figure 1c). To the best of our knowledge, coordination polymers with NiP_2 topology have never been reported. The free water molecules fill the pore through H-bonding interactions.

For crystal **2**, the in situ deaminization reaction did not take place as in **1**; instead, an in situ intramolecular amination cyclization reaction occurred, which produced an indazole cycle ligand L2 (Scheme 1).[14] A structure search with Scifinder suggests that L2 is a new organic compound.

Among the hydro(solvo)thermal in situ reactions reported, the in situ intramolecular amination cyclization reaction is rare.[15] This is the first case in which an indazole cycle is formed through an in situ intramolecular amination cyclization reaction. Compound **2** is a 2D net. As shown in Figure 2a, there are two different Cu^{II} centers in crystal **2**. Cu1 has a slightly distorted tetragonal pyramidal geometry, coordinated by two $N_{pyridyl}$ atoms of two different ligands, one oxygen atom of a nitrate group and two bridged oxygen atoms, whereas Cu2 is hexacoordinated by two $N_{triazole}$ atoms, two bridged O atoms and two water molecules. The distance between Cu2 and the two coordination water molecules is 2.478 Å, which is longer than that for the other copper centers because of the Jahn–Teller effect. The generated C–N bond is 1.346 Å, which is in the normal range for a single C–N bond. Two Cu1 atoms and one Cu2 atom connected by oxygen atoms form a $Cu_3O_4(NO_3)_2$ unit. Each ligand molecule bridges three different $Cu_3O_4(NO_3)_2$ units to build up a 2D layer (Figure 2a). Crystal **2** has a kgd topology here (Figure 2b). Its point (Schläfli) symbol for a net is $(4^3)_2(4^6.6^6.8^3)$. According to the search results of RCSR (Reticular Chemistry Structure Resource), it is also a rare net.[16] The adjacent 2D layers are interconnected through weak interactions to form a 3D supramolecular net.

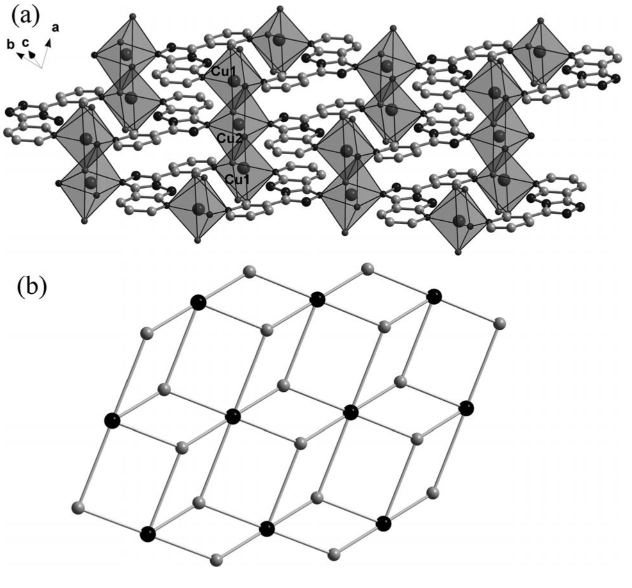

Figure 2. (a) The 2D layer of compound **2**; (b) the kgd topology of compound **2**.

Magnetic Properties

Variable-temperature, solid-state magnetic studies were performed on powdered crystalline samples of complexes **1** and **2** in a 1000 Oe (0.1 T) field and in the temperature range 2.0–300 K. As shown in Figure 3, the $\chi_m T$ product for **1** of 1.943 $cm^3 K mol^{-1}$ at room temperature is slightly larger than that expected (1.125 $cm^3 K mol^{-1}$) for three magnetically uncoupled Cu^{II} ions ($S = 1/2$). The $\chi_m T$ value gradually decreases with decreasing temperature to a plateau value of 1.098 $cm^3 K mol^{-1}$ at 10 K, then sharply falls below this temperature and reaches a value of 0.768 $cm^3 K mol^{-1}$ at 2.0 K. The room temperature $\chi_m T$ value for **2** is 0.251 $cm^3 mol^{-1} K$, much lower than the spin-only values of 0.375 $cm^3 mol^{-1} K$. Upon cooling, the $\chi_m T$ value for **2** decreases continuously. These features, in both cases, indicate a strong antiferromagnetic coupling. The rapid decrease for the two compounds at the lower temperatures can be due to intermolecular interactions.

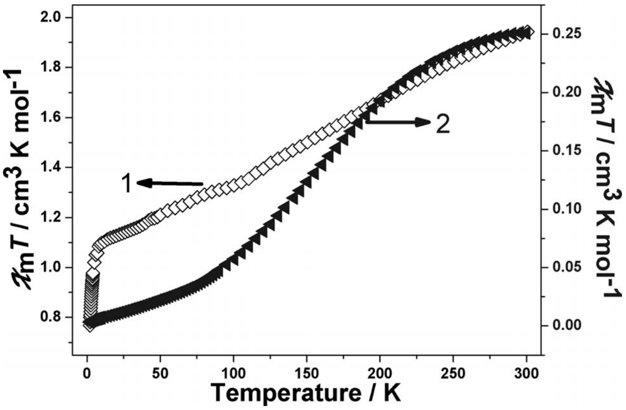

Figure 3. Magnetic susceptibility data for compounds **1** and **2**: $\chi_m T$ ($cm^3 K mol^{-1}$) vs. T in a field H = 1000 Oe.

Conclusions

In summary, two copper coordination polymers with unusual NiP_2 and kgd topologies have been formed through hydro(solvo)thermal in situ reactions, a deaminization reaction and an intramolecular amination cyclization reaction, which provides a new strategy for the preparation of coordination polymers and nitrogen heterocycles. The magnetic properties of the coordination polymers were studied. We will continue to work in this area, and we expect more progress to be made on the present reaction, for example, by changing the current ligands to other ligands with the same 4-amino-1,2,4-triazole backbone.

Experimental Section

Synthesis of 1: The hydrothermal reaction of 4-bpt (0.012 g, 0.05 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.041 g, 0.17 mmol), NaH_2PO_4 (0.056 g, 0.36 mmol), H_2O (3 mL), and glycol (3 mL) at 125 °C for 6 d produced blue block crystals of **1** (0.012 g). Yield: 24% (based on copper). $C_8H_{9.5}CuN_{2.5}O_{6.5}$ (308.22): calcd. C 31.15, H 3.08, N 11.35; found C 31.40, H 2.99, N 11.48. IR: $\tilde{\nu}$ = 3622 (m), 3454 (s), 2721 (w), 1705 (s), 1614 (s), 1293 (s), 789 (m) cm^{-1}.

Synthesis of 2: The hydrothermal reaction of 3-bpt (0.012 g, 0.05 mmol), $Cu(NO_3)_2 \cdot 3H_2O$ (0.159 g, 0.66 mmol), and H_2O (5 mL) at 120 °C for 8 d produced deep blue block crystals of **2** (0.013 g). Yield: 7% (based on copper). $C_{24}H_{20}Cu_3N_{14}O_{10}$ (855.16): calcd. C 33.68, H 2.34, N 22.92; found C 33.72, H 2.25, N 23.30. IR: $\tilde{\nu}$ = 3467 (s), 1636 (m), 1484 (s), 1377 (s), 1293 (s), 1178 (m), 697 (w) cm^{-1}.

X-ray Structure Determinations: The data collection and structural analysis of crystal **1** were performed on a Bruker SMART CCD diffractometer equipped with a graphite monochromator. The SMART software was used for data collection, for indexing the reflections, and for determining the unit cell parameters; the collected data were integrated by using the SAINT software. The data collection and structural analysis of crystal **2** were performed on a Rigaku RAXIS-RAPID equipped with a narrow-focus, 5.4-kW sealed tube X-ray source (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å). The data processing was accomplished with the PROCESS-AUTO processing program. All data were collected at a temperature of 20 ± 2 °C. Direct methods were used to solve the structure by using the SHELXL crystallographic software package. All non-hydrogen atoms were refined anisotropically. Crystal data for **1**: M_r = 855.16, triclinic, space group $P\bar{1}$, a = 8.3322(17) Å, b = 8.6563(17) Å, c = 11.581(2) Å, α = 68.79(3)°, β = 74.25(2)°, γ = 70.99(3)°, V = 725.0(3) Å^3, Z = 2, $\rho_{calcd.}$ = 1.959 mg m^{-3}, R_1 = 0.0446 [$I > 2\sigma(I)$]. Crystal data for **2**: M_r = 308.22, monoclinic, space group $C2/c$, a = 30.6444(17) Å, b = 9.2536(7) Å, c = 8.2410(5) Å, β = 103.093(4)°, V = 2276.2(3) Å^3, Z = 8, $\rho_{calcd.}$ = 1.799 mg m^{-3}, R_1 = 0.0408 [$I > 2\sigma(I)$]. CCDC-794681 and -794682 (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.

Magnetic Properties: Variable-temperature magnetic susceptibility data were obtained with a SQUID magnetometer (Quantum Design, MPMS-5) in the temperature range 2–300 K by using an applied field of 1000 Oe. Pascal's constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibility to give the molar paramagnetic susceptibility (χ_m).

Acknowledgments

This work was supported by the Foundation of the National Natural Science Foundation of China (No. 20671040, 20971054 and 90922034), the New Century Excellent Talents in University, and the Key Project of Chinese Ministry of Education.

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Received: October 5, 2010