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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 have been studied.\textsuperscript{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 were reported in recent years.\textsuperscript{2}

Here we report in this paper new coordination polymers [Cu\textsubscript{3}(trz)\textsubscript{3}][Cl\textsubscript{2}·6H\textsubscript{2}O (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\textsubscript{3}(trz)\textsubscript{3}][Cl\textsubscript{2}·6H\textsubscript{2}O 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.\textsuperscript{3,4} This ligand has two different coordination modes depending on its protonation. One is to act as anionic triazole (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.\textsuperscript{5,6} 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.\textsuperscript{7} 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\textsubscript{3}(trz)\textsubscript{3}][Cl\textsubscript{2}·6H\textsubscript{2}O (1) was synthesized by adding 1,2,4-triazole (0.14g 2mmol) in 10ml H\textsubscript{2}O solution to CuCl\textsubscript{2}·2H\textsubscript{2}O(0.34g 2mmol) in 50ml H\textsubscript{2}O 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\textsubscript{2}·2H\textsubscript{2}O (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\textsubscript{3}(trz)\textsubscript{3}][μ-γ-OH)]Br\textsubscript{2}·6H\textsubscript{2}O (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.\textsuperscript{a,b} 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.\textsuperscript{a} 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\textsubscript{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\textsubscript{3}(trz)\textsubscript{3}][μ-γ-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. 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...
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/Na₂CO₃ and HBr/Na₂CO₃ for 1 and 2, respectively. 5 g of virgin powder crystals as synthesized, which will be called as mother compound G₀, were suspended in 100 ml Na₂CO₃ 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 (G₁). 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 G₁ was used for successive conversion at pH=9.00, which produces G₂. Similar conversions were successively conducted for pH= 8.00 to 0.31, producing G₁ to G₁₄ stemmed from mother compound 1. At each step of conversion, powder crystals Gᵢ (i=1~15) were filtrated within a few minutes after Gᵢ₋₁ was suspended in 100 ml of pH controlled HCl/Na₂CO₃ 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/Na₂CO₃ 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 increased 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 CuCl₂/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 within several hours. This result indicates that compounds G₁₃, G₁₄ and G₁₅ are obtainable only in the presence of crystal template of G₁₋₁. Similar result was also observed for 2. We determined compositional formula of powder specimens G₁ ~ G₁₅ 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 as shown in Fig. 2, e was observed for 2₃ series of conversion with increasing pH after 1₃ series, and f was observed for 3₃ series of conversion with decreasing pH after 1₅ and 2₅ series. Color of diffraction pattern almost corresponds to the sample color. Cu-3α irradiation (λ =1.5444Å) was used for PXRD at 25°C.

Fig. 2 Relative composition of each element to 3N of trz for successively converted powder specimens from 1, G₁ ~ G₁₅ plotted as a function of pH of HCl/Na₂CO₃ solution.

Fig. 3 Powder X-ray diffraction pattern of specimens after successive conversions. a and f were calculated for 1 and [CuCl₂(H-trz)](3) from single-crystal data, respectively. b, c and d correspond to G₁, G₆, G₁₅ derived from 1 in the 1š series of successive conversions with decreasing pH as shown in Fig. 2, e was observed for 2₅ series of conversion with increasing pH after 1₅ series, and f was observed for 3₅ series of conversion with decreasing pH after 1₅ and 2₅ series. Color of diffraction pattern almost corresponds to the sample color. Cu-3α irradiation (λ =1.5444Å) was used for PXRD at 25°C.
[CuCl$_3$(H-trz)] (3) as pH decreased. The crystal structure of 3 is known to have one-dimensional chain 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$_2$O during the conversion. The conversions from 1 to 2 and 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$_2$O, 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$_2$X and incorporating H$_2$O. 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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†† IR spectra of 1 and 2 were recorded for KBr pellets. 1: (cm$^{-1}$): 3356w, 3140(s), 2979(s), 1767(s), 1513(m), 1295(s), 1260(s), 1062(s), 888(w), 668(m). 2: IR(cum$^{-1}$): 3371(w), 3134(s), 2067(w), 1514(m), 1295(m), 1207(s), 1173(m), 1170(m), 1002(s), 836(w), 666(m).

††† Absorption corrections were made. The structure was solved by a direct method (SAP919) and refined by least-squares methods on F$^2$ using the Crystal Structure program package. In these analyses, H atom, six H$_2$O and Cl or Br atoms were not refined because of small cross section of H atom and disorder.

Crystal data for 1: Cu$_3$N$_2$H$_4$Cl$_2$; M = 590.82, cubic, a=24.734(4), V=15148(4)$^3$, T=140K, space group Fd3c (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$_3$N$_2$H$_4$Br$_2$; M = 769.72, cubic, a=24.734(4), V=15104(8)$^3$, T=26K, space group Fd3c (no. 228), Z=32, 31859 reflections measured, 31859 unique (Rint=0.0354) 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. Caled for 4: C 13.29, H 1.67, N 3.25, Br 44.21; Found: C 13.23, H 1.72, N 23.04, Br 47. Caled 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.  


