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Crystal-to-Crystal Transformation from a Chain Compound to a Layered Coordination Polymer

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A crystal-to-crystal transformation was observed from green chain compound $\text{CuBr}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ (1**) to brown layered compound $(\text{CuBr}_2)_3(1,4\text{-dioxane})_2$ (**2**). The hydrogen bonds connecting chains in **1** were replaced by $\mu\text{-Br}$ bridge in **2** and the antiferromagnetic interaction between metal atoms in **2** became stronger than in **1**.**

Metal organic frameworks (MOFs) have received much attention in the past decades due to their intriguing structures and potential applications. Combining inorganic and organic components and possessing extended structures through coordination bonds, these materials have shown a wide spectrum of interesting properties and functionalities, such as porosity and the related properties, the most popularly and actively investigated, optical properties, framework dynamics, and so on.¹ In the field of crystal engineering, the dynamic molecular crystals capable of crystal-to-crystal transformations involve changes in the coordination environment of transition metal atoms, dimensionality, colour, and physical properties including magnetism, absorption, and chirality. Using these crystals in molecular device applications, such as switches and sensors, is very attractive.² So far, the crystal-to-crystal transformation were observed between different dimensionality coordination compounds, such as 0D (zero-dimension) to 2D, 0D to 3D, 1D to 2D, 1D to 3D, and 2D to 3D.^{3,4} Herein, we present a crystal-to-crystal transformation from 1D chain compound $\text{CuBr}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ (**1**) to a 2D layered coordination polymer $(\text{CuBr}_2)_3(1,4\text{-dioxane})_2$ (**2**) accompanied by changes in the crystal colour, cell parameters, space group, crystal structure, coordination environments of Cu^{2+} , and magnetic properties.

Green crystal **1** was obtained from CuBr_2 in a mixture of $\text{CH}_3\text{OH}/(1,4\text{-dioxane})/\text{H}_2\text{O}$ with a yield of 68.3%. Elemental analysis (%): calc. for $\text{C}_8\text{H}_{20}\text{O}_6\text{Br}_2\text{Cu}$ (435.57): C 22.06, H 4.59; found: C 22.27, H 4.66. When **1** was heated at an elevated temperature (such as 90 °C for 5 minutes) or exposure to dry air, it transformed completely into brown crystal **2** and **2** remained stable until 135 °C. During the transformation, the weight loss was 35%. Elemental analysis (%): calc. for $\text{C}_8\text{H}_{16}\text{O}_4\text{Br}_6\text{Cu}_3$ (846.27): C 11.35, H 1.91; found: C 11.54, H 2.01. Attempts to resolvent **2** to obtain pure product **1** have not been successful yet; therefore, desolvation from **1** to **2** is irreversible. The crystal-to-crystal transformation from **1** to **2** was confirmed by the X-ray diffraction experiments. When **1** desolvates into **2**, the space group changes from $P\bar{1}$ into $C2/m$ with changes in the cell parameters and crystal structures.

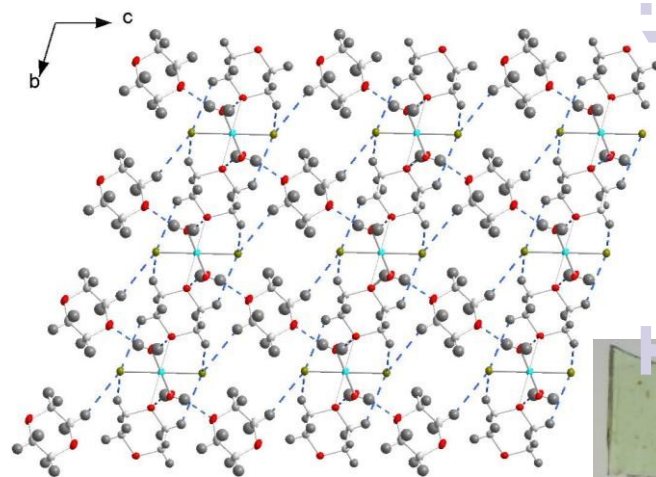


Figure 1 View of structure of chain coordination polymer along *a* axis of $\text{CuBr}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ (**1**) with thermal ellipsoids at 50% probability. Colour code: Cu, turquoise; C, light grey; O, red; Br, brown; H, grey. Hydrogen bonds, dashed blue lines.

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† Electronic supplementary information (ESI) available: experimental details, thermogravimetric analysis, X-ray powder diffraction patterns, UV-Vis spectra, CCDC 14110544–14110545.

Table 1 Crystallographic data of $\text{CuBr}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ (1) and $(\text{CuBr}_2)_3(1,4\text{-dioxane})_2$ (2).

Compound	(1)	(2)
Colour	green	brown
<i>F</i> , w.	435.60	846.29
<i>T</i> , K	173	173
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/m$
<i>a</i> , Å	5.571(2)	7.919(5)
<i>b</i> , Å	6.978(2)	12.382(7)
<i>c</i> , Å	10.303(3)	9.560(6)
α , °	103.643(3)	90.00
β , °	101.225(3)	107.177(8)
γ , °	101.936(5)	90.00
<i>V</i> , Å ³	368.2(2)	895.6(10)
<i>Z</i>	1	2
<i>D</i> _{calcd} , g/cm ³	1.965	3.138
$\mu(\text{Mo } K\alpha)$, mm ⁻¹	6.921	16.922
Cryst. size, mm	0.24x0.14x0.11	0.21x0.10x0.14
<i>T</i> _{min} , <i>T</i> _{max}	0.3196, 0.5237	0.0868, 0.3719
θ_{min} , θ_{max} , deg.	3.9011, 29.9947	2.2285, 7.4659
No. total reflns.	4709	3604
No. unique reflns(<i>R</i> _{int})	1662(0.0377)	1078(0.0534)
No. obs. ($I \geq 2\sigma(I_0)$)	1613	1032
<i>R</i> ₁ , <i>wR</i> ₂ [$I \geq 2\sigma(I_0)$]	0.0244, 0.0614	0.0393, 0.0950
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0260, 0.0628	0.0413, 0.0962
CCDC	1410544	1410545

As is shown in Figure 1, compound 1 consists of neutral chains of $\text{CuBr}_2(1,4\text{-dioxane})(\text{H}_2\text{O})_2$ and isolated 1,4-dioxane molecules, which is similar to $\text{CoBr}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ and $\text{NiCl}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$, different to what we have obtained 0D compound of $\text{CuCl}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$.⁴⁻⁶ Within the chain, each Cu^{2+} ion is octahedrally coordinated by two Br^- ($\text{Cu}-\text{Br}$ 2.4198(6) Å), two H_2O ($\text{Cu}-\text{O}$ 1.935(2) Å), and two 1,4-dioxane ($\text{Cu}-\text{O}$ 2.661(1) Å). There are two types of chair-conformed 1,4-dioxane molecules in 1. One

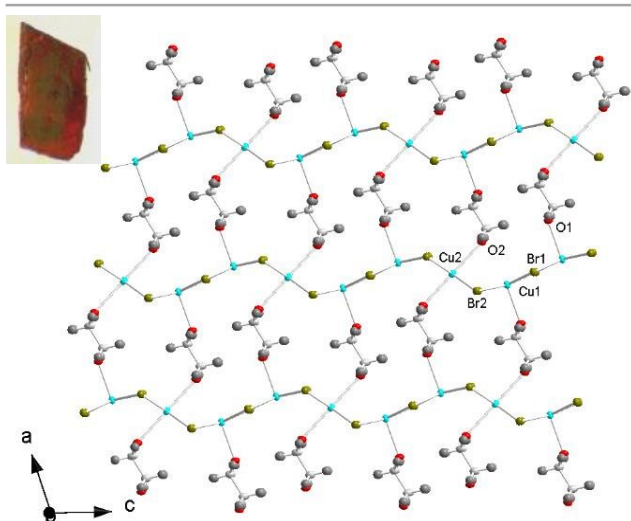
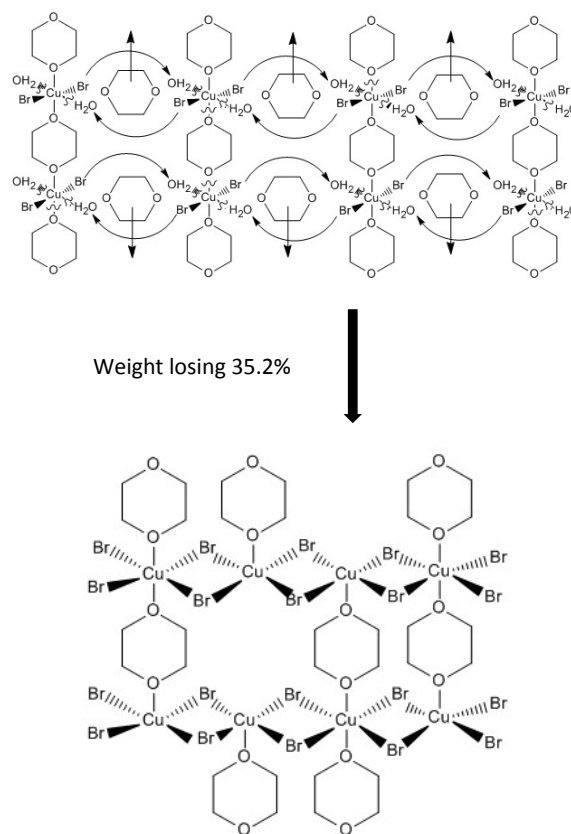


Figure 2 The structure of layered coordination polymer in $(\text{CuBr}_2)_3(1,4\text{-dioxane})_2$ (2) with thermal ellipsoids at 50% probability. Colour code: Cu, turquoise; C, light grey; O, red; Br, brown; H, grey.



Scheme 1 Schematic drawing of the possible route of crystal-to-crystal transformation from $\text{CuBr}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ (1) to $(\text{CuBr}_2)_3(1,4\text{-dioxane})_2$ (2).

acts as a guest molecule, which is tilted to the *ab* plane. The other is an end-to-end bridging ligand, which is approximately perpendicular to the *ab* plane. Moreover, the two hydrogens from H_2O interact with the O (one from the bridging 1,4-dioxane molecules, another from the guest 1,4-dioxane molecules) with hydrogen bonds forming a three-dimensional framework, which is shown in Figure 1. In *ab* plane, $\text{CuBr}_2(1,4\text{-dioxane})(\text{H}_2\text{O})_2$ running along the (110) direction is connected by hydrogen bonds through $\text{O}-\text{H}\cdots\text{O}$ between coordinated H_2O molecule and 1,4-dioxane molecule. The coordinated 1,4-dioxane molecules and metal atoms form a square lattice with one metal atom surrounded by four 1,4-dioxane molecule, vice versa.

Compound 2 consists of layered coordination polymer of $(\text{CuBr}_2)_3(1,4\text{-dioxane})_2$ as shown in Figure 2, this feature is similar to what is observed in $(\text{CuCl}_2)_3(1,4\text{-dioxane})_2$.⁴ Cu1 has a square-pyramidal geometry and is coordinated by four Br^- (two Br1, two Br2 in the equatorial plane ($\text{Cu1}-\text{Br1}$ 2.431(1) Å, $\text{Cu1}-\text{Br2}$ 2.430(1) Å) and one O (O1) atom with a $\text{Cu}-\text{O}$ distance of 2.361(5) Å from the 1,4-dioxane molecule in the chair conformation axially. A weaker $\text{Cu}-\text{O}$ (O2) 2.873(6) Å bond completes the distorted octahedral of Cu1. Cu2 is octahedrally coordinated by four Br2 with 2.426(1) Å and two O2 from 1,4-dioxane with $\text{Cu}-\text{O}$ 2.494(5) Å. Br1 bridges Cu1 with $\text{Cu1}-\text{Br1}-\text{Cu1}'$ angle of 92.887(9)°, Br2 connects Cu1 and Cu2 with a $\text{Cu1}-\text{Br2}-\text{Cu2}$ angle of 83.76(2)°, the dihedral angle between two CuBr_4 in the plane of neighboring Cu1 and Cu2 is 52.65(4)°.

The CuBr_2 chain is formed along the c axis. CuBr_2 chains are connected through 1,4-dioxane molecules along the a axis and formed a layered network on the ac plane. In ac plane, the metal atoms connected through Br and 1,4-dioxane molecules form a long and short brick network with the Schläfli symbols of $(4\cdot6^2)_2(4^2\cdot6^2)$. The $\text{Cu}\cdots\text{Cu}$ distance bridged by Br^- is 3.524(2) Å between two Cu1 and 3.242(2) Å between Cu1 and Cu2. There are no hydrogen bonds between the layers.

When **1** was heated at 70–135 °C or exposed to dry air, then H_2O and 1/3 of the 1,4-dioxane content desolvated from **1** to **2**. The transformation suggests that the connecting mode of Br^- changed from terminal model in **1** to bridged model in **2** and the chain molecule $\text{CuBr}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ transformed into layered coordination polymer $(\text{CuBr}_2)_3(1,4\text{-dioxane})_2$ as scheme 1.

Due to the hydrogen bonds in **1** and $\mu\text{-Br}$ bridge in **2**, the magnetic properties of these compounds have been studied.

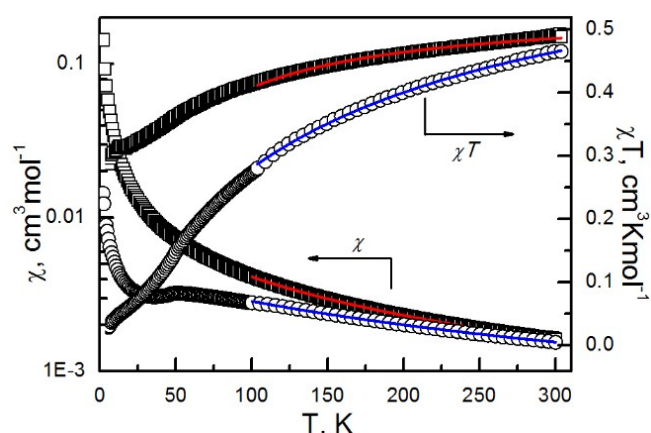


Figure 3 χ -vs- T and χT -vs- T plot of $\text{CuBr}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ (**1**, black square) and $(\text{CuBr}_2)_3(1,4\text{-dioxane})_2$ (**2**, black circle) and data fitted the Curie-Weiss law (**1** with red line, **2** with blue line).

The temperature dependent susceptibility measurement was carried out under an applied field of 1000 Oe in the range 2–300 K. On a plot of χ versus T of **1**, the χ value increased smoothly with the temperature decreasing and reached $0.1441 \text{ cm}^3 \text{ mol}^{-1}$ at 2 K. At 300 K, the χT value was $0.488 \text{ cm}^3 \text{ K mol}^{-1}$, which is significantly larger than the value of $0.375 \text{ cm}^3 \text{ K mol}^{-1}$ expected for an isolated, spin-only ion with $S = 1/2$ and $g = 2.00$ and close to the reported value.⁷ The χT value decreased smoothly upon cooling and reached $0.29 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The susceptibility data above 100 K fit the Curie-Weiss law well, giving Curie and Weiss constants of $C = 0.5277(6) \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -27.7(2) \text{ K}$, respectively, with $R = 1.87 \times 10^{-5}$. The negative Weiss value means strong antiferromagnetic interactions between Cu^{2+} ions.

On the plot of χ versus T of **2**, a broad heap was observed at 51.3 K (Figure 3) as observed for Cu^{2+} compounds.⁸ Below 51.3 K, the χ decreased and reached a minimum groove of $0.0031 \text{ cm}^3 \text{ mol}^{-1}$ at 36.5 K, and then increasing with upon cooling and reached $0.0144 \text{ cm}^3 \text{ mol}^{-1}$ at 2 K. At 300 K, the χT value was $0.465 \text{ cm}^3 \text{ K mol}^{-1}$, in the same range as that obtained for **1**. The susceptibility data above 100 K fits the Curie-Weiss law well, giving Curie and Weiss constants of $C = 0.686(3) \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -139.9(17) \text{ K}$, respectively, with $R =$

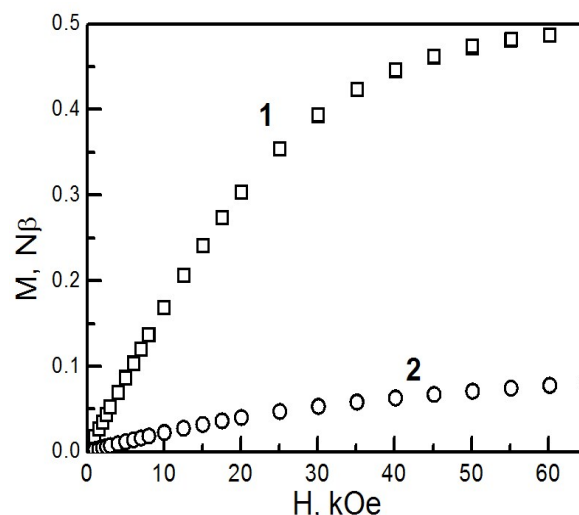


Figure 4 M -vs- H plot of $\text{CuBr}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ (**1**, black square), $(\text{CuCl}_2)_3(1,4\text{-dioxane})_2$ (**2**, black circle) at 2 K.

3.70×10^{-5} . This means the antiferromagnetic interaction in **2** is stronger than in **1**, in contrast to the antiferromagnetic interaction from $\text{CuCl}_2(1,4\text{-dioxane})_2(\text{H}_2\text{O})_2$ to $(\text{CuCl}_2)_3(1,4\text{-dioxane})_2$ becomes weakened. The antiferromagnetic interaction between Cu^{2+} in **2** is much stronger than that in $(\text{CuCl}_2)_3(1,4\text{-dioxane})_2$ with $\theta = -3.2(1) \text{ K}$, which indicates that $\mu\text{-Br}$ bridge introduces a stronger coupling than $\mu\text{-Cl}$ bridge.

The magnetic interaction of **1** could be analysed as an antiferromagnetic chain with $J = -24.3(5) \text{ K}$. The magnetic interaction between Cu atoms on the ac plane structure of **2** belong to one-dimensional $S = 1/2$ trimer system.⁹ The antiferromagnetic interaction is $-56.0(5) \text{ K}$ in **2** and it is stronger than in $(\text{CuCl}_2)_3(1,4\text{-dioxane})_2$ with -16.2 K and corresponded with magnetic measurements.¹⁰

As is shown in Figure 4, the isothermal magnetization at 2 K increased with increased field in **1** and **2** and no hysteresis loop was observed. The magnetization grows faster in **1** and reached $0.491 \text{ N}\beta$ at 65 kOe. This value is higher than in **2** where isothermal magnetization reached $0.081 \text{ N}\beta$ at 65 kOe at 2 K. These results confirm that the antiferromagnetic interaction in **2** is stronger than in **1**, which suggests that $\mu\text{-Br}$ bridge take the key role in magnetic exchange between magnetic atoms.

Conclusions

In summary, the crystal **1** composed of chain compound with a hydrogen-bonded three-dimension framework can be transformed to crystal **2** composed of layered coordination polymer by desolvation with changes in the crystal composition, colour and structure. The antiferromagnetic interaction enhanced and the Weiss constants changed from $\theta = -27.7 \text{ K}$ (**1**) to $\theta = -139.9 \text{ K}$ (**2**). These results show a way to obtain crystals quantitatively by crystal-to-crystal transformation with drastic changes in the molecular formula, crystal structure, crystal colour, and magnetism and provide crystalline materials to be used as sensors or switches in the future.

Acknowledgements

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