

Porous Coordination Polymers of Zinc(II)-dicarboxylate-diamine and Their Gas Sorption Properties*

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Abstract

Despite a short history, the research on porous coordination polymers is gaining importance in inorganic chemistry thanks to facile synthesis, unambiguous characterization by X-ray diffraction and potentials as high-surface-area materials. Recently, gas sorption properties of various porous materials are under active investigations in order to know whether it is possible to store industrially important gases through physisorption, and porous coordination polymers are one of the most promising candidates for such a purpose. This article reviews two recent papers reporting a series of isomorphous frameworks based on Zn(II), dicarboxylate and diamine ligands and their gas sorption properties.

1. Introduction

The study of network solids composed of transition-metal ions and polytopic organic ligands, often termed as 'metal-organic frameworks' or simply 'coordination polymers', has now become one of the most actively pursued topics in inorganic chemistry.¹⁾ It is somewhat surprising and, even, amazing to see this development since, in the wildest stream of nano-related sciences and technologies, the area having its origin and methodologies in rather traditional or conventional chemistry stands so high.

It is not a demanding task to understand that application possibilities are the major driving forces for studying coordination polymers since one can easily envision interesting physical properties due to the repeating metal-ligand-metal bonds. However, it must have been quite a surprise to many when a coordination polymer has been proven to possess reversible gas sorption properties,²⁾ a territory long belonged to conventional porous materials, such as zeolites, silicas and carbons. Since then, a myriad effort has been made towards 'porous' coordination polymers, and not long after reported was an experimentally determined surface area up to $5,900 \text{ m}^2 \text{ g}^{-1}$ for a porous chromium(III)-terephthalate framework.³⁾ It is noted that throughout the history of mankind, no known material, crystalline or amor-

phous, has come close to the range in terms of experimentally measured surface area, not by a long shot.

As a porous material coordination polymers do not enjoy the status of its pure inorganic counterpart, zeolites, which is understandable; however, it would be fallacious to rule coordination polymers out of porous materials.⁴⁾ For example, coordination polymers are practically the only remaining class of porous materials which have not been disproved with respect to the gas-storage applications.⁵⁾

It is both bothering and intriguing to ask why most of 'porous' coordination polymers are metal-carboxylates.⁶⁾ The question is bothering because it may imply a limitation of expandability, and at the same time the question is intriguing because there are many other organic ligands that can play a similar role in coordination network structures. The author regrettably does not have an agreeable answer to the question; however, it is quite apparent that there is a well-established synthetic protocol for coordination polymers of metal-carboxylates. The method is called solvo- (or less frequently solvato-) thermal synthesis, a smart variation of conventional hydrothermal reactions. This one-step, one-pot synthesis takes advantage of the fact that carboxylates can easily be deprotonated to strongly coordinate to transition metal ions and that some organic solvents, N,N'-dimethylformamide (DMF) and sorts, undergo

thermal decompositions to release dialkylamines in a controlled manner. In typical hydrothermal reactions, heating under autogenous pressure is used simply to convert an amorphous phase to a crystalline one. In solvothermal methods, in contrast, all the reactants are clearly dissolved in the beginning, and upon heating in a sealed vessel metal ions and organic ligands self-assemble into a polymeric form with a preferred connectivity. The slow and controlled release of base from the reaction medium seems to be the key for the formation of single-crystalline products. Originally reported by O. M. Yaghi and coworkers,⁷⁾ this simple and powerful synthetic protocol has been the source of explosive outpouring of metal-carboxylate coordination polymers.

Along with a coworker under the supervision of Kimoon Kim at POSTECH, the author has also garnered significant results in carboxylate-based coordination polymer system, and wishes to re-present some of the earlier publications.

2. Gas Sorption Properties of Zn(II)-dicarboxylate-diamine Frameworks

The combination of Zn^{2+} and terephthalate has already produced one of the (if not *the*) most well-known named material in coordination polymers, namely MOF-5.^{2d} In fact, the same group that reported MOF-5 has apparently carried out extensive screening processes for rigid dicarboxylates with an aromatic backbone.⁷⁾ Similar attempts with other metal ions followed from other groups elsewhere, which only resulted in intermittent success stories.

It was a turning point when a colleague of the author decided to use an aliphatic diamine along with Zn^{2+} and terephthalic acid for a new metal-organic framework. At first it did not look like a smart strategy since the diamine will immediately deprotonate terephthalic acid and give an amorphous precipitate of polymeric nature. Indeed, the solution mixture of $Zn(NO_3)_2 \cdot 6H_2O$, terephthalic acid (H_2bdc) and 1,4-diazabicyclo[2,2,2]octane (*a.k.a.* dabco) in DMF gives a white precipitate. It was noted, however, that the amount of the precipitate was not that much compared to the amount of reactants used, and therefore, the precipitate was removed and the

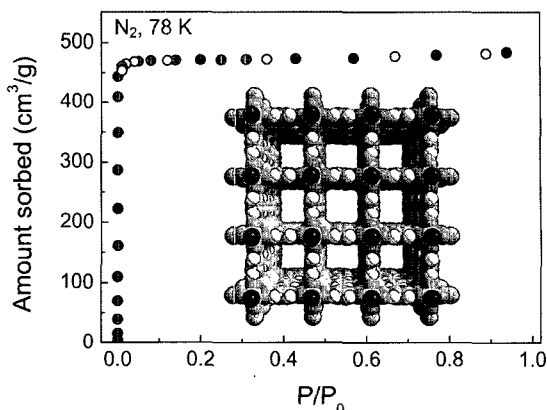


Fig. 1. The nitrogen gas sorption isotherm for $[Zn_2(bdc)_2(dabco)]$ whose crystal structure is shown as inset. The filled and open circles represent sorption and desorption, respectively.

filtrate was subject to heating in a sealed glass tube. After about 12 hours of heating at $110^\circ C$, block-shaped single-crystals were visible inside the tube and they were found to be a new metal-organic porous material with the formula $[Zn_2(bdc)_2(dabco)]$ (Fig. 1).^{5a)}

The framework material possesses interesting dynamic properties. That is, the overall structure shown in Fig. 1 is distorted when organic solvents occupy the empty channels which account for 62% of the crystal volume. The X-ray crystal structures of evacuated and DMF- and benzene-containing frameworks are shown in Fig. 2 along with corresponding X-ray powder diffraction profiles.

The porous framework material (ZBD hereafter) has advantages over the famous MOF-5. First, ZBD is permanently stable and maintains the original porous structure under the ambient condition in the air. Meanwhile, not many are aware of the fact that MOF-5, when evacuated, slowly turns to a non-porous form in contact to moisture from the air. Therefore, MOF-5 should be stored either in organic solvents, such as $CHCl_3$, or under a tight vacuum or dry atmosphere. Second, unlike MOF-5 which contains only one type of ligand (bdc), ZBD allows structural variations of two kinds, dicarboxylate (bdc) and diamine (dabco). For example, it is possible to replace bdc with longer or bulkier dicarboxylate and/or dabco with longer diamines, such as

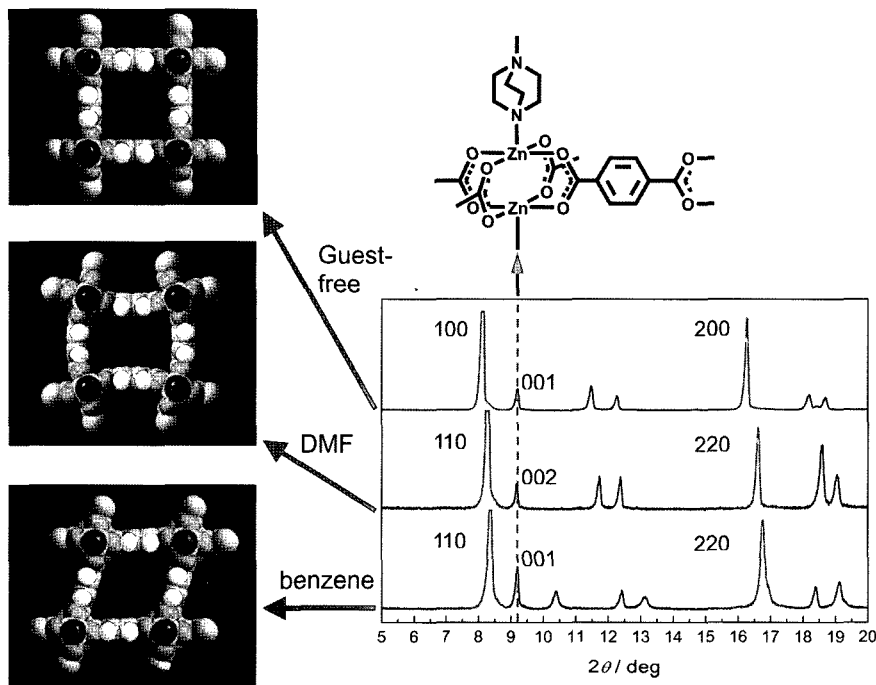
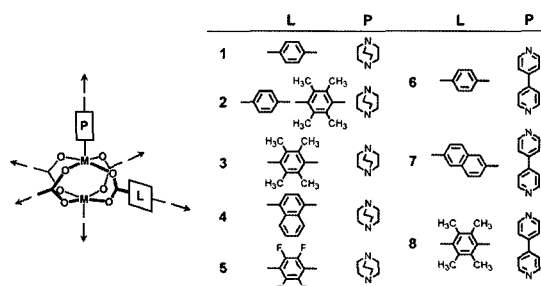


Fig. 2. X-ray crystal structures and XRD profiles of the framework ZBD when evacuated (top) and DMF (middle) or benzene (below) occupies the channels. Note that the 2θ values for peaks (001) and (002) do not change.

4,4'-dipyridyl. These anisotropic structural modifications mean various changes of the pore environment in which gas molecules are supposed to adsorb. Then, the observed differences in the gas sorption behavior may be correlated to the structural features to draw a useful conclusion for better materials towards gas storage by physisorption.

A scheme shown below has been devised and the same synthetic protocol as that for ZBD has been applied to obtain a series of isomorphous porous materials.⁸⁾

As one can easily notice from the scheme, substituents on the phenyl ring of the dicarboxylates are chemically different since they are aliphatic, aromatic and halogenic in 3, 4 and 5, respectively. Furthermore, their stereochemical demands in network structures are also different. Attempts to enlarge the pore space by using longer linkers and pillars, as in the case of 6 and 7, worked out, but two- and three-fold interpenetrations of the same nets, respectively, were observed. The interpenetration could be avoided when tetramethylterephthalate



Scheme 1. Linkers (L) and pillars (P) in paddle-wheel based nets.

(tmbdc) was used instead of bdc in the case of 8.

The changes occurred in the pore environments of the prototype ZBD are more than evident from the computer-generated plots of solvent-accessible surface of frameworks 3 and 5.

The surface plots clearly show that the nano-meter sized pores in ZBD are interconnected through wide-open windows ($\sim 8 \text{ \AA}$); however, the window size is smaller in tetrafluoroterephthalate (tfbdc) analogue 5, and even smaller in tmbdc analogue 3. The

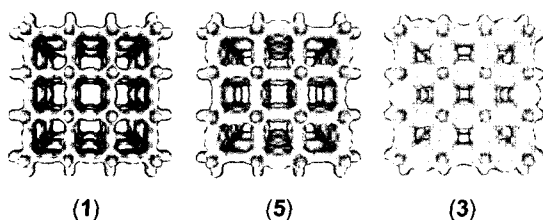


Fig. 3. Solvent-accessible surface of framework 1, 3 and 5 viewed down the *c* axis. A probe with the radius of 1.4 Å was used.

window size in 3 is around 3.5 Å which is just large enough for small gas molecules to pass through.

The results of gas sorption experiments with nitrogen were not shockingly different from expectations: the bulkier the substituents are, the smaller the amounts of sorbed nitrogen gas are. The measured surface areas assuming a monolayer coverage of all sorbed nitrogen range from 1,400 (3) to 2,090 (ZBD, 1) m² g⁻¹. The sorbed amounts are equivalent to the porosity (in volumetric sense) of at least 50% in 3 and 4, and as high as 62% in 1.

The results of hydrogen sorption experiments are shown in Fig. 4.

What is most apparent from the isotherms in Fig. 4 is that the sorption capacities of the materials

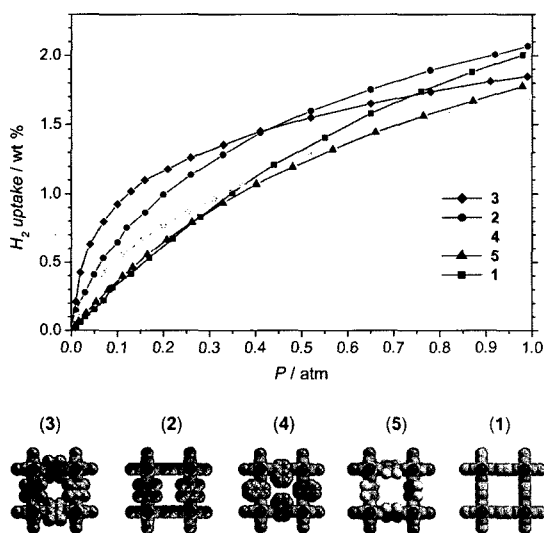


Fig. 4. Hydrogen sorption isotherms for isomorphous frameworks 1~5 and their crystal structures showing pore-connecting windows.

measured at 1 atm pressure do not vary much, even though their available surface areas are quite different. The amounts of hydrogen sorbed at 1 atm are 187~230 cm³ g⁻¹ or 1.7~2.1 wt%. The numbers become more uniform when translated into molecular terms, that is 5.7 H₂ for 1 and 4 to 6.5 H₂ in 2 per paddlewheel unit. Also it can be seen that there is no attractive interactions between H₂ and aromatic or halogen side groups. These results suggest that attempting to influence hydrogen sorption chemically is not a good strategy. The isotherms are far from being saturated and thus it is difficult to draw a conclusion on the hydrogen uptake capacities of each framework. However, the sorption traces at a low pressure range (<0.4 atm) show large differences in the H₂ uptake. For example, at 0.1 atm framework 3 adsorbs approximately 3 times more than the prototype 1. It is interesting to note that framework 1 and 3 are those with the highest and smallest, respectively, surface areas. In fact, the slopes of the curves up to 0.4 atm are inversely proportional to available surface areas, or more precisely, to the size of free apertures connecting the pores. It is not difficult to imagine the pore structures of framework 1 and its analogues, and doing so will naturally lead to a conclusion that frameworks with indented channels and high curvatures are preferred by hydrogen molecules, judging from the slopes of the sorption curves below 0.4 atm. The results of the hydrogen sorption experiments have been compared to other well-known metal-organic porous materials and a similar conclusion could be drawn: some frameworks show higher affinity towards H₂ molecules than others and they are those with wavy channels and limited free passages rather than those with straight channels and large openings. Based on the structures of the frameworks in this work and others in literature, it is proposed that a porous material with surface area of 2,000 m² g⁻¹ or above, a void fraction of 60% or more, and free windows of 6 Å or less may show an unprecedented H₂ storage capacity.

3. Conclusion

Among the many application possibilities, the

research of coordination polymer has a bright prospect in porous materials. Porous materials are widespread in our lives and they can be applied at all levels, from macroscopic level with sponges to atomic level with zeolites. Also, as a material it is an undisputable advantage to be crystalline because it is possible to obtain structural information with atomic resolution. Crystalline materials are also advantageous compared to amorphous ones since one can expect certain physical properties in homogeneous, consistent and reproducible way. The facile synthesis and easiness to get crystalline form will further broaden the scope in this area. There are skeptical views, too; however, coordination chemistry will come out to the central stage again with a breakthrough in materials science.

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Notes

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