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Reversible reconstructive transition of $[\text{CuZn}(\text{CN})_4]^-$ framework host induced by guest exchange

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The framework host $[\text{CuZn}(\text{CN})_4]^-$, a coordination polymer composed of tetrahedral Cu(I) and Zn(II) ions and CN^- bridges, exhibits a reversible reconstructive transition in the solid-state between a cristobalite-like framework and a tridymite-like one induced by guest exchange between water and acetonitrile molecules.

The framework host $[\text{CuZn}(\text{CN})_4]^-$ is derived from one of the simplest clathrates $\text{Cd}(\text{CN})_2 \cdot \text{G}$.¹ A 3D coordination polymer, $\text{Cd}(\text{CN})_2$ consists of tetrahedral Cd(II) ions with linking CN^- bridges.² It is particularly worth noting that the $\text{Cd}(\text{CN})_2$ framework shows wide structural variations which have been revealed by many preparative and X-ray diffraction studies.^{3,4} To understand these structural variations, Iwamoto *et al.* introduced the concept of 'mineralomimetic chemistry', in which the crystal structure of a compound is considered based on the structures of minerals.⁵ In the case of $\text{Cd}(\text{CN})_2$, by regarding Cd(II) and CN^- ions as Si^{4+} and O^{2-} ions, respectively, and considering the polymorphism of SiO_2 , the structural variations of the $\text{Cd}(\text{CN})_2$ frameworks can be systematically and simply classified and understood. The first prepared $\text{Cd}(\text{CN})_2$ framework host exhibited a β -cristobalite-like (designated as CRI) structure. Subsequently, β -tridymite-like (TRI) and α -cristobalite-like structures were found.⁴ In the $[\text{CuZn}(\text{CN})_4]^-$ framework host, Cu(I) and Zn(II) ions take the place of Cd(II) ions. The host framework of the first prepared clathrate of this type, $[(\text{CH}_3)_4\text{N}][\text{CuZn}(\text{CN})_4] \cdot n\text{CCl}_4$, which included CCl_4 molecules as well as $(\text{CH}_3)_4\text{N}^+$ ions for charge neutralization of the host, adopted the CRI form (Figs. 1(a) and (b)).¹ Subsequently, $[\text{K}(\text{H}_2\text{O})_n][\text{CuZn}(\text{CN})_4]$, in which the TRI-form host included hydrated K^+ ions, was prepared (Figs. 1(c) and (d)).⁶

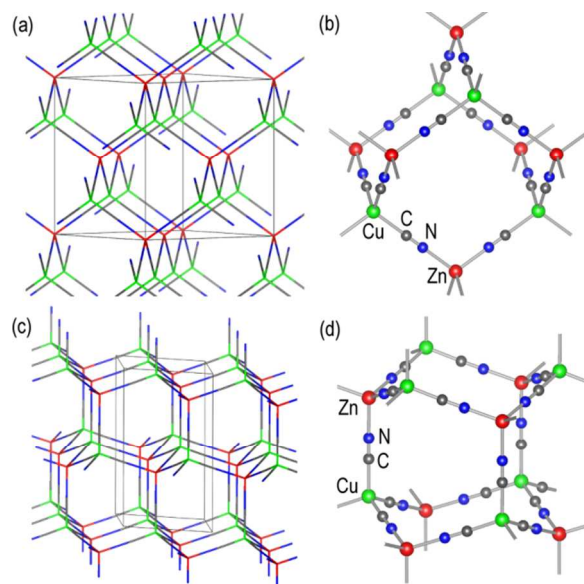


Fig. 1 Structures of $[\text{CuZn}(\text{CN})_4]^-$ framework (left) and cavity (right). (a), (b) CRI form found in $[(\text{CH}_3)_4\text{N}][\text{CuZn}(\text{CN})_4] \cdot n\text{CCl}_4$ (ref.1); (c), (d) TRI form found in $[\text{K}(\text{H}_2\text{O})_n][\text{CuZn}(\text{CN})_4]$ (ref.6).

These two structures could be prepared separately under different conditions. In the presence of only $(\text{CH}_3)_4\text{N}^+$, $[(\text{CH}_3)_4\text{N}][\text{CuZn}(\text{CN})_4]$ was obtained, which possessed an empty internal framework.^{1,7} However, in the presence of both $(\text{CH}_3)_4\text{N}^+$ and a neutral guest G (CHCl_3 , CH_2Cl_2 or CCl_4), inclusion products of the type $[(\text{CH}_3)_4\text{N}][\text{CuZn}(\text{CN})_4] \cdot n\text{G}$ ($n = 0.9 - 0.96$, depending on G) was obtained,¹ with CRI-form $[\text{CuZn}(\text{CN})_4]^-$ framework. In contrast to these cases, under the conditions in which $(\text{CH}_3)_4\text{N}^+$ and G were absent, $[\text{K}(\text{H}_2\text{O})_n][\text{CuZn}(\text{CN})_4]$ was obtained.⁶ These results suggest that the molecular shape of the cationic guest controls the geometry of the host framework, as has been observed in studies of

$\text{Cd}(\text{CN})_2$ type clathrates.⁴ In this study, we initially sought to more closely investigate the geometrical effects of the cationic guest on the host framework. Instead of $(\text{CH}_3)_4\text{N}^+$, which is highly symmetrical and non-polar, the smaller, less symmetrical and polar $(\text{CH}_3)_3\text{NH}^+$ was examined. In the presence of $(\text{CH}_3)_3\text{NH}^+$, $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4] \cdot n\text{H}_2\text{O}$ was obtained in the CRI form. Interestingly, this host framework was found to interconvert between the CRI and TRI forms upon exchange of the neutral guest. This structural change requires the breaking and reforming of coordination bonds—*i.e.*, it is a reconstructive transition.

The new clathrate $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4] \cdot n\text{H}_2\text{O}$ was obtained as a white powder from an aqueous solution containing $\text{K}_2[\text{Zn}(\text{CN})_4]$, CuCN , KCN , and $(\text{CH}_3)_3\text{N} \cdot \text{HCl}$ (electronic supplementary information, ESI†). The IR spectrum showed that the compound included H_2O molecules. Thermogravimetric (TG, Fig. ESI-1†) and elemental analyses suggested the water molecule stoichiometry (n) to be 1.5. The powder X-ray diffraction (XRD) pattern was almost identical to that of $[(\text{CH}_3)_4\text{N}][\text{CuZn}(\text{CN})_4]$, whose framework is the CRI form. The observed diffraction peaks were assignable in the same manner as for $[(\text{CH}_3)_4\text{N}][\text{CuZn}(\text{CN})_4]$, and the derived cell parameters were similarly very close. (Figs. 2(a) and (b), Figs. ESI-2(a) and (b)†, and Table ESI-1†)

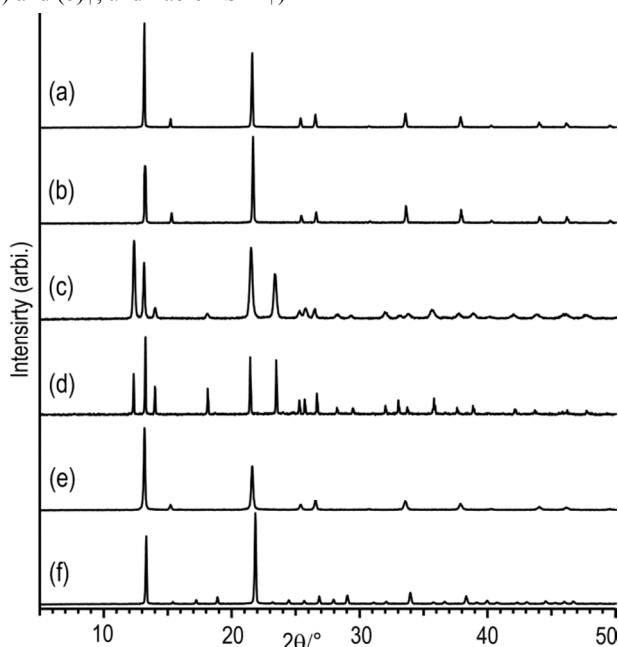


Fig. 2 XRD patterns of (a) $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4] \cdot 1.5\text{H}_2\text{O}$, (b) $[(\text{CH}_3)_4\text{N}][\text{CuZn}(\text{CN})_4]$, (c) $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4] \cdot \text{CH}_3\text{CN}$, (d) $[\text{K}(\text{H}_2\text{O})_n][\text{ZnCu}(\text{CN})_4]$, (e) $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4] \cdot \text{CH}_3\text{CN}$ after standing in H_2O vapour for 1 d, (f) $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4] \cdot 1.5\text{H}_2\text{O}$ after standing acetonitrile vapour for 30 m.

Upon exposing $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4] \cdot 1.5\text{H}_2\text{O}$ powder to the vapour of a volatile liquid such as acetonitrile, MeOH , EtOH , CCl_4 , CHCl_3 , CH_2Cl_2 or acetone at room temperature, the H_2O molecules were replaced. These guest exchanges were confirmed spectroscopically by IR. For most of the guest molecules, the powder XRD patterns of the samples after guest exchange were almost the same as that of the parent. (Fig. ESI-3†) However, in the case of acetonitrile, the pattern was completely different. Here, the pattern was very similar to that of $[\text{K}(\text{H}_2\text{O})_n][\text{CuZn}(\text{CN})_4]$, which exhibits the TRI-form framework. The diffraction peaks could be assigned in the same manner as for $[\text{K}(\text{H}_2\text{O})_n][\text{CuZn}(\text{CN})_4]$, and calculated cell parameters were also very close. (Figs. 2(c) and (d), Figs. ESI-2(c) and (d)†, and Table ESI-1†) These findings suggest that the

$[\text{CuZn}(\text{CN})_4]^-$ host was transformed from the CRI to the TRI form upon the water-to-acetonitrile guest exchange. Elemental analysis of the sample after guest exchange showed an acetonitrile content of 1: $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4] \cdot n\text{CH}_3\text{CN}$ ($n = 1$). The CRI-to-TRI transition required *ca.* 10 d at room temperature (16 - 20 °C), and could be shortened to *ca.* 5 d at 30 °C.

Upon standing in room or water vapour-saturated air, the acetonitrile in $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4] \cdot \text{CH}_3\text{CN}$ was replaced with water and the host structure returned to the CRI form. In water vapour-saturated conditions, the conversion required *ca.* 2.4 d and *ca.* 1 d at room temperature and 30 °C, respectively. Under room air, *ca.* 4 d were required. The guest exchange and structural transition were confirmed by IR spectroscopy (Fig. ESI-4†) and XRD (Fig. 2(e)). The CRI-form sample underwent structural retransformation to the TRI-form by re-exposure to saturated acetonitrile vapour. Successive change from the TRI to the CRI form also took place. (Fig. ESI-5†) These changes were confirmed over more than 10 cycles. The time required for the conversion became shorter as the cycles progressed: the CRI-to-TRI conversion was completed within 1 d at the 10th cycle at 30 °C.

During the transition from the CRI to the TRI form, new diffraction peaks not belonging to either structure appeared within a few minutes after the sample was placed in acetonitrile vapour (Figs. 2(f) and ESI-2(f)†). These peaks can be assigned to those which were originally absent due to the extinction rule for an all-face centered cubic cell ($F\bar{4}3m$) of the CRI form. (Table ESI-1†) This finding suggests the existence of an intermediate phase which is cubic but has reduced crystal symmetry compared to the original CRI structure, as well as slightly smaller parameters. (Table ESI-1†) The peaks of the intermediate phase gradually disappear and those of the TRI form gradually appear. In the transition from the TRI to the CRI form, however, the diffraction pattern change takes place simply as the appearance and disappearance of the TRI and CRI patterns. Extra peaks suggesting the intermediate phase or another phase are not observed. (Fig. ESI-5†)

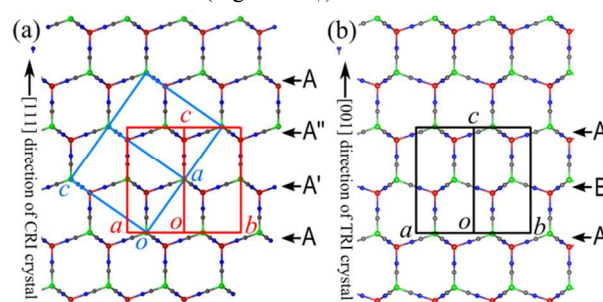


Fig. 3 (a) CRI form lattice of $[(\text{CH}_3)_4\text{N}][\text{CuZn}(\text{CN})_4]$ and its unit cell (blue). The red cell indicates a possible position of the unit cell of TRI form after the conversion. (b) TRI form lattice of $[\text{K}(\text{H}_2\text{O})_n][\text{CuZn}(\text{CN})_4]$ and its unit cell (black)

Comparing the patterns of the CRI and TRI forms, the two diffraction peaks at $2\theta = 13.18^\circ$ and 21.61° remain nearly unchanged, although the cell parameters shrink transiently due to the appearance of the intermediate phase, as mentioned above (Fig. ESI-6†). Based on this finding, the relationship between the two lattices before and after the transition can be estimated as shown in Figs. 3(a) and ESI-7†. This relationship is the same as that observed in the transition of a single crystal of true tridymite to cristobalite.⁸ The structure of the CRI framework is described as a stacking of 2D honeycomb sheets along the $[111]$ direction of the crystal, although CN^- ligands link adjacent sheets. The 2D honeycomb sheet is composed of chair-form hexagonal rings formed from Cu, Zn and CN^- ligands, with a wavy appearance from the side. At each layer, the sheet is shifted to the

[112] direction such that the stacking pattern for the CRI framework is AA'A"AA'A". (Fig. 3(a)) The structure of the TRI framework can also be represented as a stacking of 2D honeycomb sheets. However, as shown in Fig. 3(b), its stacking pattern is ABAB, where B is A rotated by 180° about the axis perpendicular to the sheet.

Solid-state NMR spectra were acquired to obtain information about the dynamic states of the trapped $(\text{CH}_3)_3\text{NH}^+$ ions, water, and acetonitrile molecules and their surroundings. Figs. 4(a) and (b) and ESI-8† show ^{13}C -NMR spectra of the samples in the CRI and TRI forms. Spectra acquired in the absence of magic angle spinning showed clear differences between the two forms. The featureless sharp peak observed in the CRI form suggests that $(\text{CH}_3)_3\text{NH}^+$ undergoes isotropic rotational motion. On the other hand, the spectrum of the TRI form displayed a so-called axial powder pattern. This line shape suggests that the $(\text{CH}_3)_3\text{NH}^+$ undergoes rotational motion about the molecular principal axis (C_3 axis). Information for the water and acetonitrile molecules was obtained from ^2H -NMR powder pattern measurements carried out using samples that included deuterated water and acetonitrile molecules, respectively. The ^2H -NMR spectra of the CRI form shown in Figs. 4(c) and ESI-9† clearly suggest that the water molecules undergo very rapid isotropic rotational motion. The spectra for the TRI form presented an axial powder pattern (Figs. 4(d) and ESI-10†), which is often observed for a methyl group undergoing rotational motion. This suggests that there is no re-orientational motion of the acetonitrile molecule. The isotropic motions observed for the $(\text{CH}_3)_3\text{NH}^+$ and water molecules are reasonable considering a cavity structure with T_d symmetry in the CRI-form host. In contrast, their orientations are fixed—*i.e.*, the guests are packed tightly—in the TRI form. A model that can be considered for the included guests shows them trapped in the space between the stacked 2D sheets of the TRI-form crystal, with their molecular principal axes parallel to the planes of the sheets. The volume of the space is just sufficient to accommodate the guests. However, the orientation of the molecular axes in the space is unclear. Although an imaginable representation of guest molecule packing is presented in Fig. ESI-11(b)†, other arrangements are possible. Another candidate for the guest space is the channel-like space perpendicular to the 2D sheets, which penetrates the stack. However, this configuration can be discarded because the packing of the guests into this space is loose and does not satisfy the stoichiometry of the acetonitrile guest.

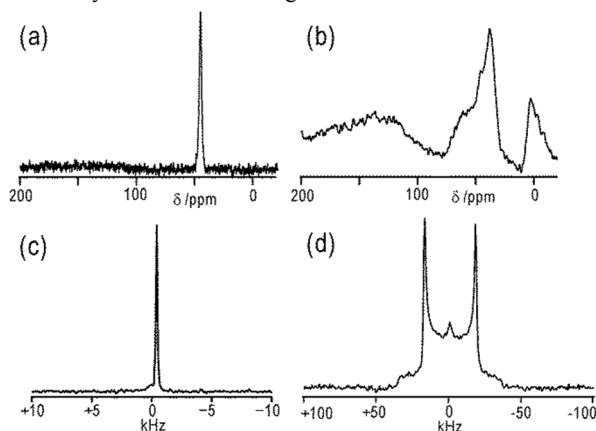


Fig. 4 Solid-state ^{13}C -NMR spectra of (a) $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4]\cdot 1.5\text{H}_2\text{O}$ and (b) $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4]\cdot \text{CH}_3\text{CN}$. ^2H -NMR powder patterns of (c) $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4]\cdot n\text{D}_2\text{O}$ and (d) $[(\text{CH}_3)_3\text{NH}][\text{CuZn}(\text{CN})_4]\cdot \text{CD}_3\text{CN}$.

In addition to acetonitrile, CH_2Cl_2 induces the same structural change (Fig. ESI-3(g)†), albeit inconsistently. Sometimes the reconfiguration was observed, sometimes not. Although CH_2Cl_2 is

not a perfectly linear molecule, the Cl-C-Cl angle is nearly linear. Also, considering the van der Waals radii, its molecular size is almost the same as that of acetonitrile (Fig. ESI-12†). Perhaps the shape and size of the replaceable guest are important factors for this transformation.

Recently, interesting structural changes were observed in $\text{Zn}(\text{CN})_2$, which is considered to be a compound related to our host.⁹ The $\text{Zn}(\text{CN})_2$ structure comprises the interpenetration of two frameworks with the CRI form so that it has no function as a clathrate host. At high pressure (0.9 - 1.8 GPa) and in a fluid medium, the interpenetration is broken and the framework acquires pores that can trap molecules from the fluid medium. These changes vary depending on the conditions. Among the changed frameworks, CRI and TRI structures are involved. These structural changes might be a common property of $\text{M}(\text{CN})_2$ -type compounds, including our case. Another remarkable property of $\text{Zn}(\text{CN})_2$ is negative thermal expansion,¹⁰ and a similar property, near-zero thermal expansion was observed in $[(\text{CH}_3)_4\text{N}][\text{CuZn}(\text{CN})_4]$.¹¹ It is interesting that these thermal expansion properties and the structural changes are the properties which are related to the structural flexibility.

In conclusion, a reconstructive transition of the $[\text{CuZn}(\text{CN})_4]^-$ framework between the CRI and TRI forms was described. This structural change involves the breaking and reforming of coordination bonds. In coordination chemistry, especially in the field of metal-organic frameworks (MOFs) and porous coordination polymers (PCPs), the control of framework structure is a significant research theme. The ligand design, combination of metals and ligands, and selection of guests or templates have also been important targets. Post-synthetic transformations in which rearrangements are effected in existing compounds are increasingly of interest.¹² Understanding the dynamic behaviour of frameworks has also become an important research objective, such as the impact of breathing effects on guest absorption,¹³ which is transformation without topological change. In this respect, our study adds a new facet to the dynamic behaviour of MOFs and PCPs. However, such structural changes—including ours—have been discovered serendipitously.¹⁴ For general consideration, the accumulation of more examples is necessary at this stage. Further investigation of this compound emerges by consideration of the trapped $(\text{CH}_3)_3\text{NH}^+$ and H_2O , which are both polar and bear an acid/base relationship. Here, dielectric properties and/or the possibility of proton transfer could be expected.

Notes and references

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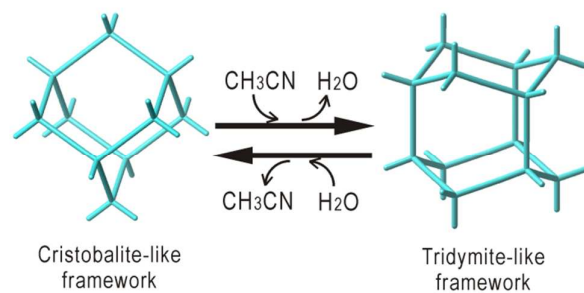
† Electronic Supplementary Information (ESI) available: sample preparation, data of TG, IR, PXRD, NMR and additional figures are included. See DOI: 10.1039/c000000x/

‡ In Figure 1 showing the structures of the CRI and TRI forms, the positions of Cu, Zn, C and N are ordered. However, the disorder of their positions is possible in the TRI and CRI forms generated from the reconstructive transition.

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A graphical and textual abstract for the Table of contents



Framework host $[\text{CuZn}(\text{CN})_4]^-$ exhibits a reversible reconstructive transition in the solid-state between cristobalite-like framework and tridymite-like one induced by guest exchange.