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Pore-controlled formation of 0D metal complexes in anionic 3D metal–organic frameworks†

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The host–guest chemistry between a series of anionic MOFs and their trapped counterions was investigated by single crystal XRD. The PCN-514 series contains crystallographically identifiable metal complexes trapped in the pores, where their formation is controlled by the size and shape of the MOF pores. A change in the structure and pore size of PCN-518 indicates that the existence of guest molecules may reciprocally affect the formation of host MOFs.

The study of host–guest chemistry has attracted an enormous amount of attention in the past few decades.^{1–3} Due to their structural diversity and convenient association and dissociation of guest molecules by non-covalent interactions, host–guest compounds can be potentially applied in many areas, including molecular recognition,^{4–6} reaction capsules,^{7–9} small molecule structural determination,^{10–12} sensors,^{13–15} biological applications,^{16–18} and many others. Clathrate compounds^{19–21} are a unique category of host–guest complexes that consist of completely encapsulated guest molecules residing in cages formed by the crystal lattices of host molecules. Due to their crystalline nature, crystallographic tools can be conveniently applied to study their structures for the purpose of understanding the host–guest interactions of these compounds.

The utilization of a host compound with cavities of definite size and shape for selective inclusion of guest molecules

is of vital significance for the successful design of host–guest systems.²² Many porous media with intrinsic cavities or openings, including cyclic compounds,^{23–25} self-assembled molecular cages,^{26–28} zeolites,^{29–31} hydrogen-bonded frameworks,³² and metal–organic frameworks (MOFs),^{10–12,33} have been utilized for the construction of host–guest complexes. Different from traditional porous materials, MOFs exist as 3D coordination networks consisting of metal-containing units and organic linkers.^{34–36} They have widespread potential applications, such as in energy storage, separation processes, carbon capture, catalysis, luminescent materials, and biomedical applications.^{37–39} With regard to host–guest chemistry, MOFs appear to be very promising host materials due to their large porosities, customizable cavities, and crystalline nature. For simplicity, in this manuscript, we use the term “MOF clathrates” to describe any MOF-related host–guest compounds in which discrete guest molecules enclosed by MOF cavities are in ordered arrangements throughout the entire framework and can be studied by crystallographic methods. Due to their crystalline nature, MOFs consist of uniform cavities in ordered and periodic arrangements throughout the 3D space with long-range regularity. Upon incorporation of guest molecules that possess appropriate interactions with specific tunable features in MOF pores, they are likely to adopt a particular or preferred conformation and orientation depending on the size, shape, polarity, and alignment of the MOF cavities. This will significantly facilitate the formation of the MOF clathrates. Nevertheless, single-crystal X-ray diffraction (XRD) studies of these compounds are still rare,⁴⁰ presumably due to the lack of appropriate host–guest interactions between MOFs and the guest molecules. In fact, the guest molecules incorporated in MOFs can rarely be observed by X-ray crystallography.¹⁰ In recent years, the Fujita group has reported a series of MOFs as “crystalline sponges”. Due to the high affinity and molecular-recognition ability of the cavities to the target molecules, the molecules absorbed by these MOFs can be regularly placed throughout the MOF lattice, where the molecular structure of these guest

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molecules, along with their host frameworks, can be conveniently determined by single crystal XRD.^{10–12} In this work, we report a series of MOF clathrates with incorporated metal complexes as guest molecules. In these MOFs, all of the guest metal complexes are formed *in situ* and are incorporated into the host framework *via* Coulombic interactions. Unlike the “crystalline sponge” nature of those reported in Fujita’s work, the MOFs utilized in this work serve as “reaction containers”, where the formation of the encapsulated metal complexes is controlled by the size, shape, and electric charge of the cavities of the host MOF. These metal complexes are otherwise not likely to form without the presence of the host framework.

A host MOF that is suitable for the formation of MOF clathrates should possess several distinctive attributes. First, this MOF should possess cavities with an appropriate size. These cavities should be adequately large to contain the guest molecules. Nevertheless, excessively large pores are likely to reduce their host–guest interactions. Second, MOFs with low-symmetry cavities are usually more suitable for obtaining a crystallographic image of the guest molecules. Spherical-shaped cavities are typically not preferred because isotropic host–guest interactions are more likely to result in crystallographic disorders inside the cavities. Low symmetry cavities are more likely to result in a preferred alignment orientation for the guest molecules. Third, suitable host–guest interactions, such as Coulombic attraction, hydrogen bonding, and $\pi\cdots\pi$ interactions, will facilitate the ordered arrangements of guest molecules inside the MOFs.

PCN-514 (PCN represents “Porous Coordination Network”) appears to be a promising host for making MOF clathrates.⁴¹ It is an ionic framework consisting of an 8-connected trinuclear cadmium cluster (Fig. 1(a)) connected by a tetratopic ligand, TCPS (TCPS = 4,4',4'',4'''-tetrakis(carboxyphenyl)silane), in a 1:2 ratio. It crystallizes in the triclinic space group $P\bar{1}$, exhibiting a fluorite (flu) topology⁴² with a solvent accessible volume⁴³ of 52.40%. It possesses a unique type of cavity with a diameter of 8.4 Å. This cage possesses C_i symmetry with an inversion center located in the geometric center. It is surrounded by four TCPS ligands connected to four trinuclear cadmium clusters (Fig. 1(b) and (c)). It is this cage that controls the formation of a variety of cadmium complexes under different solvothermal conditions. Due to its anionic nature and appropriate pore size, unanchored Cd complexes with coordinating solvents can form inside this cage as counterions of this MOF. The vast majority of previously discovered anionic MOFs typically contain alkylammonium cations that originate from the decomposition of the reaction solvents as their counterions. Examples of positively charged metal-containing coordination complexes formed *in situ* that fill the MOF cavities as counterions still remain scarce.^{44,45} It is even rarer for the metal complexes filling the MOF cavities to be crystallographically identified by single crystal XRD studies. In fact, two of these metal-complex-incorporated MOFs were already reported by our group.⁴¹ Nevertheless, their host–guest chemistry remains completely

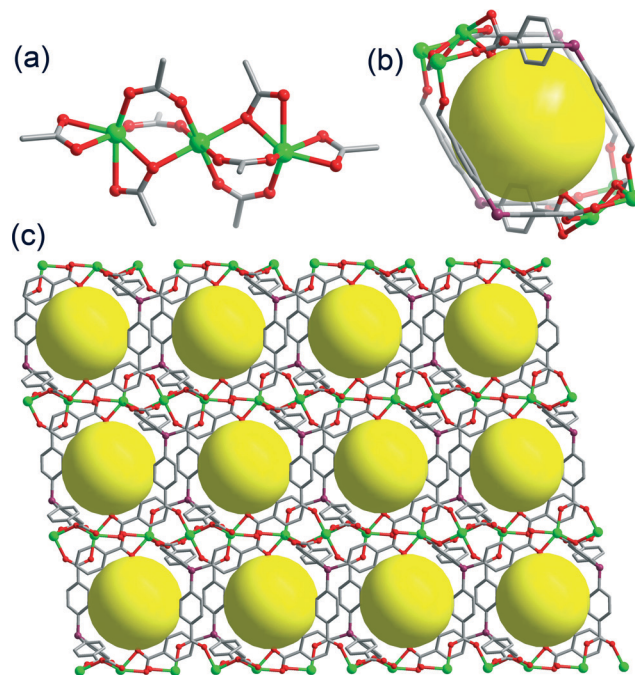


Fig. 1 (a) A graphic representation of the trinuclear cadmium cluster. (b) The cage where the cadmium complex is encapsulated. (c) The crystal structure of the PCN-514 framework (the host MOF). For simplicity, the trapped Cd complexes (the guest molecules) are not shown. Color scheme: C, gray; O, red; Cd, green. H atoms were omitted for clarity.

undiscussed in the previous manuscript. Herein, we would like to provide a systematic study of the host–guest chemistry of the PCN-514 series and illustrate how the utilization of different solvents results in the formation of different metal complexes with the assistance of MOF cavities.

The anionic framework PCN-514 can be generated under a variety of solvothermal conditions. Different metal complexes will form when different solvents are used, while the formation of these trapped metal complexes is controlled by the size and shape of the cavities of this MOF. All of these metal complexes consist of a Cd ion and six coordinating solvent molecules. When bulkier solvents are used, a decreasing number of bulky solvent molecules are observed to coordinate to the metal (see Fig. 2). When DMF (*N,N*-dimethylformamide) was used, the resulting complex consists of one Cd ion and six DMF molecules, yielding a $[\text{Cd}(\text{DMF})_6]^{2+}$ cation residing in the center of each cavity of this framework. When a bulkier solvent, DMA (*N,N*-dimethylacetamide), was used, the $[\text{Cd}(\text{DMA})_4(\text{H}_2\text{O})_2]^{2+}$ cation formed. Each water molecule connects to one free DMA solvent and one Cd₃ cluster through hydrogen bonds. When the DMA/NMP (NMP = *N*-methyl-2-pyrrolidone) mixture was used, formation of $[\text{Cd}(\text{DMA})_2(\text{NMP})_2(\text{H}_2\text{O})_2]^{2+}$ was observed. In other words, it is the MOF cavities that control the formation, size, and coordination chemistry of the trapped Cd complex. Single crystal XRD studies reveal that all of these Cd complexes possess C_i symmetry with an inversion center located on the Cd metal ion, which is consistent with the symmetry of their host cages.



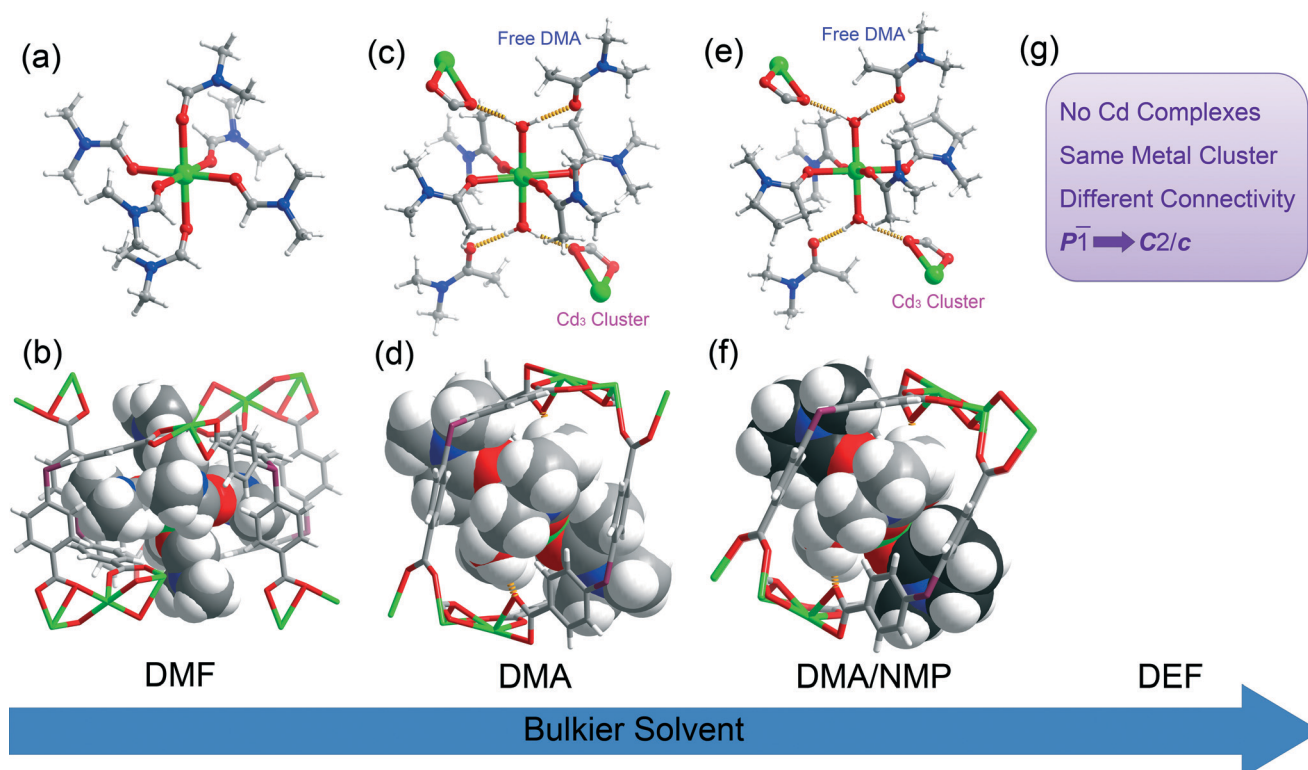


Fig. 2 The top row illustrates the single crystal structures of the Cd complexes trapped in the corresponding MOF cavities. The bottom row illustrates the space filling models of these complexes and their interactions with the MOF cavities. (a, b) The Cd(DMF)₆ complex. (c, d) The Cd(DMA)₄(H₂O)₂ complex. Each water molecule connects to one free DMA solvent and one Cd₃ cluster through hydrogen bonds (yellow dashed lines). (e, f) The Cd(DMA)₂(NMP)₂(H₂O)₂ complex. For clarity, the carbon atoms of NMP molecules are shown as dark gray spheres. Color scheme: C, gray; O, red; N, blue; Cd, green; Si, purple; H, white. (g) A topologically different framework without any trapped Cd complex is formed when using DEF as the solvent.

Further exploration of the utilization of bulkier solvents has led to the discovery of a novel MOF, designated as PCN-518. Single crystal XRD studies reveal that it crystallizes in the monoclinic group *C2/c*. Similar to the PCN-514 series, it is also an anionic MOF that possesses the same Cd clusters (Fig. 1(a)) linked by the TCPS ligand. Nevertheless, even though the cluster of PCN-518 is the same (an 8-connected trinuclear Cd cluster) as that of PCN-514, the connectivity of this cluster is different (Fig. 3(a)). This has resulted in the formation of a topologically different framework, which contains the Cd₃ cluster and the tetrahedral ligand in a 1:2 ratio to exhibit an *alb/P* topology.^{41,46} Interestingly, this framework does not contain any metal complexes as counterions. Instead, it is expected to contain alkylammonium cations trapped in its pores as counterions, which cannot be investigated by crystallographic tools due to their disordered nature. The solvent accessible volume⁴³ of PCN-518 is 48.90%. The diameter of its largest cavities is 6.4 Å (Fig. 3(b)), which is significantly smaller than that of PCN-514. It should be noted that the formation of the PCN-518 framework with trapped Cd-DEF complexes was not observed under solvothermal conditions, presumably because the PCN-518 cavity is too small for any type of Cd-DEF complex to fit into. Without the presence of bulky metal-solvent complexes, the formation of

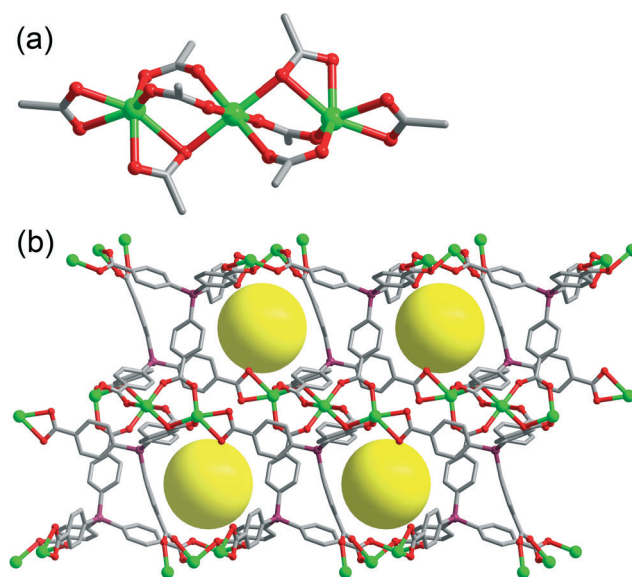


Fig. 3 (a) The trinuclear cadmium cluster in PCN-518. Its surrounding carboxylates have a different connectivity from those of PCN-514. (b) The crystal structure of PCN-518. The yellow spheres indicate the empty spaces inside its cavities. This MOF does not contain any metal complexes. Color scheme: C, gray; O, red; Cd, green. H atoms were omitted for clarity.



PCN-518 is more energetically favored because the smaller cavities of PCN-518 will significantly enhance the host–guest interactions by increasing the Coulombic attraction between the alkylammonium cations and the host framework. This illustrates a rare example indicating that the existence of guest molecules can reciprocally affect the formation of host frameworks.

Conclusions

In summary, we have reported a series of anionic Cd MOFs in this work. Their host–guest chemistry was investigated by single crystal XRD. The PCN-514 series contains metal–solvent complexes that are generated *in situ* as counterions. These are rarely seen examples of MOF clathrates whose incorporated metal complexes can be crystallographically identified. The formation of these metal complexes is controlled by the size and shape of MOF cavities, where these reactions are otherwise not likely to happen without the host framework. PCN-518 is a topologically different framework without any metal–solvent complexes. It indicates that the formation of host frameworks may be reciprocally controlled by the presence of these metal–solvent complexes as well. Furthermore, this work has provided some insight into the design of MOF-related host–guest systems, where their mutual interactions can be conveniently studied.

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Notes and references

- 1 S. Stepanow, M. Lingenfelder, A. Dmitriev, H. Spillmann, E. Delvigne, N. Lin, X. Deng, C. Cai, J. V. Barth and K. Kern, *Nat. Mater.*, 2004, 3, 229–233.
- 2 G. D. Stucky and J. E. Mac Dougall, *Science*, 1990, 247, 669–678.
- 3 D. J. Cram and J. M. Cram, *Science*, 1974, 183, 803–809.
- 4 R. M. K. Calderon, J. Valero, B. Grimm, J. de Mendoza and D. M. Guldi, *J. Am. Chem. Soc.*, 2014, 136, 11436–11443.
- 5 H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.*, 1991, 30, 1417–1436.
- 6 M. Yamamura, T. Saito and T. Nabeshima, *J. Am. Chem. Soc.*, 2014, 136, 14299–14306.
- 7 M. Yoshizawa, J. K. Klosterman and M. Fujita, *Angew. Chem., Int. Ed.*, 2009, 48, 3418–3438.
- 8 D. H. Leung, D. Fiedler, R. G. Bergman and K. N. Raymond, *Angew. Chem., Int. Ed.*, 2004, 43, 963–966.
- 9 D. Fiedler, D. H. Leung, R. G. Bergman and K. N. Raymond, *Acc. Chem. Res.*, 2004, 38, 349–358.
- 10 Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, *Nature*, 2013, 495, 461–466.
- 11 Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai and M. Fujita, *Nat. Protoc.*, 2014, 9, 246–252.
- 12 G.-H. Ning, Y. Inokuma and M. Fujita, *Chem. – Asian J.*, 2014, 9, 466–468.
- 13 F. L. Dickert and P. A. Bauer, *Adv. Mater.*, 1991, 3, 436–438.
- 14 F. L. Dickert and A. Haunschild, *Adv. Mater.*, 1993, 5, 887–895.
- 15 R. V. Slone, K. D. Benkstein, S. Bélanger, J. T. Hupp, I. A. Guzei and A. L. Rheingold, *Coord. Chem. Rev.*, 1998, 171, 221–243.
- 16 T. Douglas and M. Young, *Nature*, 1998, 393, 152–155.
- 17 E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem., Int. Ed.*, 2003, 42, 1210–1250.
- 18 G. C. R. Ellis-Davies, *Nat. Methods*, 2007, 4, 619–628.
- 19 J. L. Atwood, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
- 20 S. A. Bourne and M. R. Caira, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2014.
- 21 T. Iwamoto and D. F. Shriver, *Inorg. Chem.*, 1972, 11, 2570–2572.
- 22 K. Odashima, A. Itai, Y. Iitaka and K. Koga, *J. Am. Chem. Soc.*, 1980, 102, 2504–2505.
- 23 C. A. Stanier, M. J. O'Connell, W. Clegg and H. L. Anderson, *Chem. Commun.*, 2001, 493–494.
- 24 A.-J. Avestro, D. M. Gardner, N. A. Vermeulen, E. A. Wilson, S. T. Schneckel, A. C. Whalley, M. E. Belowich, R. Carmieli, M. R. Wasielewski and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2014, 53, 4442–4449.
- 25 J. Storsberg and H. Ritter, *Macromol. Rapid Commun.*, 2000, 21, 236–241.
- 26 M. Fujita, *Chem. Soc. Rev.*, 1998, 27, 417–425.
- 27 C.-Y. Su, Y.-P. Cai, C.-L. Chen, F. Lissner, B.-S. Kang and W. Kaim, *Angew. Chem., Int. Ed.*, 2002, 41, 3371–3375.
- 28 C. J. Bruns, D. Fujita, M. Hoshino, S. Sato, J. F. Stoddart and M. Fujita, *J. Am. Chem. Soc.*, 2014, 136, 12027–12034.
- 29 G. Calzaferri, S. Huber, H. Maas and C. Minkowski, *Angew. Chem., Int. Ed.*, 2003, 42, 3732–3758.
- 30 J. A. Incavo and P. K. Dutta, *J. Phys. Chem.*, 1990, 94, 3075–3081.
- 31 S. Megelski and G. Calzaferri, *Adv. Funct. Mater.*, 2001, 11, 277–286.
- 32 M. J. Prakash and S. C. Sevov, *Inorg. Chem.*, 2011, 50, 12739–12746.
- 33 K. Uemura, S. Kitagawa, K. Fukui and K. Saito, *J. Am. Chem. Soc.*, 2004, 126, 3817–3828.
- 34 H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, 402, 276–279.
- 35 M. Zhang, M. Bosch, T. Gentle and H.-C. Zhou, *CrystEngComm*, 2014, 16, 4069–4083.



- 36 W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle, M. Bosch and H.-C. Zhou, *Chem. Soc. Rev.*, 2014, **43**, 5561–5593.
- 37 J. R. Long and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1213–1214.
- 38 H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673–674.
- 39 M. Zhang, Z.-Y. Gu, M. Bosch, Z. Perry and H.-C. Zhou, *Coord. Chem. Rev.*, 2014, DOI: 10.1016/j.ccr.2014.05.031.
- 40 B. Chen, S. Xiang and G. Qian, *Acc. Chem. Res.*, 2010, **43**, 1115–1124.
- 41 M. Zhang, Y.-P. Chen and H.-C. Zhou, *CrystEngComm*, 2013, **15**, 9544–9552.
- 42 M. Zhang, Y.-P. Chen, M. Bosch, T. Gentle, K. Wang, D. Feng, Z. U. Wang and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2014, **53**, 815–818.
- 43 A. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.
- 44 J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2009, **131**, 8376–8377.
- 45 F. Bu and S.-J. Xiao, *CrystEngComm*, 2010, **12**, 3385–3387.
- 46 L. Wen, P. Cheng and W. Lin, *Chem. Sci.*, 2012, **3**, 2288–2292.

