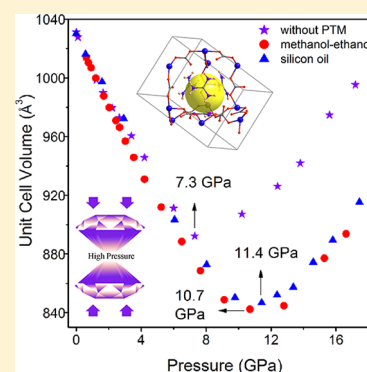


High-Pressure Studies of Abnormal Guest-Dependent Expansion in $\{[\text{Cu}(\text{CO}_3)_2](\text{CH}_6\text{N}_3)_2\}_n$ Qian Li,^{†,§} Shourui Li,^{†,§} Kai Wang,^{*,†} Jing Liu,[‡] Ke Yang,[§] Bingbing Liu,[†] Guangtian Zou,[†] and Bo Zou^{*,†}[†]State Key Laboratory of Superhard Materials, Jilin University, Qianjin Street 2699, Changchun 130012, P. R. China[‡]Beijing Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China[§]Shanghai Synchrotron Radiation Facilities, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China

S Supporting Information

ABSTRACT: High-pressure guest-dependent behaviors of porous coordination polymer $\{[\text{Cu}(\text{CO}_3)_2](\text{CH}_6\text{N}_3)_2\}_n$ (GCC) are investigated using synchrotron X-ray diffraction (XRD) and Raman techniques. In GCC, the host framework of 3D $[\text{Cu}(\text{CO}_3)_2]^{2-}$ coordination network presents a diamond-like topology, with guest guanidinium cations locating at the window of the pores through N–H···O hydrogen bonds. Above a critical pressure, the external force can squeeze the guanidinium ions into the pores, leading to the abnormal expansion of the structure. Meanwhile, the critical pressure for expansion can be effectively lowered when no pressure transmitting medium is employed. Moreover, nonhydrostatic effects can promote the insertion of guanidinium ions, along with the amorphization of the structure, and thus affect the reversibility of the structure after releasing the pressure. Our results show that pressure is an effective tool to tune the host–guest relationship and to prepare high-pressure phase host–guest materials. Meanwhile, this study broadens the understanding of host–guest chemistry and offers a new strategy for fabricating novel materials with applications of pressure switches and zero contraction material in porous coordination polymers.



■ INTRODUCTION

In the past decade, porous coordination polymers (PCPs), which are also known as metal–organic frameworks (MOFs), have attracted considerable attention owing to the aesthetics of their flexible structures and the observation of novel phenomena therein.^{1–5} The wide variety of unique functional properties of PCPs make them attractive candidates for promising applications, including gas separation and storage, molecular and chemical sensing, heterogeneous catalysis, luminescence, and biomedicine.^{6–10} In their practical applications, extreme conditions will be routinely encountered. Consequently, for the further practical use of PCPs, explorations of their high-pressure properties have become a necessary prerequisite. Indeed, it has been recently recognized that the structural versatility and flexibility of PCPs make them sensitive to the external force, affording novel and unpredictable pressure-induced phenomena and generating new structures and new properties.^{11,12} In particular, pressure-induced expansion is expected to be discovered in PCPs where there exists void space.

Pressure, the most effective thermodynamic variable to investigate structural stabilities, can tune the phase, pore size, and shape of PCPs, so as to control their guest content and selectivity.^{13–16} Afforded by the open structures, PCPs displays anomalous guest-dependent behaviors under high pressure,

which is associated with the pressure-induced expansion. In MOF-5 ($\text{Zn}_4\text{O}(\text{BDC})_3$, BDC = 1,4-benzenedicarboxylate), inclusion of pressure-transmitting medium (PTM) as a function of pressure makes the framework more resilient to compression, delaying the onset of amorphization and expand the volume of unit cell.¹⁷ Similarly, in Cu-btc ($[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_3]_n$, TMA = benzene-1,3,5-tricarboxylate), pressure forces the hydrostatic medium to enter the pores of framework, causing the sample to expand.^{18,19} Moreover, when using methanol and ethanol as PTM, the pore volume and media content in ZIF-8 ($\text{Zn}(\text{MIm})_2$, MIm = 2-methylimidazole) are increased with the compression.²⁰ Further investigations show that the storage of CO_2 in ZIF-8 can also be enhanced by the pressure.²¹ Recently, it has been reported that within small-molecule fluids at high pressure, diamondoid framework $\text{Zn}(\text{CN})_2$ can be transferred to a new phase with large fluid-filled pores, accompanied by near two-fold volume expansions.²² The material's volume expansion upon compression is counterintuitive and violating the thermodynamics dictates. Hence, pressure-induced expansion is associated with the composition change of the PCPs, hyperfilling of the pore

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network. The confined fluids, acting as both PTM and guest molecules, can be forced by the external pressure to enter the pores of PCPs, resulting in the volume expansion of the structure. Such pressure-induced expansion is benefit for the application of PCPs and the development of pressure switches and zero contraction materials.

High-pressure investigation on the relationship between the host framework and guest molecules is conducive to expand the application of PCPs. Meanwhile, it is benefit for broadening the area and understanding of host–guest chemistry. However, there are only a few kinds of molecules for high-pressure host–guest studies so far. Most investigations focus on how the “outer” guest molecules (PTM or gas molecules) influence the guest-free PCPs under high pressure.^{17–22} Nevertheless, because the guest molecules can help stabilize the structure, more PCPs are based on the host–guest structures. High-pressure exploration on the guest-dependent behavior of a host–guest system itself has more realistic significance.

Following the strategy of combining host–guest chemistry and high-pressure technique, we choose a model host–guest system of 3D PCP, $\{[\text{Cu}(\text{CO}_3)_2](\text{CH}_6\text{N}_3)_2\}_n$ (GCC), a guanidinium-containing carbonate compound.²³ As shown in Figure 1, the host framework of 3D $[\text{Cu}(\text{CO}_3)_2]^{2-}$ coordina-

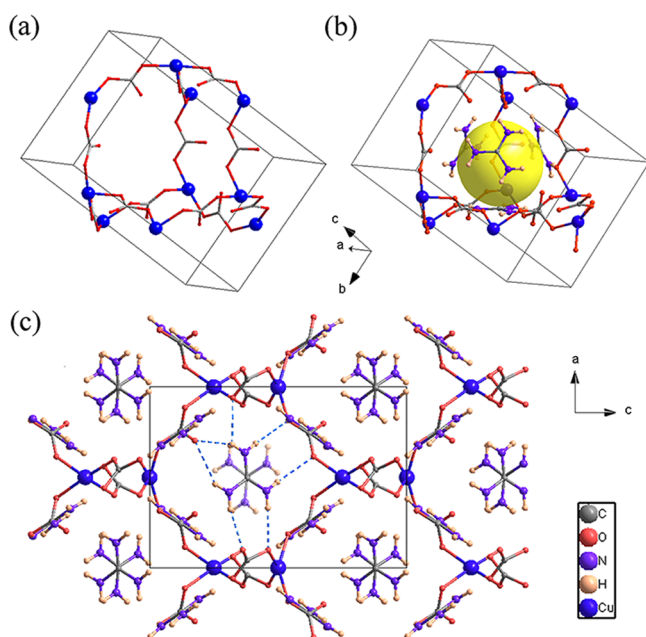


Figure 1. Crystal structure of GCC at ambient conditions: (a) the anion framework; (b) guanidinium cations at the windows and the space among guanidinium ions inside pores (pale yellow shows the empty space); and (c) selected hydrogen bonds in GCC.

tion network presents a diamond-like topology, in which tetrahedral nodes are the O_4 -coordinated copper. The $\text{Cu}(\text{CO}_3)_2^{2-}$ plays as the negative charge, and template counter-cation is $(\text{CH}_6\text{N}_3)^+$. Guanidinium ions, which are connected to the carbonate oxygen atoms through the $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, are the guests in the pores of $\text{Cu}_6(\text{CO}_3)_6$ to block the window. These template-to-framework hydrogen bonds play an important role in determining the structure. Moreover, the rigid ligands of GCC can also help stabilize the structure at high pressure. Therefore, the structure of GCC is expected to be stable in a wide pressure range. Such nature of GCC makes it a valuable model to investigate the host–guest properties.

Previously, Spencer et al. performed a high-pressure X-ray diffraction investigation on GCC single crystal.²⁴ The experiments are carried out in a relatively narrow pressure range of 0–4 GPa only. It is suggested that GCC undergoes a reversible softening at pressures above 2.5 GPa, which results from the changes in coordination geometries of copper ions, and the high-pressure behaviors of GCC cannot be affected by the PTM molecules (methanol–ethanol and anhydrous isopropanol). However, there is no information on the relationship between guanidinium ions and host framework. The host–guest behaviors of GCC above 4 GPa are still open questions.

For the stable nature of GCC, investigations on its behaviors in the higher pressure region (in excess of 4 GPa) are believed to obtain new phenomena and properties so as to provide insightful information on host–guest relationships. Such high-pressure studies require the consideration of the nonhydrostatic effects. Different PTM can be used to tune the pressure condition and then to explore whether the pressure condition can affect the host–guest behaviors in GCC. On the basis of this consideration, the well-known ethanol–ethanol mixture (4:1) and silicon oil were selected, and our high-pressure experiments were carried out with or without any PTM. We expect two questions to be answered. The first is how different pressure conditions influence high-pressure behaviors and reversibility of the PCPs. The second is whether PTM molecules can enter the pores inside the framework during the compression.

EXPERIMENTAL SECTION

GCC was prepared by following the procedure previously reported.²³ The symmetric diamond anvil cell (DAC), equipped with 0.4 mm diamond culets, was adopted for generating high pressure. The visual flawless crystals were selected and grinded to powder in a mortar with the grain size of a few micrometers. The sample chamber was a 150 μm diameter aperture drilled at the center of a preindented T301 gasket. Powdered GCC was loaded into this aperture together with two or three ruby balls so that the standard ruby technique could be applied to calibrate the pressure.²⁵ High-pressure experiments were carried out with or without any PTM. When PTM was applied during the experiments, the PTM was added to the sample chamber along with the ruby balls before closing the DAC briefly. Small alcohol fluids of methanol–ethanol (4:1 by volume) and macromolecular PTM of silicon oil were applied as PTM in this study. The silicon oil was purchased from Sigma-Adrich (viscosity 10 cst, 25 $^\circ\text{C}$), and the average molecular weight was ~ 1000 . Such silicon oil not only possesses the molecules that are too large to enter the pores in GCC but also offers the pressure condition that is very similar with the one in methanol–ethanol in the low-pressure range. All of the experiments were performed at room temperature.

In situ angle-dispersive X-ray diffraction (ADXRD) measurements of GCC were performed at the 4W2 High Pressure Station of Beijing Synchrotron Radiation Facility (BSRF). Portions of this work were performed on the BL15U1 beamline at the Shanghai Synchrotron Radiation Facility (SSRF). In all runs of ADXRD experiments, the monochromatic X-ray 0.6199 \AA beam was utilized as the incidence light source. Meanwhile, the spot sizes at the 4W2 High Pressure Station of BSRF and SSRF are $\sim 20 \times 30$ and $\sim 5 \times 13 \mu\text{m}^2$, respectively. CeO_2 was used as the standard sample to do the calibration. The 2D XRD images were converted into 1-D patterns using FIT2D

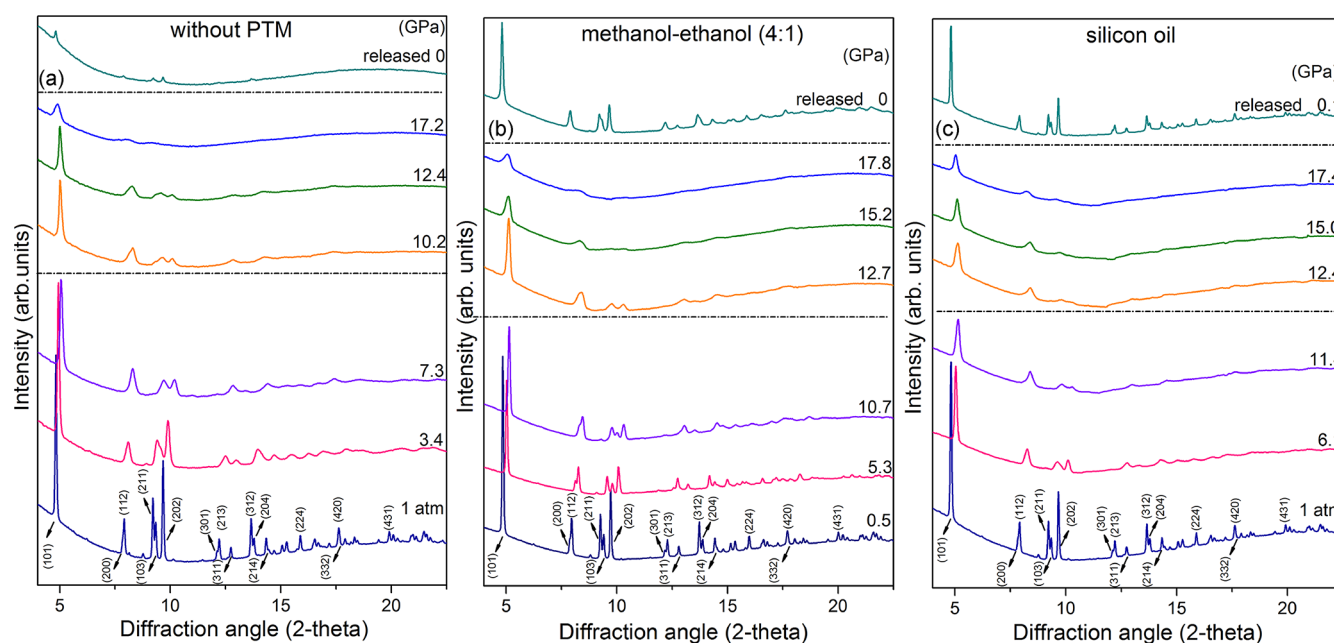


Figure 2. Selected ADXRD patterns of GCC (a) when no pressure transmitting medium (PTM) is applied and (b,c) when methanol–ethanol mixture and silicon oil are applied as PTM, respectively. The top patterns are collected after releasing the pressure, showing the partial reversibility of the transition.

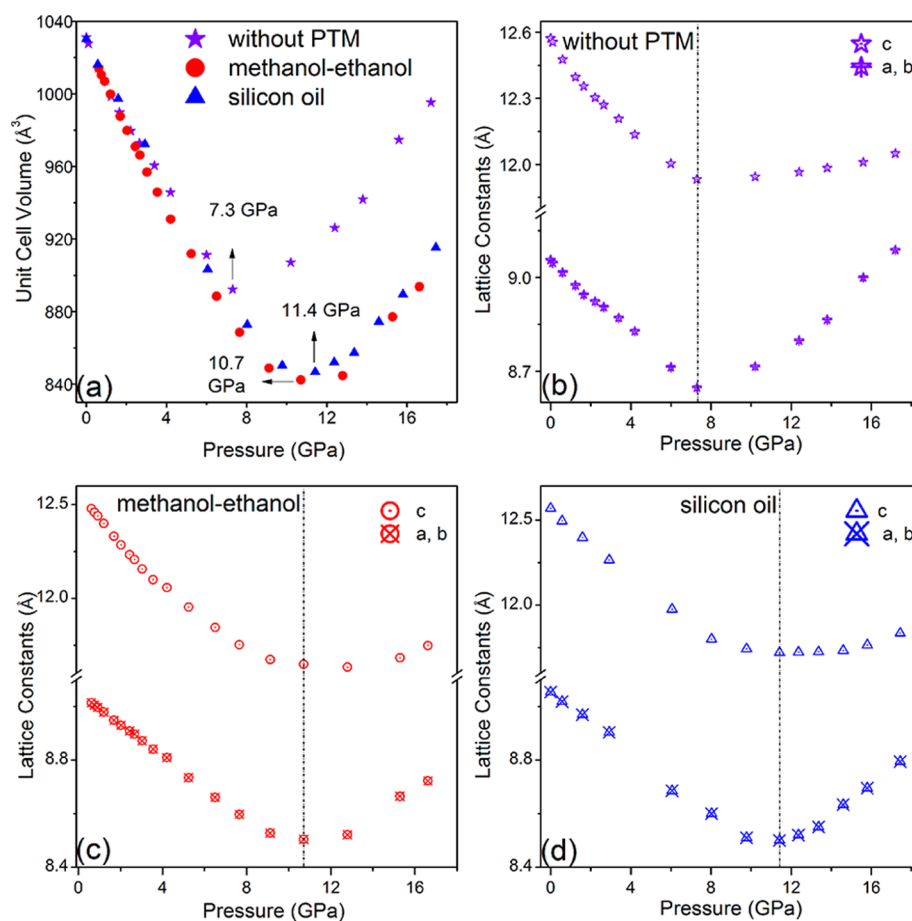


Figure 3. (a) Compression of unit cell volume as a function of pressure (without PTM and with methanol–ethanol mixture and silicon oil as PTM). (b) Pressure dependence of lattice constants without PTM. (c,d) Pressure dependence of lattice constants with methanol–ethanol and silicon oil as PTM, respectively.

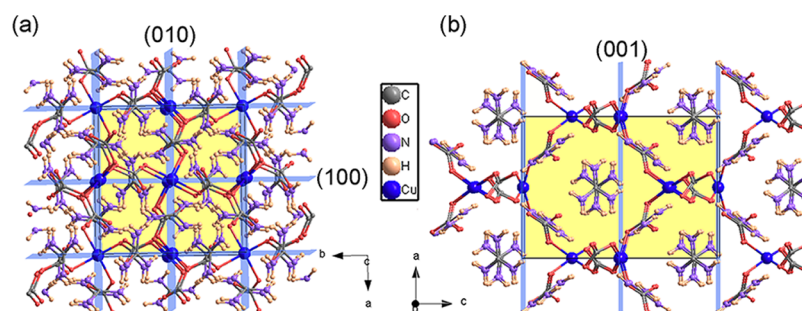


Figure 4. Projection of the structure with response to the Miller planes. The structure of GCC is shown along (a) c and (b) b axes. Blue planes show the Miller planes of (100), (010), and (001), respectively. Pale yellow shows the empty space.

software.²⁶ Further analysis of ADXRD data, pressure dependence of lattice constants, and cell volume was obtained by the Pawley refinement, using the reflex module combined in the commercial program Materials Studio 5.5.

High-pressure Raman spectra were recorded by ARC-SP 2558 spectrograph (Princeton Instruments) equipped with the liquid-nitrogen-cooled charge-coupled detector (CCD) PyLon: 100B. The excitation source is the 532 nm radiation from the diode pumped solid-state (DPSS) laser with the output power of 10 mW. Integration time for each spectrum was 60 s.

RESULTS AND DISCUSSION

Detailed identification of the diffraction peaks are shown in Figure S1 in the Supporting Information. In all of the experiments, the diffraction patterns decrease their intensity gradually during compression, and some diffraction peaks are too weak to be distinguished at high pressure, implying that the structure of GCC tends to be disordered upon compression (Figures 2). Below 4 GPa, our powdered X-ray diffraction data coincide the previous single crystal results very well. The softening of the structure above ~ 2.5 GPa can also be observed in our study (Figure S2 in the Supporting Information).

When no PTM is used, all diffraction peaks shift to higher angles below 7.3 GPa (Figure 2a). The cell volume and lattice constants decrease gradually, as expected (Figure 3), suggesting that GCC keeps a sustained contraction in this pressure range. However, with further compression above 7.3 GPa, all of the diffraction peaks start to shift toward lower angles until the highest pressure of 17.2 GPa. The cell volume and lattice constants begin to increase with compression, indicating the gradual expansion of the structure. Along with the transition, some weak diffraction peaks tend to disappear gradually, implying the collapse trends of the structure. Therefore, when no PTM is applied, GCC shows a pressure-induced expansion, accompanied by the collapse trends above 7.3 GPa. With the presence of PTM of methanol–ethanol mixture (4:1) or silicon oil, the results are the same in essence in two sets of experiments. In these experiments, sustained contraction of the structure can also be observed below ~ 11 GPa (Figures 2a,b and 3). Above ~ 11 GPa, the structure of GCC also expands progressively to the maximum pressure of ~ 17.6 GPa. However, the critical pressure of ~ 11 GPa with PTM is much higher than the pressure of 7.3 GPa without PTM.

No matter whether PTM is applied, GCC shows a pressure-induced expansion above a critical pressure, indicating that such expansion is not induced by the hyperfilling of the PTM molecules. As is well known, silicon oil is a kind of macromolecular material. The molecule is too big to enter the pores in GCC. The similarity of these two sets of

experimental results shows that both silicon oil and methanol–ethanol mixture have not entered into the pores at high pressure. It differs from the previous high-pressure studies of guest-free PCPs, which is attributed to the own nature of GCC.^{17–22} Because the windows of the pores are blocked by the guanidinium ions and the confined fluids cannot enter the pores, even small methanol molecules are used in PTM. However, PTM can still afford a better pressure condition during the experiments.²⁷

On the gigapascal scale, external force plays the dominate role in determining the structure and molecular interactions in GCC. Upon compression to the critical pressures, the size of the pores and pore windows is compressed, as the volume contraction.²⁰ At first, the N–H \cdots O hydrogen bonds between guanidinium ions and host framework should be strengthened by the external force.^{28,29} Because guanidinium ions at the windows can help support the window structure, the contraction of the window is expected not to reach the extent of the void-space contraction inside the pores. Such contraction continues until the critical pressures; then, the guest-induced expansion begins to balance the increasing free energy. Because PTM molecules have proven not to enter the pores, the only factor responsible for the abnormal expansion is the guest guanidinium ions already within the framework. Guanidinium ions are squeezed into the empty space (Figure 1b) inside the pores gradually, leading to the enlarged size of the pores and expansion of the framework. Meanwhile, such squeezing must be accompanied by the distortion of the guanidinium ions. The mechanism is supported by the different dependence of lattice constants versus pressure. During the expansion process, a and b axes are enlarged much more evidently than c axis (Figure 3). The framework is more compact along a and b axes than along the c axis (Figure 4). Between the Miller planes of (001), there is more space allowing the insertion of the guanidinium ions. Therefore, the expansion along the c axis is not as obvious as that along the a and b axes, as expected. Furthermore, the critical pressure without PTM is ~ 3.5 GPa lower than that with PTM. When no PTM is used, GCC experiences the poor pressure condition during the experiment. Nonhydrostatic pressure brings not only the hydrostatic pressure component but also the deviatoric stress component to the sample.³⁰ The latter component can promote the insertion trend of the guest, making it easier for guanidinium ions to enter the pores. Therefore, the threshold pressure for expansion under poor pressure condition is ~ 3.5 GPa lower.

During the expansion, periodicity of the structure can collapse more easily without the supports of guanidinium ions at the windows.^{17–22,31} Therefore, the expansion of the host framework continues along with the gradual amorphiza-

tion of the whole structure until the highest pressure. It implies that with more guanidinium ions filling into the pores, the structure becomes disordered more obviously. This is coincident with the disappearance of some weak diffraction peaks above the critical pressure. Hence, with increasing pressure, the hyperfilling of the guest guanidinium ions is inevitable, leading to the continuous expansion and collapse of GCC. In general, the amorphization of MOFs occurs at a low pressure, such as 0.34 GPa of ZIF-8 and 3.5 MPa of MOF-5.^{16,31} When the pressure reaches ~ 17.5 GPa, the highest pressure in all experiments, we can still distinguish the diffraction peaks of GCC, indicating that the sample has not yet completely changed to the amorphous state. This phenomenon is coincident with the point that the rigid nature of GCC makes its amorphization pressure much higher than usual carboxyl-based or guest-free MOFs. After releasing pressure from ~ 17.5 GPa, GCC returns to its original structure in all of the experimental runs, whereas the intensity of the released pattern without PTM is very weak, implying that the released sample still has collapse trends. It seems that the periodicity of sample without PTM collapses more thoroughly, so the structure becomes harder to totally recover after releasing pressure. Furthermore, the amorphization of the quenched sample can be influenced by increasing the highest pressure of the experiment (Figure S3 in the Supporting Information).

To get the more detailed local information of the structure transformation, we performed high-pressure Raman experiments. As shown in Figure 5, when no PTM is applied, below the critical pressure of 7.9 GPa, both CN_3 angle deformation modes (ν_1) and CO_3 symmetric bending modes (ν_2) exhibit normal blue shift owing to the expected decrease in interatomic distance. During further compression, when the structure begins to expand, peak positions of ν_1 keep unchanged, implying the distortion of guanidinium ions. Distortion (induce the red shift of the modes) has counteracted the compression (blue shift of the modes) of the guanidinium ions.²⁹ As we expected, such distortion makes guanidinium ions cannot keep balanced at the windows; they have to be squeezed into the empty space inside the pores during further compression. Meanwhile, peaks of ν_2 modes exhibit an obvious red shift above 7.9 GPa, which stems from the couple effect of the expanded structure and distortions of the CO_3 groups. With the presence of PTM of methanol–ethanol mixture or silicon oil, similar variation trends of Raman modes are observed; only the critical pressure rises to ~ 10.3 GPa (Figure S4 in the Supporting Information). Therefore, the expansion of the framework is accompanied by the distortion of guanidinium ions and CO_3 groups. The Raman results can match the results of ADXRD experiments and support our expected mechanism as well.

CONCLUSIONS

In summary, the behaviors of GCC are strongly influenced by the guest molecules at high pressure. The abnormal expansion of the host framework in GCC is induced by the gradual insertion of the guest guanidinium ions. When no PTM is applied, the critical pressure for expansion can be effectively lowered, implying that nonhydrostatic effects can facilitate the insertion of guest ions. Furthermore, the structure can reverse to its original state more easily with better pressure condition. The expansion of frameworks and insertion of guest ions show that host–guest relationships can be effectively tuned by high

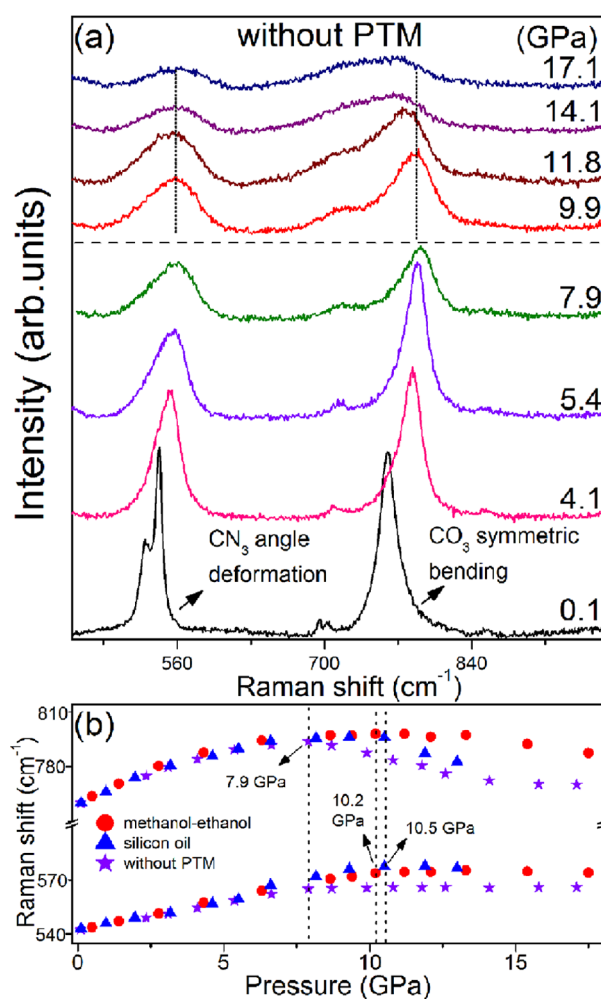


Figure 5. (a) Two vibrations of CN_3 deformation and CO_3 bending without PTM at high pressure. (b) Frequency shifts of selected modes without PTM and with methanol–ethanol mixture and silicon oil as PTM.

pressure, and high pressure can be applied to prepare new high-pressure phase host–guest materials. Significantly, this study broadens the understanding of host–guest chemistry and offers new strategy for the design and synthesis pressure sensors and switches.

ASSOCIATED CONTENT

Supporting Information

Experimental details and data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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