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Controlled *In Situ* Reaction in Assembly of Cu(II) Mixed-ligand Coordination Polymers: Synthesis, Structure, Mechanistic Insights, Magnetism and Catalysis

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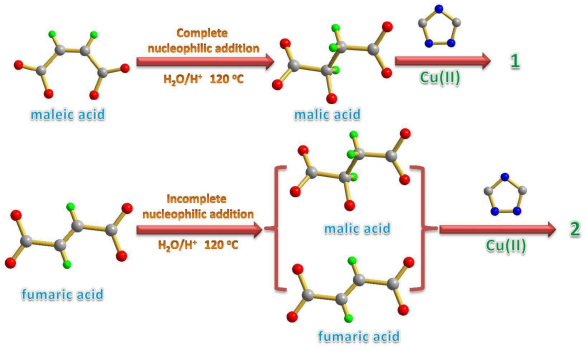
It has been a challenge to decipher the *in situ* ligand reaction mechanism in assembly process involving metal and ligand. The present study shows two crystalline mixed-ligand Cu(II) coordination polymers isolated by controlled *in situ* ligand reaction under the same hydrothermal condition. Two closely related examples provide a precious chance to access the in-depth mechanistic issues about *in situ* reaction. The solid structure of **1** demonstrated that the maleic acid was completely transformed to malic acid, whereas when fumaric acid used in the same reaction condition, incompletely transformation from fumaric acid to malic acid was observed in solid structure of **2**. Compound **1** exhibits a 3D 6-connected **sni** network based on a binuclear copper(II) secondary building unit, whereas the 3D network of **2** is classified to a (6,8)-connected topology network. The different steric hindrance between maleic acid and fumaric acid dictates the degree of in situ nucleophilic addition reaction. The comparison of synthesis and final solid structures indicates that the one-step nucleophilic addition mechanism for *in situ* generated malic acid in current reaction condition of **1** is plausible. The magnetic sensitivity measurements of **1** demonstrate overall antiferromagnetic coupling exist between Cu1 and Cu2 ions and between Cu3 and Cu4 ions. Furthermore, the obtained **1** can be an active catalyst for solvent-free silylcyanation of aromatic aldehydes under mild conditions.

Introduction

The rational design and effective construction of novel metal-organic coordination polymers are current hot topic in supramolecular and material chemistry owing to their widespread applications in many fields such as magnetism, catalysis, luminescence, porous materials, as well as their intriguing variety of architectures and topologies.[1] Generally, coordination polymers are composited by reactions of pre-synthesized or commercially available ligands and metal ions. As an effective synthetic route, *in situ* generating novel ligands under hydro- or solvothermal conditions, then incorporates the final structures has attracted considerable attention for new organic synthesis and unexpected coordination complexes,[2-6] since it was proposed by Champness and Schröder in 1997.[7] So far, numerous kinds of *in situ* ligand reactions such as carbon C-C coupling, hydroxylation, substitution, alkylation, hydrolysis, oxidation–hydrolysis, cycloaddition, acylation, amination and decarboxylation have been documented and comprehensively reviewed by Zhang and Chen.[8] In spite of such progress on *in situ* ligand reactions, it is still difficult to decipher the in-depth mechanistic issue on *in situ* ligand reaction due to the intricacy of the reaction systems and possible multi-step reactions,[9] unless comparable solid structures are isolated. For higher level of *in situ* ligand reaction in construction metal-organic coordination polymers, how to control the degree of *in situ* ligand reaction, then modulate the final solid structures is a much bigger challenge.

Scheme 1. The controlled *in situ* reaction in assembly of **1** and **2**.



In this respect, we achieved the controlled *in situ* ligand reaction by employment of different steric hindrance between maleic acid and fumaric acid. Herein, we presented the synthesis, structure, *in-situ* reaction mechanism, magnetic and catalytic properties of a new coordination polymer $\{[Cu_4(trz)_2(mal)_2(H_2O)_2]\cdot 3H_2O\}_n$ (**1**, Htrz = 1*H*-1,2,4-triazole, H_3mal = malic acid), and for comparison and discussion of controlled *in situ* ligand reaction, we then isolated the previous reported $\{[Cu_5(trz)_2(mal)_2(fma)(H_2O)_4]\cdot 2H_2O\}_n$ (**2,** H_2fma =

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fumaric acid)[10] under the same reaction condition to **1**. In this work, the maleic acid completely transformed to malic acid through nucleophilic addition, then incorporated into the solid structure of **1**, but *in situ* nucleophilic addition is just partial for fumaric acid used in the synthesis of **2** (Scheme 1). These results clearly demonstrated that i) the different steric hindrance between maleic acid and fumaric acid dictated the degree of *in situ* nucleophilic addition reaction; ii) the one-step nucleophilic addition mechanism for *in situ* generated malic acid in current reaction condition of **1** is plausible.

Results and discussion

Crystal Structural descriptions. X-ray analysis indicated that **1** is a 3D framework and crystallizes in the monoclinic space group $P2_1/c$ (Table 2). The asymmetric unit of **1** consists of four crystallographically Cu(II) ions, two trz^-, two mal^{3-} and two coordinated aqua ligand. As shown in Figure 1a, all copper(II) atoms are five-coordinated and display the distorted square pyramidal geometry (τ_5 = 0.051, 0.127, 0.308, and 0.155 for Cu1, Cu2, Cu3 and Cu4, τ_5 = Addison parameter, τ_5 = 0 for an ideal square pyramid and τ_5 = 1 for an ideal trigonal bipyramid).[11] The coordination geometry of Cu1 is defined by two N atoms from two trz^- ligands, two O atoms from one mal^{3-} ligand and one O atom of aqua ligand, in which N3, N4, O1 and O3 build the basal square plane and the axial position is occupied by the O1W with a longer bond. The Cu1–O1W bond length of 2.345(5) Å is longer than other Cu1–O/N distances from 1.939(4) to 1.979(5) Å, which is similar to those observed in many other Cu(II) MOFs.[12c-e] The *cis* and *trans* bond angles around Cu1 are in the ranges of 83.22(19)–104.0(2) and 165.9(2)–169.0(2)°, suggesting an axially elongated square pyramid due to the strong Jahn-Teller effect.[12] The Cu2 ion coordinates to one N atom from one trz^- ligand, two O atoms from one mal^{3-} ligand and another two from two separated mal^{3-} ligands, in which O3, O4, O6, and N5 build the square base and $O10^{i}$ is at the apex. The Cu3 is ligated by two O atoms (O7 and O8) from one mal^{3-} ligand and two N atoms ($N1^{ii}$ and $N6^{iii}$) from two different trz^- ligands, which construct the base of the square pyramid and the apex position is occupied by one O atom ($O2^{iv}$) from another mal^{3-} ligand. The Cu4 is coordinated in the base the square pyramid by one N atom ($N2^{ii}$) from one trz^- ligand and three O atoms (O8, O9 and $O5^{v}$), and the remaining position at the apex is occupied by terminal aqua ligand (O2W). The Htrz ligand deprotonates to trz^-, then adopts μ_3-κ^1:κ^1:κ^1 coordination mode to bind Cu(II) atoms, whereas *in situ* generated mal^{3-} ligands show μ_4-κ^1:κ^1:κ^2:κ^1:κ^1 binding fashion to Cu(II) atoms, in which carboxylate groups as *syn-anti* bridges. Every two Cu(II) atoms are connected by one mal^{3-} and one trz^- ligand to form dinuclear [Cu_2(trz)(mal)] SBUs with Cu1···Cu2 and Cu3···Cu4 distances of 3.3731(13) and 3.3824(15) Å, respectively, which then are extended by mal^{3-} and trz^- ligands to furnish a complicated a 3D porous framework with a solvent-accessible pore volume of 17.8%, calculated by PLATON (Figure 1b).

For better insight into this 3D architecture, topologically, **1** can be simplified to a 6-connected **sni** network with a point symbol of $\{4^{11}.6^4\}$,[13] if taken dinuclear [Cu_2(trz)(mal)] SBUs as 6-connected nodes (Figure 1c). In 6-connected coordination network family, the well known cases are of the **pcu**,[14] **acs**,[15] **hxg**,[16] **rob**,[17] and **hxl**,[18], but the **sni** topology is extremely rare in previous works and only a limited number of such networks have been documented.[19]

(Symmetry codes: (ii) *x*+1, −*y*+3/2, *z*−1/2; (iii) *x*+1, *y*, *z*; (iv) *x*, −*y*+3/2, *z*−1/2; (v) −*x*+1, −*y*+1, −*z*).

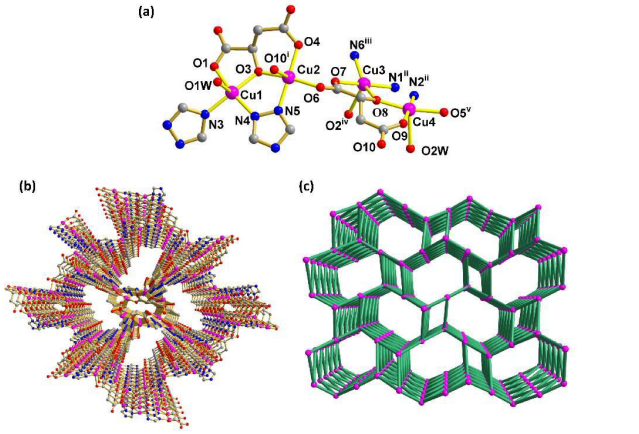

Fig 1. Structural representations of compound **1**: (a) Coordination environments of Cu(II) ions (Symmetry codes: (i) −*x*, −*y*+1, −*z*; (ii) *x*+1, −*y*+3/2, *z*−1/2; (iii) *x*+1, *y*, *z*; (iv) *x*, −*y*+3/2, *z*−1/2; (v) −*x*+1, −*y*+1, −*z*). (b) Ball-and-stick representation of the 3D network of **1** viewed along the *a* axis (Colour code: purple = Cu, red = O, blue = N, gray = C). (c) The simplified 3D 6-connected **sni** network of **1** viewed along the *a* axis (purple = [Cu_2(trz)(mal)]).

The structure of **2** has been described in details elsewhere.[10] So we just briefly comment the differences between **1** and **2**. Complex **2** contains both *in situ* generated mal^{3-} and original fma^{2-}, which is caused by incomplete *in situ* transformation of H_2fma. It contains both [Cu_2(trz)(mal)] SBU and single Cu(II) node, which act as 8- and 6-connected nodes to construct the 3D network of **2**, resulting a (6,8)-connected topology. The different degree of *in situ* nucleophilic addition reaction dictates the diverse structures of **1** and **2**.

Mechanistic insights to *in situ* reaction in transformation of maleic acid to malic acid during assembly of 1. The malic acid was not used as reactants but it was indeed unexpectedly found in the products, so it should be *in situ* originated from maleic acid or fumaric acid through nucleophilic attack by water molecules or hydroxy groups in water, which also was observed in several other literatures.[20] But controlled *in situ* nucleophilic addition reaction has not been observed in assembly of coordination polymers. The success in the isolation of two coordination polymers **1** and **2** is unambiguously dependent on the initial reactants, maleic acid and fumaric acid, which have different steric hindrance for nucleophilic addition reaction. In other words, the degree of *in situ* reaction was ingeniously controlled in this system. The conversion from maleic acid or fumaric acid to malic acid is completely or partially realized depending on different steric hindrance, as a result, the regulation of final products was achieved. It is well known that the maleic acid easily isomerizes to fumaric acid under acid conditions at elevated temperature.[21] The pH values before and after hydrothermal reaction for **1** are 2.82 and 3.60, respectively, and the temperature is 120 °C, both of which are very suitable to *cis-trans* isomerization reaction. So the maleic acid should convert to fumaric acid in the synthesis procedure of **1**. However, we have carefully checked several batches of products during synthesis of **1** and found it is always obtained as single phase as indicated by high quality Powder X-ray diffraction results (Figure S2 in SI), which definitively indicates no *cis-trans* transformation occurs before nucleophilic addition

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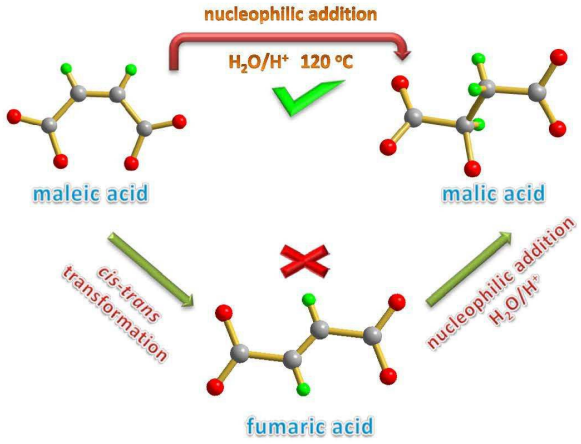
reaction for maleic acid, otherwise, it will convert to fumaric acid, then promote to the formation of **2** or mixed phases of **1** and **2** at least. When the maleic acid was replaced by the fumaric acid, under the same conditions, the crystal **2** was isolated in the presence of mixed malic acid and fumaric acid ligands, suggesting partially fumaric acid converts to malic acid. Why different degree of *in situ* nucleophilic addition reaction happened during synthesis of **1** and **2** under the same reaction condition? For *cis* maleic acid, it is easily attacked in assembly process on account of small steric effect and transformed into malic acid completely, whereas, *trans* fumaric acid is not beneficial to nucleophilic addition reaction due to large steric hindrance. Based on these observations, we can propose an *in situ* reaction mechanism that the maleic acid is subjected to nucleophilic attack by water (low pH value environment) and one-step converts to malic acid, then participates into the structure of **1**. At the same time, we also ruled out another mechanism that maleic acid firstly *cis-trans* isomerizes to fumaric acid, then suffered to nucleophilic attack by water and then completely converts to malic acid to construct the structure of **1** (Scheme 2).

Scheme 2. The proposed one-step transformation mechanism of *in situ* ligand reaction in assembly of **1**.



Magnetic investigations. The DC magnetic susceptibility was measured on polycrystalline sample in the 300 – 2 K temperature range in an applied magnetic field of 1 kOe and at constant temperature of 2 K in the magnetic field up to 70 kOe. The temperature dependent susceptibility per mole χ_M of the **1** and effective magnetic moment p_{eff} calculated per Cu atom are shown on Figure 2a after the data were corrected for three temperature independent contributions: sample holder, diamagnetism of core electrons as obtained from Pascall's tables and temperature independent paramagnetsim.[22] The susceptibility decreases with decreasing temperature already from room temperature and obtaining a minimum at approximately 50 K. Below 50 K the susceptibility increases inversely with temperature - showing a so called Curie tail. The effective magnetic moment calculated per Cu atom is 1.12 BM at room temperature. This value is reduced from expected value for non-interacting Cu^{2+} ion with spin S = 1/2 (p_{eff} = 1.9 μ_B).[23] With decreasing temperature the effective magnetic moment p_{eff} decreases and obtains a constant value of p_{eff} = 0.2μ_B below 50 K. From the measured temperature dependent χ_M and p_{eff} we can conclude the antiferromagnetic interaction between Cu^{2+} ions is effective already at room temperature. The Curie tail and the non-zero constant value of p_{eff} below 50 K are a consequence of isolated non-interacting magnetic moments. The individual magnetic moment and spin of these paramagnetic moments can be probed with the magnetization measurement at low temperature. Figure 2b shows the isothermal magnetization at 2 K measured in magnetic field between 0 and 70 kOe. The experimental data can be excellently reproduced with a Brillouin function for magnetic ions with spin S = 1/2 as shown with a full green line. Thus, the paramagnetic moments are very probable uncoupled Cu^{2+} ions with a spin S = 1/2. The concentration of this uncoupled ions is rather small as the magnetization in magnetic field of 70 kOe is only 0.009 μ_B/Cu atom while the saturation magnetization for a system of Cu^{2+} S = 1/2 ions should be 1 μ_B/Cu atom.

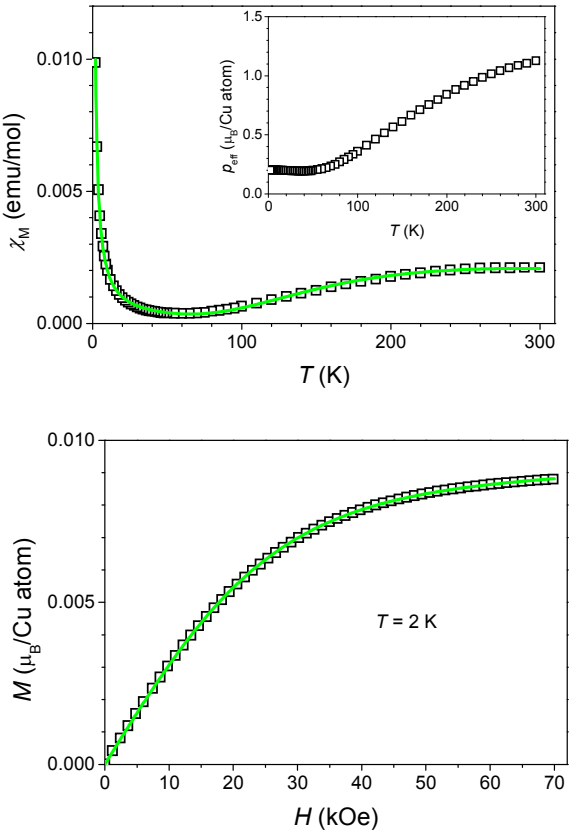


Fig 2 (a) Plots of χ_M vs T calculated per mol of **1** and p_{eff} vs T (inset) where effective magnetic moment p_{eff} was calculated per Cu atom. Full green line is the best fit of measured data with function (1). (b) Magnetization measured at 2 K. Full green line is a fit with Brillouin function for spin S = 1/2.

Finally we determined the magnitude of an interaction between Cu^{2+} ions that leads the system into prevailing antiferromagnetic state below room temperature. According to the structure of the **1** the substantial interaction can be expected between Cu1 and Cu2 ions and between Cu3 and Cu4 ions. In both cases it is a superexchange interaction mediated by oxygen atom: Cu1-O-Cu2 and Cu3-O-Cu4, leading us to two dimeric units per chemical formulae. The temperature dependence of molar susceptibility of dimeric units can be described with the Bleaney-Bowers equation[22]

$$\chi = (1-\rho)\frac{2N_A g^2 \mu_B{}^2}{k_B T(3+e^{-2J/k_B T})} + \rho\frac{N_A g^2 \mu_B{}^2}{2k_B T} \quad (1)$$

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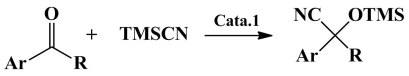
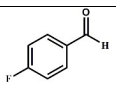
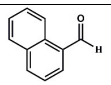
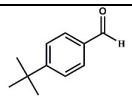
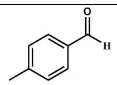
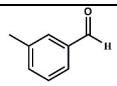
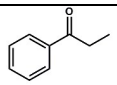
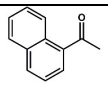
where factor 2 accounts for two dimeric unit per chemical formulae. The *J* in Eq. (1) is the magnetic spin exchange interaction according to an interaction Hamiltonian $H_{int} = -2J\, S_1 \cdot S_2$ between two copper's magnetic moments in a dimeric unit (Cu1-Cu2 and Cu3-Cu4). The second term in Eq. (1) accounts for non-interacting paramagnetic species with the factor ρ as a molar fraction of these paramagnetic moments, N_A is the Avogadro number, μ_B the Bohr magneton, k_B the Boltzmann constant. The best fit to the experimental data was obtained (full green line in Figure 2a) with J/k_B = -240 K and ρ = 1.6 %. As we can see in Figure 2a the Bleaney-Bowers equation (1) excellently describes experimental results confirming our assumption that the only considerable interaction exists only between copper Cu^{2+} ions in two dimeric units Cu1-Cu2 and Cu3-Cu4 while the interaction between next nearest neighbours Cu2-Cu3 mediated by -O-C-O group can be neglected.

Catalytic Activity. Since the porous **1** may present a surface with coordinative unsaturated metal sites once apical aqua ligand leave, the guest molecules that enter the pores can interact with the Lewis acidic metal sites, suggesting that **1** may act as a catalyst for the catalytic conversion of organic substrates.[24] To evaluate the catalytic activity of **1**, we have used the cyanosilylation of aldehydes as a test reaction catalyzed by Lewis acid. The reaction of aldehydes with trimethylsilyl cyanide (TMSCN) in the existence of a catalyst produce the relevant products, which are industrially worthy and significant intermediates in the synthesis of cyanohydrins and other biological compounds.[25] Before the test, the **1** was activated at 80 ^{o}C under vacuum for 20 mins. Then the cyanosilylation was accomplished in the presence of **1** with a 1:2 molar ratio of the selected carbonyls and TMSCN for 24h at room temperature under nitrogen. The conversions were calculated based on ^{1}H NMR spectroscopy (see SI). As shown in Table 1, benzaldehyde was availably converted to the corresponding cyanohydrin trimethylsilyl ether with the conversion of up to about 95.2 %. The use of such a catalyst can be extended to other carbonyl derivatives with different catalysis performance, which may be explained by steric hindrance or electron effects. For ketones, the activity is much lower due to the low reactivity of ketones compared with aldehydes. The size selectivity of the substrate suggested that cyanosilylation indeed occurs in the channels rather than the external surfaces.[26] Although the feasible mechanism cannot be certainly established, the catalytic reaction should involve an intermediate species with the substrate coordinated to the unsaturated Cu(II) atoms produced in the activation process.

Table 1. Results for the Catalytic Cyanosilylation of Aldehydes in the Presence of **1**.



Entry	Aldehyde/Ketone	Conversion (%)
1		95.2
2		85.5
3		95.2
4		45.9
5		38.0
6		18.0
7		87.7
8		1.8
9		~0
10		~0

Reaction conditions: aldehyde/ketone, 0.5mmol; TMSCN, 1mmol; catalyst **1**, 0.01mmol (2%); at room temperature under N_2 for 24h.

Experimental

Methods. All chemicals and solvents used in the syntheses were of analytical grade and used without further purification. IR spectra were recorded on a Nicolet AVATAT FT-IR360 spectrometer as KBr pellets in the frequency range of 4000-400 cm^{-1}. The elemental analyses (C, H, N contents) were determined on a Vario EL III analyzer. The variable-temperature magnetic susceptibilities were collected on a Magnetic Property Measurement System (MPMS), SQUID-VSM (superconducting quantum interference device-vibrating sample magnetometer) (Quantum Design, USA). Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert Pro MPD X-ray diffractometer with MoK_α radiation equipped with an X'Celerator detector. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C thermal analyzer from room temperature to 800 ° C under nitrogen atmosphere at a heating rate of 10° C/min. UV-Vis measurements (diffuse-reflectance mode) were carried on a Hitachi U-4100 UV-vis-NIR spectrophotometer at 298 K. The pH values were measured on a pHs-3C (08) digital pH-meter (REX, Shanghai, China).

Synthesis of Complexes.

$\{[Cu_4(trz)_2(mal)_2(H_2O)_2]\cdot 3H_2O\}_n$ (**1**) A mixture of 1*H*-1,2,4-triazole (13.8 mg, 0.2 mmol), maleic acid (23.2 mg, 0.2 mmol) and

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$Cu(OAc)_2 \cdot H_2O$ (60 mg, 0.3 mmol) was dissolved in 6 mL deionized water stirred for 10 min at room temperature. The resulting mixture was sealed in a 25-mL Teflon-lined stainless steel autoclave and heated at 120 °C for 3000 mins, after which, it was cooled over 13 h to room temperature. The blue flower-like crystals were isolated by filtration, washed with water, rinsed with ethanol, and dried in air. The yield was 60% based on copper. Anal. Calc. (found) for $C_{12}H_{20}Cu_4N_6O_{15}$: C, 19.41 (19.57); H, 2.72 (2.58); N, 11.32 (11.48) %. IR (KBr): ν(cm^{-1}) = 3437 (s), 3150(m), 2836(w), 1578(s), 1393 (s), 1293 (s), 1153 (s), 1080(s), 904(m), 812(w), 719(m), 654(m).

$\{[Cu_5(trz)_2(mal)_2(fma)(H_2O)_4]\cdot 2H_2O\}_n$ (**2**) Although the synthesis of **2** was already described elsewhere by Gao et al.,[10] we present here the conditions that realized its synthesis in higher yield (65%) with in a shorter heating time at a lower reaction temperature. All reactants are the same to those in the synthesis of **1**, just using fumaric acid (23.2 mg, 0.2 mmol) instead of maleic acid.

Table 2. Crystal Data for Complex **1**.

Empirical formula	$C_{12}H_{10}Cu_4N_6O_{12}$
Formula weight	684.42
Temperature/K	200(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.105(3)
b/Å	16.969(5)
c/Å	17.666(6)
α/°	90.00
β/°	102.495(5)
γ/°	90.00
Volume/$Å^3$	2372.0(13)
Z	4
ρ_{calc} mg/mm^3	1.917
μ/mm^{-1}	3.604
F(000)	1344.0
2Θ range for data collection	4.8 to 49.98°
Index ranges	$-9 \le h \le 9$, $-10 \le k \le 20$, $-20 \le l \le 20$
Reflections collected	11662
Independent reflections	4175 [R(int) = 0.0673]
Data/restraints/parameters	4175/0/302
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0560, wR_2 = 0.1423
Final R indexes [all data]	R_1 = 0.0769, wR_2 = 0.1511

Structural Crystallography. Single crystal of the complex **1** with appropriate dimensions were chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for them were collected on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 12 frames each, each frame corresponds to a 0.5° scan in 5 s, followed by spot integration and least-squares refinement. For **1**, data were measured using ω scans of 0.5° per frame for 3 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART software and refined with SAINT on all observed reflections.[27] Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS.[27] In all cases, the highest possible space group was chosen. All structures were solved by direct methods using SHELXS-97[28] and refined on F^2 by full-matrix least-squares procedures with SHELXL-97.[29] Atoms were located from iterative examination of difference *F*-maps following least squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. All structures were examined using the Addsym subroutine of PLATON[30] to assure that no additional symmetry could be applied to the models. Selected bond lengths and angles are collated in Table S1 from supporting information. The CIF data were confirmed by employing the checkCIF/PLATON service, and the CCDC numbers were obtained 1049485 (**1**) from Cambridge Crystallographic Data Center.

Conclusions

In summary, a new Cu(II) mixed-ligand coordination polymer constructed from 1*H*-1,2,4-triazole and maleic acid has been successfully synthesized under hydrothermal condition, which shows the fascinating 6-connected sni network. The preparation of **1** involves a controllable route that the maleic acid was completely *in situ* transformed to malic acid. This synthesis route caused different structures from the reaction involving fumaric acid in the same conditions. The different steric hindrance between maleic acid and fumaric acid dictates the degree of *in situ* nucleophilic addition reaction. The comparison of synthesis and final solid structures indicates that the one-step nucleophilic addition mechanism for *in situ* generated malic acid in current reaction condition of **1** is plausible. The magnetic sensitivity measurements of **1** demonstrate overall antiferromagnetic coupling in the network. Furthermore, the obtained **1** can be an active catalyst for solvent-free silylcyanation of aromatic aldehydes under mild conditions.

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Controlled in situ nucleophilic addition reaction results two Cu(II) mixed-ligand coordination polymers and the one-step nucleophilic addition for in situ reaction is proposed. The antiferromagnetism of 1 and its catalytic activation towards the solvent-free silylcyanation of aromatic aldehydes under mild conditions are discussed.