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Introduction

Recent decades have witnessed considerable progress in metal-organic frameworks (MOFs) due to their theoretical significance and potential applications in adsorption, ion exchange, sensor technology, drug delivery and catalysis. Considering the existing MOFs, one notes that numerous monometallic structures have been reported, there has been relatively little progress concerning the synthesis of heterometallic MOFs. Heterometallic MOFs have exhibited a great promise in molecular magnetism, optics and electrochemistry because of the charge-transfer properties between different metal centers. One common methodology for the construction of heterometallic MOFs is to introduce two kinds of metal cations to react with organic ligands in one system. And a construction of heterometallic MOFs is to introduce metal-oxo anions as secondary ligands to bind with metal cations. As well known, a few heavy metal-oxo anions, such as CrO$_4^{2-}$, Cr$_2$O$_7^{2-}$ and Mo$_7$O$_2$$_7^{2-}$, can form effective M-O-Cr or M-O-Mo bonds, which provides us new opportunities to construct novel heterometallic MOFs by using these metal-oxo anions as secondary ligands. The dichromate (Cr$_2$O$_7^{2-}$) has long been known to bridge metal ions forming coordination polymers. Recently, a series of heterometallic MOFs based on late transition metal ions and Cr$_2$O$_7^{2-}$ have been reported. However, the chemistry of heterometallic MOFs based on Ag$^+$ and Cr$_2$O$_7^{2-}$ is largely unexplored, although two 1-D hybrid chains based on Ag$^+$ and Cr$_2$O$_7^{2-}$ were presented. One possible reason is that Ag$^+$ is a strong oxidizing agent and can be easily reduced into silver during the reaction process; the other reason may be ascribed to the rapid formation of insoluble silver dichromate when Ag$^+$ and Cr$_2$O$_7^{2-}$ are simultaneously present in one reaction system. Therefore, the exploration of new methods for the synthesis of heterometallic MOFs based on Ag$^+$ and Cr$_2$O$_7^{2-}$ still remains a great challenge.

Recently, there has been a growing interest in crystal-to-crystal transformation of MOFs because they can provide us new chances to obtain unique compounds that cannot be obtained by direct reaction. What’s more, the structural transformation may also bring new functions, such as adsorption and magnetic properties, into the resultant materials. So far, the crystal transformation involving single-crystal to single-crystal process has been widely studied, however, the transformations through solvent-mediated process was less studied. Solvent-mediated structural transformation usually takes place under mild conditions as a result of external stimuli, such as heat, light, solvent molecules, anions, metal cations and redox reagents. It is noteworthy that in the reported solvent-mediated anion-induced crystal transformations, the external stimuli was just one kind of anion, the structural transformation driven by two kinds of anions, especially by non-coordinated anions is rare. In this work, we report the syntheses of two heterometallic MOFs based on Ag$^+$ and Cr$_2$O$_7^{2-}$ through solvent-mediated crystal-to-crystal transformations from a cationic homometallic MOF. By immersing monometallic Ag$_2$(btr)$_2$·2ClO$_4$·3H$_2$O in aqueous KPF$_6$-K$_2$Cr$_2$O$_7$ and NaBF$_4$-K$_2$Cr$_2$O$_7$, respectively, yellow crystals of Ag$_2$(btr)$_2$Cr$_2$O$_7$·0.5H$_2$O (1) and red crystals of Ag$_2$(btr)$_2$(Cr$_2$O$_7$)$_2$·PF$_6$·6H$_2$O (2) were successfully obtained in three months, respectively (Scheme 1). It should be mentioned

Solvent-mediated crystal-to-crystal transformations from a cationic homometallic metal-organic framework to heterometallic frameworks

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Two unprecedented heterometallic metal-organic frameworks (MOFs), Ag$_2$(btr)$_2$·Cr$_2$O$_7$·0.5H$_2$O (1) and Ag$_2$(btr)$_2$(Cr$_2$O$_7$)$_2$·PF$_6$·6H$_2$O (2) [btr = 4,4′-bis(1,2,4-triazole)], were synthesized through crystal-to-crystal transformation when a monometallic MOF Ag$_2$(btr)$_2$·2ClO$_4$·3H$_2$O was immersed into the aqueous solution of KPF$_6$-K$_2$Cr$_2$O$_7$ and NaBF$_4$-K$_2$Cr$_2$O$_7$, respectively. The transformation follows a solvent-mediated anion-induced mechanism through the dissolving-reaction-crystallization process. Single-crystal X-ray diffraction analyses reveal that both 1 and 2 are three-dimensional structures based on Ag$^+$, Cr$_2$O$_7^{2-}$ and btr. In 1, Cr$_2$O$_7^{2-}$ adopts a bidentate bridging mode, and Ag$^+$ ions are linked by Cr$_2$O$_7^{2-}$ and btr into a neutral framework. However, Cr$_2$O$_7^{2-}$ in 2 exhibits two types of unprecedented bridging modes through bridging four and five Ag$^+$ ions, respectively. Ag$^+$ ions in 2 are bridged by Cr$_2$O$_7^{2-}$ and btr to form a cationic framework. The non-coordination anions BF$_4^-$/PF$_6^-$ show a structure-directing effect during the crystal-to-crystal transformations and can be considered as structure-directing agents. The second-harmonic-generation (SHG) measurement shows that 1 is a non-linear optical complex.
that the presence of KPF_6 and NaBF_4 in aqueous K_2Cr_2O_7-
solution plays a key factor for the formation of 1 and 2. The
attempts to prepare 1 and 2 in the absence of KPF_6 or NaBF_4
were fruitless under the same conditions. To the best our
knowledge, 1 and 2 is the first series of 3-D heterometallic
MOFs based on Ag^+ and Cr_2O_7^{2-}.

**Scheme 1** Synthetic route for 1 and 2

![Scheme 1](image1)

**Results and discussion**

**Syntheses**

Both 1 and 2 were prepared through crystal-to-crystal
transformations, however, either direct one-step reaction or
the absence of KPF_6 and NaBF_4 failed to give rise to 1 and 2.
Their formation was considered to follow a solvent-mediated
mechanism.\(^{16,17}\) It is well known that the reversible nature of
metal coordination chemistry allows the crystals of a complex
to dissolve slightly in certain solution, the dissolved complex
may interact with the compositions in the solution, the subtle
precipitation-dissolution equilibrium will be broken in the
presence of extra inductive interaction, in turn unleashing the
dissolving. When crystals of the homometallic precursor of 1
and 2 were immersed in an aqueous solution of KPF_6-K_2Cr_2O_7-
or NaBF_4-K_2Cr_2O_7, Cr_2O_7^{2-} will interact with trace amount of
Ag^+ ions in the aqueous solution, but it is quite hard to be
observed since the reaction rate is very slow and the newly
formed compounds are too tiny to be seen with the naked
eyes. As time goes on, the dissolving-reaction-crystallization
process continues and the crystals of the newly formed
products become large enough for X-ray diffractions, then 1
and 2 were formed. It is noteworthy that the uncoordinated
anions PF_6^- and BF_4^- are important for the formation of 1 and 2.
When PF_6^- and BF_4^- were remove from the system, 1 and 2
cannot be isolated. Thus, the uncoordinated anions PF_6^- and
BF_4^- may have a structure-inducing effect in the reassembly
process. Interestingly, PF_6^- in 2 locates in the 1-D channels
and acts as charge compensation anion to balance the cationic
framework. Although BF_4^- does not appear in 1, BF_4^- is
indispensable for the formation of 1.

**Figure 1** View of the coordination environment of Ag^+ in 1.

![Figure 1](image2)

**Figure 2** View of the 2-D layer based on Ag^+ and Cr_2O_7^{2-} and
tetradentate btr ligands.

![Figure 2](image3)

**Figure 3** View of the 3-D framework of 1.

**Structural Descriptions**

Ag_2(brt)_2Cr_2O_7·0.5H_2O (1) Single-crystal X-ray
diffraction analysis revealed 1 crystallizes in the orthorhombic
non-symmetric space group *Pbca*, and the asymmetric unit is
made up of two Ag^+ ions, two btr ligands and one Cr_2O_7^{2-}
anion. As shown in **Figure 1**, Ag^+ is four-connected by three
nitrogen atoms from three different btr ligands and one
oxygen atom from Cr_2O_7^{2-} in a distorted tetrahedral geometry.
The Ag-N and Ag-O bond distances are in the range of 2.187(3)–2.445(3) and 2.555(3)–2.682(2) Å, respectively (Table S1). Two crystallographically independent Ag⁺ ions (Ag1 and Ag2) are connected by four nitrogen atoms (N11, N12, N7a and N8a) to form a binuclear six-membered Ag₉N₆ metalloccycle (Figure 1). In the metalloccycle, the Ag⋯Ag distance (Ag1-Ag2) is 4.139(9) Å, which is much longer than that of its precursor (3.719(6) Å). btr ligands adopt two types of coordination modes, one acts as a bidentate bridge connecting two Ag⁺ ions (Scheme 2a), the other serves as a tetradentate linker binding to four Ag⁺ ions (Scheme 2e). In addition, the inorganic Cr₂O₇²⁻ anion joins two Ag⁺ ions with Cr-O bond distances from 1.600(3) to 1.792(3) Å (Scheme 2d), which is consistent with those in the reported 1-D hybrid chain containing Ag⁺ and Cr₂O₇²⁻. In 1, the Ag₉N₆ metalloccycles are connected by Cr₂O₇²⁻ and tetradentate btr ligands to generate a 2-D layer (Figure 2), which is further extended by bidentate btr ligands into a 3-D neutral framework (Figure 3). In the 3-D framework, two types of channels (A and B) are formed along the crystallographic c axis, and the big one (A) hosts the lattice water molecules. To the best of our knowledge, 1 is the first example of 3-D neutral heterometallic MOF based on Ag⁺ and Cr₂O₇²⁻.

Ag(btr)₃(ClO₄)₁·PF₆·6H₂O (2) 2 crystallizes in the triclinic space group P-1, and its asymmetric unit consists of four and a half Ag⁺ ions, three btr ligands, two Cr₂O₇²⁻ anions, three isolated water molecules and one half of PF₆⁻ anion. One of interesting structural features in 2 is that Ag⁺ ions exhibit three kinds of coordination geometry (Figure 4a). Both Ag1 and Ag3 are five-coordinated by three nitrogen atoms from different btr and two oxygen atoms from Cr₂O₇⁻ in a slightly distorted tetragonal pyramid configuration. Ag1 is coordinated by two oxygen atoms from one Cr₂O₇⁻ to form a six-membered chelating ring (Figure 4b), while Ag3 is bonded by two oxygen atoms from different Cr₂O₇⁻ (Figure 4d). Ag2 and Ag4 are four-connected in a slightly distorted square-planar environment. Ag2 is coordinated by two nitrogen atoms from different btr ligands and two oxygen atoms from two Cr₂O₇⁻ anions (Figure 4e), while Ag4 is coordinated by three nitrogen atoms from three btr and one oxygen atom from Cr₂O₇⁻ anion (Figure 4e). Different from Ag2 and Ag4, four-connected Ag5 ion adopts a distorted tetrahedral geometry and is surrounded by one nitrogen atom from btr, two terminal oxygen atoms and one bridging oxygen atoms from three independent Cr₂O₇⁻ anions (Figure 4f). The Ag-N and Ag-O bond distances in 2 are in the range of 2.178(3)–2.258(3) and 2.271(3)–2.667(3) Å, respectively (Table S2), which are within the normal range in reported Ag complexes.19 Worthy of mention is the coordination modes of Cr₂O₇²⁻ anions, the other interesting structural character in 2. Two crystallographically independent Cr₂O₇²⁻ anions exhibit two types of different coordination modes binding to Ag⁺ ions, which are much different from simple bidentate bridging mode in 1. The first mode is that Cr₂O₇⁻ bridges four Ag⁺ ions through three terminal oxygen atoms (Scheme 2e), the other is that Cr₂O₇⁻ connects five Ag⁺ ions through three terminal oxygen atoms and one bridging oxygen atom (Scheme 2f). To our knowledge, such two types of coordination modes have not been reported hitherto, though a lot of coordination modes of Cr₂O₇⁻ were presented in the literatures.6,12 In addition, btr ligands in 2 also show two types of bridging modes. One links three Ag⁺ ions in a tridentate mode (Scheme 2b) and the other bridges four Ag⁺ in a tetradentate mode (Scheme 2e), which are different from that of the precursor and 1. In 2, Ag⁺ ions were connected by Cr₂O₇⁻ anions to form a 2-D inorganic layer (Figure 5) which is further bridged by btr ligands, leading to the formation of a 3-D cationic framework (Figure 6). The framework possesses 1-D channel with diameter about 5.6 Å along the crystallographic a axis. The PF₆⁻ anions are located in the channel, playing the role of charge compensation and stabilizing the cationic framework. As far as we know, 2 not only represents the first example of 3-D cationic heterometallic MOF based on Ag⁺ and Cr₂O₇⁻, but also is the first MOF that contains PF₆⁻ and Cr₂O₇⁻ in one structure.

![Figure 4](image)

**Figure 4** a) View of the coordination environment of Ag⁺ ions in 2; b–f) View of the coordination environment of Ag1-Ag5. All hydrogen atoms are omitted for clarity.

![Figure 5](image)

**Figure 5** View of the 2-D inorganic layer structure based on Ag⁺ and Cr₂O₇⁻ in 2.
**Figure 6** View of the 3-D framework of 2.

**PXRD, IR, TGA and Non-linear optical property**

The phase purity of complexes 1 and 2 was checked by X-ray powder diffraction (XRPD) at room temperature using the as-synthesized samples. As shown in Figure S1 and S2, the peak positions of the experimental patterns are in good agreement with the simulated ones, which clearly indicates the good purity of the complexes. In infrared (IR) spectra of 1 and 2 (Figure 7 and 8), characteristic vibration bands of Cr₂O₇⁻² and PF₆⁻ are located at 771 cm⁻¹ [18] and 843 cm⁻¹ [21], respectively, which are consistent with their single-crystal structural analysis. Thermogravimetric analysis (TGA) curves (Figure 9) revealed that the weight loss of 1.45% from 30 to 150 °C in 1 is attributed to the loss of lattice water molecules (calcd 1.26%). For 2, the removal of free water molecules occurs in the range of 30 to 150 °C (found 3.72%, calcd 3.57%). Drastic framework decompositions in 1 and 2 were observed after 215 and 200 °C, respectively, due to high nitrogen content and good oxygen balance, which is common in energetic MOFs.²⁰ In addition, 1 crystallizes in the nonsymmetric space group Fdd2, the non-linear optical property of 1 was studied. As shown in Figure S3, the second harmonic generation property of 1 is about 0.4 times that of KDP.

**Figure 7** IR spectrum of 1.

**Figure 8** IR spectrum of 2.

**Figure 9** TGA curves of 1 and 2.

**Conclusions**

Two unprecedented heterometallic MOFs have been prepared through solvent-mediated crystal-to-crystal structural transformations using a monometallic cationic MOF as a precursor. The structures represent the first series of 3-D heterometallic MOFs based on Ag⁺ and Cr₂O₇⁻². The inorganic Cr₂O₇⁻² anion can act as an effective secondary ligand in the construction of heterometallic MOFs. Two new coordination modes of Cr₂O₇⁻² are presented for the first time. The non-coordination anions are firstly considered as structure-inducing agents during the solvent-mediated structural transformations. This work not only provides a new strategy in searching unique materials that cannot be obtained through conventional methods, but also enriches the structural diversity of heterometallic MOFs.

**Experimental Section**

**Materials and General methods**

The precursor Ag₂(btr)_2·2ClO₄·3H₂O was prepared according to the literature method.¹⁹ All other chemicals were obtained from commercial sources and were used without further purification. Elemental analyses of C, H and N were carried out with a Vario EL
III elemental analyzer. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR infrared spectrophotometer. Thermal analyses were performed in a dynamic nitrogen atmosphere with a heating rate of 10 °C/min, using a NETZSCH STA449C thermal analyzer. Powder XRD patterns were obtained using a Philips X'Pert-MPD diffractometer with CuKα radiation (λ = 1.54056 Å). The SHG measurements are carried out on the powder samples by the Kurtz-Perry method at room temperature. Fundamental 1064 nm light was generated with a nanosecond pulsed Q-switched Nd:YAG laser.

Synthesis of Ag2(btr)2Cr2O7·0.5H2O (1)

As-synthesized Ag2(btr)2·2ClO4·3H2O (37 mg, 0.05 mmol) was immersed in an aqueous solution (20 mL) of K2Cr2O7 (0.0025 mol) after 3 months. Yield 11 mg (30% based on Ag(btr)). IR (KBr, cm⁻¹): 3446(m), 3146(m), 2367(w), 1496(m), 1305(m), 1292(w), 1223(vw), 1087(s), 1063(s), 983(m), 954(vs), 936(vs), 906(m), 844(s), 769(vs), 611(vs), 576(v). Elemental analysis (%) calcd for C8H9N12O7.5Cr2Ag2 (713.01): C 13.47, H 1.27, N 23.58; found: C 13.58, H 1.33, N 23.73.

Synthesis of Ag9(btr)6(Cr2O7)4·PF6·6H2O (2)

Complex 2 was prepared according to a similar procedure to that of 1, excepted for the replacement of NaBF4 by equimolar KPF6 (92 mg, 0.5 mmol). Yield 9 mg (25% based on Ag(btr)2·2ClO4·3H2O). IR (KBr, cm⁻¹): 3436(s), 3145(w), 3056(m), 3001(m), 2962(m), 1629(m), 1496(m), 1384(w), 1305(m), 1291(m), 1223(vw), 1079(vs), 1063(m), 995(m), 983(m), 955(vs), 936(vs), 906(m), 885(s), 843(vs), 768(vs), 611(vs), 652(m), 482(m). Elemental analysis (%) calcd for C24H36N36O34F6PCr8Ag9 (2904.69): C 9.92, H 1.37, N 17.36; found: C 10.13, H 1.37, N 17.60.

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X-Ray Crystallography

X-ray diffraction data for 1 and 2 were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) at room temperature. The program SADABS was used for the absorption correction. The structures were solved by the direct method and refined on F² by full-matrix least-squares methods using the SHELX-97 program package. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of hydrogen atoms on the organic ligands were generated geometrically and refined using a riding model. CCDC 988556-988557 contain the supplementary crystallographic data for this paper. The summary of crystallographic data and structure refinements for 1 and 2 is listed in Table 1. The selected bond lengths and angles of complexes 1 and 2 are listed in Table S1 and S2 in the Supporting Information, respectively.
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Notes

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† Electronic supplementary information (ESI) available: Selected bond lengths and bond angles for 1 and 2, PXRD patterns. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

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20 (a) G. M. Sheldrick, SHELXS97, Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL97, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.