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Reversible Solid State Structural Conversion between Three-dimensional Network and One-dimensional Chain of Cu(II) Triazole Coordination Polymers in Acidic/Basic- Suspensions or Vapors

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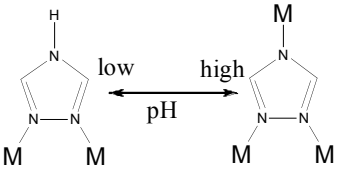
New Cu(II) triazole coordination polymers with 3D network were synthesized and reversible structural conversion between 3D network and 1D chain with color change was realized by pH controlled acidic and basic-suspensions or vapors. For each conversion process of decreasing and increasing pH, conversion was accomplished with high yield, in which the crystal before conversion played a role of a solid state crystal template.

A lot of metal-organic frameworks (MOFs) and metal coordination polymers (MCPs) with characteristic physical properties have been synthesized and relation between their structures and functional properties has been studied.[1] The functional ability of MOF and MCP is sensitive to their structures. Therefore, a drastic structural conversion of MOF and MCP based on the original crystal structure as a template is one of the challenging strategies to control their structures and physical properties. Only a few structural transformations with external stimuli such as temperature, pH or photo-irradiation without dissolution was reported in recent years.[2]

Here we report in this paper new coordination polymers $[Cu_3(trz)_3(\mu_3\text{-}OH)]X_2{\cdot}6H_2O$ (X = Cl, Br, trz = triazolate), which could be transformed in the solid state from three-dimensional coordination network to one-dimensional chain structure under acidic condition. The present copper metal coordination polymers are almost insoluble in water and thus convenient to study structural conversion in the solid state. A pronounced character of $[Cu_3(trz)_3(\mu_3\text{-}OH)]X_2{\cdot}6H_2O$ is having 1,2,4-triazole as ligands. 1,2,4-triazole is known as a useful ligand for constructing a variety of MOFs and MCPs.[3,4] This ligand has two different coordination modes depending on its protonation. One is to act as anionic triazolate (trz) ligand which forms tridentate coordination to a metal ion and the other is to act as neutral triazole (H-trz) ligand which constructs bidentate coordination to a metal ion.[4,5] Protonation of trz can be controlled by pH. Since pKa of H-trz is 2.2, trz is dominant at higher pH and H-trz is dominant at lower pH as shown in Scheme 1.[6] These two possible coordination modes make one structure of MCPs transform largely to another structure depending on external condition of pH. Structural conversions, which are induced by pH stimuli and based on the original structure as a template, are presented in this paper.

Powder specimen of $[Cu_3(trz)_3(\mu_3\text{-}OH)]Cl_2{\cdot}6H_2O$ (**1**) was synthesized by adding 1,2,4-triazole (0.14g 2mmol) in 10ml H_2O solution to $CuCl_2{\cdot}2H_2O$(0.34g 2mmol) in 50ml H_2O with stirring. Blue powder crystals immediately precipitated with c.a. 90% yield. Single crystals were prepared by diffusion method in U-type glass tube which was filled with carefully prepared tetramethoxysilane (TMOS)-water gel of pH=1.9. 1,2,4-triazole (2mmol) in 5 ml water and $CuCl_2{\cdot}2H_2O$ (2mmol) in 5ml water were used. After a few months, single crystals suitable for X-ray structure determination were obtained. Powder specimen and single crystal of $[Cu_3(trz)_3(\mu_3\text{-}OH)]Br_2{\cdot}6H_2O$ (**2**) were prepared similarly. Blue powder precipitated in a few days with c.a. 90% yield. Elemental analysis and IR spectra of **1** and **2** were examined.[§,‡] Each composition formula of **1** and **2** was determined by single-crystal X-ray diffraction, elemental analysis and TG-DTA measurement shown in Electronic Supplementary Information (ESI). Single-crystal X-ray diffraction experiments were performed on synchrotron radiation BL08A at Photon Factory in High Energy Accelerator Research Organization (KEK) with λ=0.6884 Å around 20 K and Rigaku R-AXIS rapid imaging plate diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) at 140 K.[†] Synchrotron X-ray was used to obtain precise diffractions with higher resolution From single-crystal X-ray diffraction, it was found that the two compounds have cubic symmetry $Fd\bar{3}c$ with large unit cell (a = 24.743(4) at 140K and 24.719(8) Å at 26 K for **1** and **2**, respectively). The crystals are constructed from equilateral triangular units of Cu(II) ions; details are presented in ESI. Three copper ions of this unit are linked by an oxygen atom at the center of the equilateral triangle and each two copper ions of a triangular unit are bridged by two adjacent nitrogen atoms of trz, leading to a $[Cu_3(trz)_3(\mu_3\text{-}OH)]$ building block as shown in Fig. 1 and Fig. S1 in ESI. Although this type of structure has been reported recently by other groups, the reported compounds have no Cl or Br ion in contrast to our present compound **1** and **2**.[7] In our compounds, four water molecules and two X ions locate at six axial coordination positions of three copper ions of a triangular unit with random disordering at all temperatures investigated. Other two water molecules exist in the space of three-dimensional network as crystal water, which was also confirmed by TG/DTA. For **1** and **2**, rest nitrogen atom of each trz of triangular unit coordinates to adjacent triangular unit, leading to form three-dimensional network structure as shown in Fig. 1 and Fig. S2 in ESI. We found considerable space in the crystal. This space makes the three-dimensional network flexible and gives advantage to transform to another structure by external stimuli.

Two different external pH stimuli were used for solid state



Scheme 1 Possible coordination modes of a 1,2,4-triazole at high and low pH conditions.

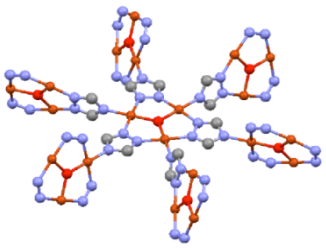


Fig. 1 Framework of seven building blocks of $[Cu_3(trz)_3(\mu_3\text{-}OH)]$. Each copper triangular unit is connected to adjacent six units by Cu-N bonding with dihedral angle of +(-)70.5°. H atoms and part of triazolate were omitted for simplicity. Color: red, O; orange, Cu; purple, N; gray, C.

structural conversion of **1** and **2**, *i.e.* firstly acidic/basic suspensions and secondly acid/base vapors. Since **1** and **2** are almost insoluble in water, acidic/basic aqueous solutions with several pH = 0.2 ~10 were prepared by HCl/Na_2CO_3 and HBr/Na_2CO_3 for **1** and **2**, respectively. 5 g of virgin powder crystals as synthesized, which will be called as mother compound G_0, were suspended in 100 ml Na_2CO_3 solution of pH=9.84. Then the color of the suspended powder crystals immediately changed and a few minutes later suspended powders were filtrated with almost 100% yield which will be called as generation 1 (G_1). A part of this powder specimen was used for powder X-ray diffraction measurements (PXRD) and elemental analysis of H, C, N and Cl (halogen). The rest major part of G_1 was used for successive conversion at pH=9.00, which produces G_2. Similar conversions were successively conducted for pH= 8.00 to 0.31, producing G_3 to G_{15} stemmed from mother compound **1**. At each step of conversion, powder crystals G_i (i=1~15) were filtrated within a few minutes after G_{i-1} was suspended in 100 ml of pH controlled HCl/Na_2CO_3 solution. For mother compound **2**, similar conversions were conducted. The color of the powder specimens stemmed from **1** changed from navy to pale blue-green as the pH value of HCl/Na_2CO_3 solution was decreased from 10.0 to 0.31, while the two-step color change was observed for the powder specimens derived from **2**, which is from blue (pH = 10.0) to pale blue-green (pH ~ 0.6) and from pale blue-green to brown (pH << 0.24). Colors of the filtrated powders are shown in Fig. S3(a) for **1** and in Fig. S3(b) for **2**, respectively. For highly acidic conditions, *i.e.* pH < 0.6, yield was decreased but more than 65% at least and filtrate was slightly colored blue for a family of **1** and green for **2**, indicating that a part of copper ions dissolved in the HCl or HBr solution. As a reference, we tried to obtain precipitate from uniform solution by mixing acidic $CuCl_2$/HCl aqueous solution (pH=0.5) and H-trz/HCl aqueous solution (pH=0.5) under the same condition of relative amount of Cu ion, trz ion and HCl aqueous solution. However, no precipitate appeared

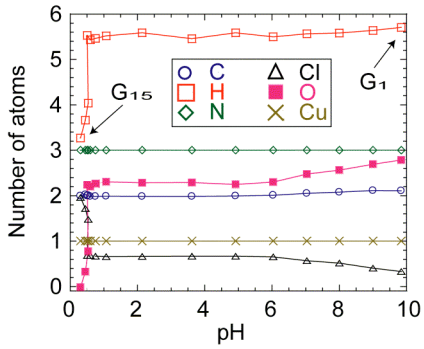


Fig. 2 Relative composition of each element to 3N of trz for successively converted powder specimens from **1**, $G_1 \sim G_{15}$ plotted as a function of pH of HCl/Na_2CO_3 solution.

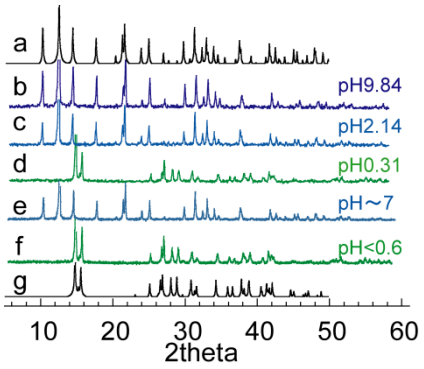


Fig. 3 Powder X-ray diffraction pattern of specimens after successive conversions. a and f were calculated for **1** and $[CuCl_2(H\text{-}trz)]$ (**3**) from single-crystal data, respectively.[8] b, c and d correspond to G_1, G_8, G_{15} derived from **1** in the 1st series of successive conversions with decreasing pH as shown in Fig. 2, e was observed for 2nd series of conversion with increasing pH after 1st series, and f was observed for 3rd series of conversion with decreasing pH after 1st and 2nd series. Color of diffraction pattern almost corresponds to the sample color. Cu-K α irradiation (λ =1.5444Å) was used for PXRD at 25°C.

within several hours. This result indicates that compounds G_{13}, G_{14} and G_{15} are obtainable only in the presence of crystal template of G_{i-1}. Similar result was also observed for **2**. We determined compositional formula of powder specimens $G_1 \sim G_{15}$ stemmed from **1** by elemental analysis of H, C, N, Cl (halogen) and relative compositions of each element to 3N of trz were plotted as a function of pH of HCl/Na_2CO_3 solution in Fig. 2 for $G_1 \sim G_{15}$. A similar conversion for **2** is summarized in Fig. S4. Relative composition of Cu to N was assumed to 1:3 as expected from crystal structure of virgin sample and converted specimen as described below. Composition of O was estimated as the residual element of the analysis. The structural conversions with different pH values were confirmed by PXRD. The crystallinity was kept good during three cycles of successive conversions as shown in Fig. 3. For pH = c.a. 1 ~ 6, compositional formula was kept constant as $[Cu_3(trz)_3(\mu_3\text{-}OH)]X_2{\cdot}6H_2O$, which is the same as that of virgin specimen, while Cl ion was gradually exchanged by OH ion in higher pH region attending to $[Cu_3(trz)_3(\mu_3\text{-}OH)]X(OH){\cdot}6H_2O$ at pH = 9.84. At higher pH, pure $[Cu_3(trz)_3(\mu_3\text{-}OH)](OH)_2{\cdot}6H_2O$ could not be obtained but unknown mixture appeared. On the contrary, for pH < 0.6 relative composition of Cl ion suddenly decreased to reach

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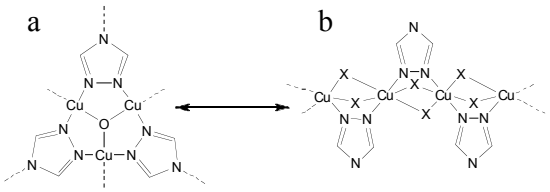

Scheme 2 Reversible structural conversion between 3D network and 1D chain. a shows **1** or **2**, b shows 1D chain of $[CuX_2(H\text{-}trz)]$.[8]

$[CuCl_2(H\text{-}trz)]$ (**3**) as pH was decreased. The crystal structure of **3** is known to have one-dimensional chain as shown in Scheme 2-b.[8] PXRD pattern of our specimen obtained from **1** under pH < 0.6 coincides very well to the reported structure of **3**. The same conversion process was observed for **2** (Fig. S5), except intermediate one-dimensional structure of $[CuBr_2(H\text{-}trz)_2]$ (**4**), which appeared around pH ~ 0.6.‖ In case of **2**, 1D MCP $[CuBr_2(H\text{-}trz)]$(**5**) was finally obtained at highly acidic condition.

In the next step, we tried to transform the three-dimensional network of **1** and **2** to one-dimensional chain structure not by acidic/ basic suspension but with acid/ base vapor. It was found that conversion from three-dimensional network of **1** and **2** to one-dimensional chain occurred under HCl and HBr gas flow, respectively. Within a few minutes after injecting acid gas, the conversion completed macroscopically as shown in Fig. S6, where water droplets were seen because of removing OH ion and H_2O during the conversion. The conversions from **1** and **2** to **3** and **5**, respectively, were confirmed by PXRD and elemental analysis like in the case of suspension. Although the successive reverse conversions from **3** (**5**) to **1** (**2**) by NH_3 gas was not successful at present, it is noteworthy that drastic change of the structure in the solid state can be accomplished by acid gas.

Finally, a possible mechanism of drastic change of coordination structure found by us will be discussed below. Conversion of coordination modes between three-dimensional network of **1** and **2** and one-dimensional chain of **3** and **5** possibly occurs through removing of OH ion, addition of proton and X ion to trz and Cu by acid and then rotation of trz, translation of Cu, and reconstruction of coordination bond on the template of original 3D structure. This conversion only requires addition of HX and removing H_2O, which can be easily accomplished in acid gas atmosphere. On the contrary, the reverse conversion by NH_3 gas flow requires removing HX as a solid salt NH_4X and incorporating H_2O. These processes are hard to occur in dry gas atmosphere. This reverse process easily occurs on the solid-liquid interface of powder crystals suspended in aqueous solution.

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Notes and references

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§ Elemental analysis (%) calcd for **1**: C 12.20, H 3.24 N 21.33, Cl 12.00; Found: C 12.31, H 2.98, N 21.58, Cl 12.08. Calcd for **2**: C 10.60, H 2.82, N 18.55, Br 23.51; Found: C 10.93, H 2.45, N 18.49, Br (24).

‡ IR spectra of **1** and **2** were recorded for KBr pellets. **1**: (cm^{-1}):3356(w), 3140(s), 2097(w), 1767(s), 1513(m), 1295(m), 1206(s), 1172(m), 1100(m), 1038(m), 1002(s), 888(w), 668(m). **2**: IR(cm^{-1}):3371(w), 3134(s),2067(w), 1514(m), 1295(m), 1207(s),1173(m), 1173(m), 1101(m), 1002(s), 886(w), 666(m).

† Absorption corrections were made. The structure was solved by a direct method (SAPI91) and refined by least-squares methods on F^2 using the Crystal Structure program package.[9] In these analyses, H atom, six H_2O and Cl or Br atoms were not refined because of small cross section of H atom and disorder. Crystal data for **1**: $Cu_3C_6N_9H_{19}Cl_2$; M = 590.82; cubic, a=24.743(4), V=15148(4)Å^3, T=140K, space group $Fd\bar{3}c$ (no. 228), Z=32, 31859 reflections measured, 31859 unique (Rint=0.0354) which were used in refinement. The final wR(F^2) was 0.0688 (all data.). Crystal data for **2**: $Cu_3C_6N_9H_{19}Br_4$; M= 679.72; cubic, a=24.719(8), V=15104(8)Å^3, T=26K, space group $Fd\bar{3}c$ (no. 228), Z=32, 40808 reflections measured, 2641 unique (Rint=0.0681) which were used in refinement. The final wR(F^2) was 0.1205 (all data.)

‖ The compositional formula of **4** and **5** were determined by elemental analysis. Calcd for **4**: C 13.29, H 1.67, N 23.25, Br 44.21; Found: C 13.23, H 1.72, N 23.04, Br (47). Calcd for **5**: C 8.21, H 1.03, N 14.37, Br 54.65; Found: C 8.43, H 1.15, N 14.63, Br (60). Br percentage has less accuracy because of a limit of ion-chromatography under coexistence of Cu ion. Their colors correspond to the two-step color change of a family of **2** described in the text.[10]

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