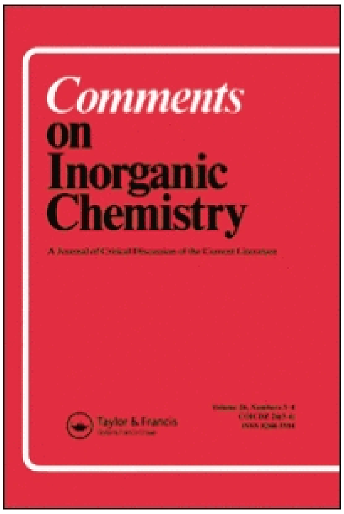

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Pillared layer compounds based on metal complexes. Synthesis and properties towards porous materials

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Pillared Layer Compounds Based on Metal Complexes. Synthesis and Properties Towards Porous Materials

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Microporous materials have been studied extensively because of their useful properties such as gas adsorption, ion exchange, and heterogeneous catalysis. Pillared-layer structure is a representative of porous structural motifs. Not only the channel size and shape but also the chemical and physical properties could be readily designed and realized by pillar modules. A large number of pillared layer compounds, mainly in inorganic and organic-inorganic hybrid compounds, have been synthesized and characterized. On the other hand, pillared layer compounds based on coordination compounds are still sparse. We describe new types of pillared layer compounds, constructed from together with coordination compounds, focusing on structures, properties and advantages as materials, future prospects.

Keywords: *microporous materials; pillared-layer structure; adsorption; coordination polymer; rational construction*

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INTRODUCTION

Microporous compounds have been extensively studied due to their unique properties such as separation, adsorption, ion exchange, heterogeneous catalysis, and so on.[1–6] However, the porous properties have been restricted to inorganic or carbon materials whose preparations and structures have been studied in great detail. Zeolites and activated carbons are representative of microporous materials. Activated carbons have high porosity, however, incompatible with a regular pore, while zeolites possess the opposite characteristics. On the other hand, other molecularly inorganic-organic hybrid compounds, such as coordination polymers, could provide not only well-designed uniform pores but also low-density light materials. It is useful to take advantage of the coordination complexes as porous materials. In this context, metal complex-assembled compounds are demonstrated to be relevant for the purposes although they have been still undeveloped and prepared for only structure models of zeolites.

Creation of novel porous compounds with unique frameworks is one of the most attractive and challenging targets. Coordination compounds constructed from transition metal ions and bridging organic ligands could make it possible to afford a new type of robust porous solids. The rational synthetic strategy is of significance for preparation of porous frameworks. In macroscopic scale pillared-layer structures have been found in ancient buildings such as the Parthenon. Utilization of pillared-layer structure is one of the most rational methods for construction of microporous compounds because of he controllable nature. In this review, we focus our interest mainly on porous materials with pillared-layer structures based on transition metal complexes. In particular, we mention synthesis, structures and properties of coordination polymers.

INORGANIC PILLAED-LAYER COMPOUNDS

It is well known that clays such as montmorillonite and bentonite have layer structures, which are constructed of vertex- and edge-sharing octahedra and tetrahedra. It has been found that introducing certain types of large guest cations into smectic clays can provide permanent microporosity, which is known as pillaring.[7] The species exchanged into the inter-lamellar region is selected for size. General method to obtain these microporous materials is to exchange the interlayer cations of the clays with bulky inorganic cations followed by calcinations. Representative clays used for this purpose are shown in Table I.[8] Host materials having cation-exchange properties other than clay minerals are layered acid salts having the general formula of M^{IV} $(HXO_4)_nH_2O$ (M^{IV} = Zr, Ti, Sn, Ge; X=P,As) such as metal(IV) hydrogen phosphate and metal(IV) hydrogen arsenate, and layered oxygen acid salts having the general formula of $A_xM_yO_z$ (A=alkaline metal, alkaline earth metal, Ag; M=transition element (Ti, V, Nb, Mo, W, U)) including titanated vanadates, niobates, molybdates, tungstates, and uranates.[9–13] The most widely pillaring species are of the polynuclear hydroxide cluster having $Al_{13}O_4(OH)_{28}^{3+}$, $Zr_4(OH)_{16-n}^{n+}$, and $Si_8O_{12}(OH)_8$ formula. On heating, the intercalated cations are converted to metal oxide clusters to separate the layers as pillars and generate interlayer space which agrees with metal oxide cluster size. Consequently, thermally stable inorganic materials with pillared-layer structures and surface areas (200~500 m^2/g) were made, which are called pillared interlayer clays or cross-linked clays. Various host materials other than smectite clays have also been employed for this purpose. Much of the current interest in pillared clays focuses on their utility as shape-selective heterogeneous catalysis.[14–17]

TABLE I General Formulas of Some Important Clay Host Materials[a]

name of mineral	*interlayercation*	*cation in the octahedral layer*	*cation in the tetrahedral layer*	*anion*
smectic group				
montmorillonite	Mx	$Al^{III}_{2-x}Mg^{II}_x$	Si^{IV}_4	$O_{10}(OH)_2$
beidellite	Mx	Al_2	$Si_{4-x}Al_x$	$O_{10}(OH)_2$
nontronite	Mx	Fe^{III}_2	$Si_{4-x}Al_x$	$O_{10}(OH)_2$
saponite	Mx	Mg_3	$Si_{4-x}Al_x$	$O_{10}(OH)_2$
hectorite	Mx	$Mg_{3-x}Li^I_x$	Si_4	$O_{10}(OH)_2$
vermiculite group				
vermiculite	Mx	Mg_3	$Si_{4-x}Al_x$	$O_{10}(OH)_2$
mica group				
Na-taeniolite	Na	Mg_2Li	Si_4	$O_{10}(F)_2$
Na-tetrasilicic	Na	$Mg_{2.5}$	Si_4	$O_{10}(F)_2$

a. reference 2 (K. Ohtuka, Chem. Mater 1997, 9, 2039).

ORGANIC PILLARED-LAYER COMPOUNDS[18–22]

Organic pillared-layer materials based on two-dimensional (2D) hydrogen-bonded networks constructed by guanidium ions and the sulfonate groups of alkane- or arene-sulfonate ions were prepared. Figure 1 shows a schematic structure of these compounds. Spacers of disulfonates, R, separate 2D sheet composed by guanidium cations and sulfonate groups to form 3D pillared-layer structure. These sheets have the flexibility because they are constructed by hydrogen bonding between guanidinium and sulfonate group. The sulfonate ion act as pillar that connects opposing hydrogen bonded sheets and form nanoporous structures with one-dimensional (1D) channels. The flexibility of the hydrogen bonded network acts significantly for self-organization of pillared-layer structures constructed from guanidium ions/ disulfonates/guest molecules. The disulfonate pillar is a key structural factor to adjust the gallery heights, together with guest molecules that occupy the channels. The layering motif would depend on the sizes of the pillar and guest molecules that may occupy these voids. Sterically undemanding pillars and small guests would favor a bilayer motif, whereas large guests would favor a continuous single-layer-stacking motif. Large pillars would favor only single-layer motifs with small guests or might even exclude guest molecules. As shown above, using guanidinium and sulfonate group can produce many porous materials with pillared-layer structure. This is one of the first steps to synthesize rationally organic pillared compounds. The disadvantage of this system is that the frameworks cannot be maintained when a pillar is exchanged, for instance, from a shorter pillar to a longer one. This structure owes to a kind if assembled dissolved reassembles process.

HYBRID PILLARED-LAYER COMPOUNDS

Porous metal phosphates have been synthesized by pillaring organic molecules.[23] Phosphonate salts of di-, tri-, and tetravalent metals are typically insoluble lamellar solids, which are crystallized hydrothermally, from the appropriate metal salts and phosphonic acids. Early attempts to make open solids by using a mixture of pillaring diphosphonates (O_3P-R-PO_3) and monophosphonates (O_3P-R) led to apparently porous materials.[24] Vanadyl phosphonates, $VO(O_3PR)\cdot H_2O\cdot C_6H_5CH_2OH$, lose $C_6H_5CH_2OH$ topochemically upon heating to form porous materials.[25]

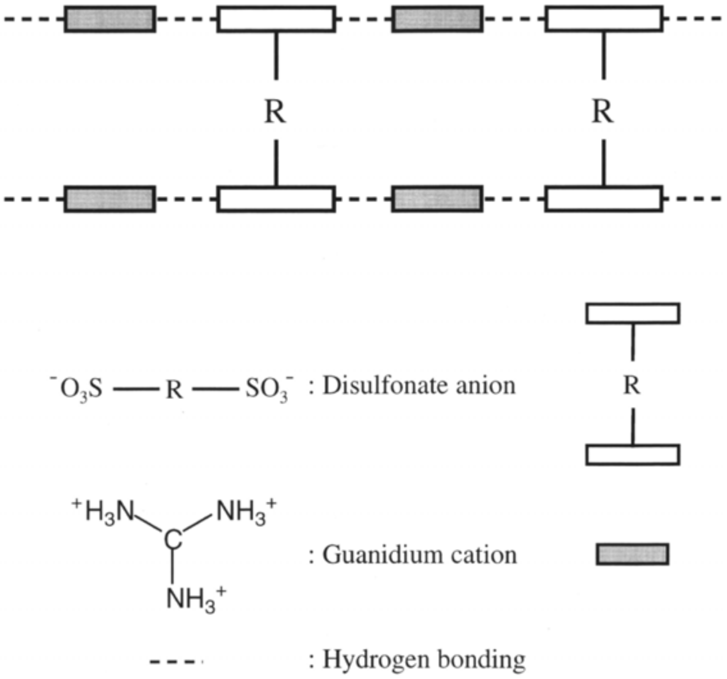


FIGURE 1

Layered zirconium derivatives containing organic pillar were synthesized by reaction of zirconium phosphate ($[ZrPO_4\{O_2P(OH)_2\}]\ 2H_2O$) and diphosphonic acid ($H_2O_3P\text{-}R\text{-}PO_3H_2$).[26–28] Diphosphonic acid is added to exfoliated lamellae ZrP in water/organic solvent with heating to form 3D pillared-layer structure. The size, shape, and chemical function of free interpillar spaces may be designed by choosing the appropriate organic moieties, R, and controlling the degree of pillaring.

During the latest ten years a number of compounds of general formulae $[H_3N(CH_2)_6NH_3]MX_4$, $H_3N(CH_2)_6NH_3]MX_4$, $[C_6H_5CH_2CH_2NH_3]_2MX_4$ (M=Pb,Sn,Ge,Cu,Mn,etc.; X=I, Br, Cl) have been prepared and studied.[29–31] Most of these compounds have a layered Perovskite structure consisting of layers of MX_6 corner-sharing octahedra sandwiched between the organic alkylammonium spacers. Figure 2 shows the struc-

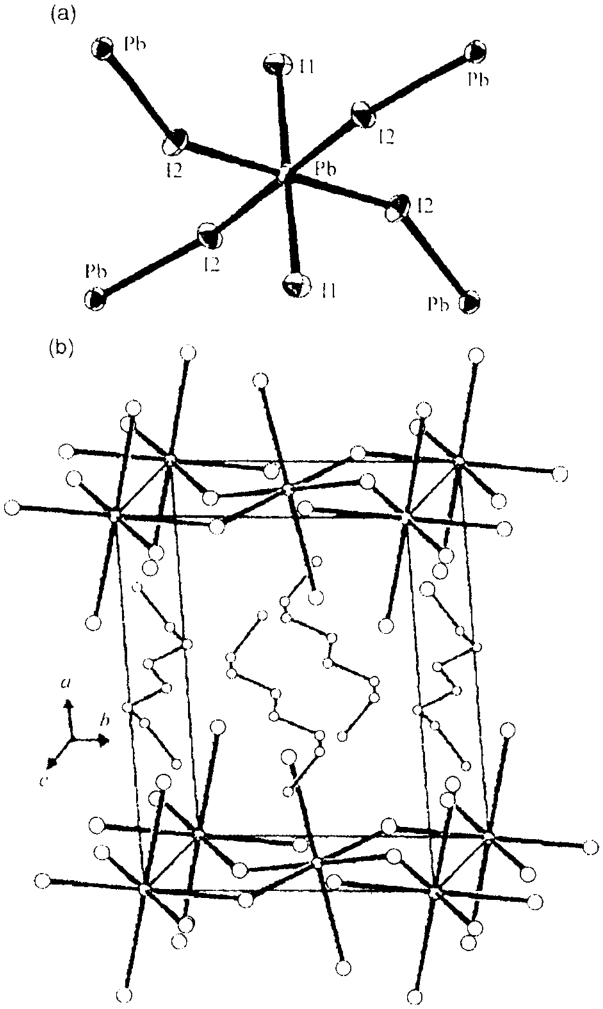


FIGURE 2

ture of the $(H_3N(CH_2)_6NH_3)[PbI_4]$ consisting of ordered perovskite sheets constructed from comer sharing PbI_6 octahedra, which alternate with the $H_3N(CH_2)_6NH_3$ sheets.

A series of organodiamine-molybdenum oxide composite materials are prepared and characterized.[32–37] By reaction of MoO_3 and $Cu(NO_3)$ and 4,4′-bpy at high temperature, porous material with pillared-layer structure with formula $[Cu(bpe)(MoO_4)]$ (bpe=1,2-bis(4-pyridyl)ethene) is synthesized. Figure 3 shows this structure. This structure is constructed by $\{Cu(bpe)\}^{+2}$ liner chains bridged though $\{MoO_4\}^{2+}$ tetrahedra into a 3D framework. In another word, each molybdenum group bridges three neighboring Cu atoms to produce bimetallic oxide layer and these layers are linked by bpe to form 3D pillared-layer framework.

Lamellar nanocomposites with conducting polymers are of interest in relation to novel properties that result from the molecular level interaction of the two dissimilar chemical components. These composites have been synthesized by various intercalative methods, such as (1) in situ redox intercalative polymerization, (2) monomer intercalation followed by polymerization, (3) encapsulative precipitation from solutions of exfoliated lamellar solids, and (4) other methods. Among these, method (1) is the most direct and least disturbs the crystalline structure of the host.[16] The reaction with the oxidizing hosts has been limited to FeOCl,[17] V_2O_5,[17] and $VOPO_4$.[18] Recently, $RuCl_3$ was utilized for the reaction,[16] which has a lamellar structure composed of hexagonal sheet of Ru atoms sandwiched between two hexagonal sheets of Cl atoms with ABC stacking. The reaction of acetonitrile solution of aniline with $RuCl_3$ causes intercalative redox polymerization to polyaniline (PANI) within the gallery space of $RuCl_3$. In the process of intercalation, a fraction of Ru^{3+} atoms is reduced to Ru^{2+}, resulting in a mixed valence compounds. The electric conductivity of $(PANI)_xRuCl_3$ at room temperature is 2 Scm^{-1}, 3 orders of magnitude higher than that of $RuCl_3$. This material is a hole conductor with a room temperature Seebeck coefficient of +22 μ V/K.

METAL COMPLEX-ASSEMBLED COMPOUNDS

Pillared-layer structures constructed by hydrogen bond and coordination bond

Metal complexes of 1,4-dihydroxy-benzoquinone and its homologues ($H_2C_6X_2O_4$) are reported.[38–40] The crystal structures have afforded a

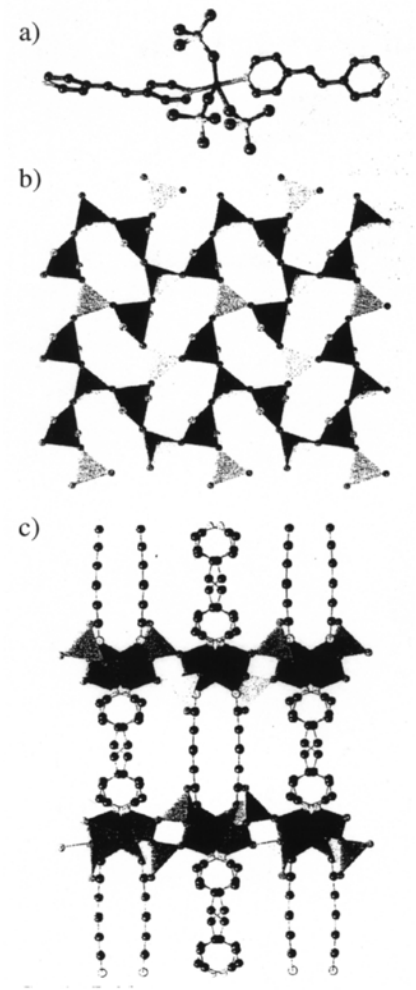


FIGURE 3

variety of frameworks together with voids. The frameworks are listed as chains, ladders, grids, honeycombs, and so on while voids are classified in cavities, channels and space between layers, illustrating an alternative of inorganic zeolites and clays. 1,4-Dihydroxy-benzoquinone derivatives and metal cations form 2D sheet and various guests are included interlayer space to form three dimensional pillared-layer structures.[41] There are two types of layers; one is composed of 1D coordination polymer motif of $[M(C_6X_2O_4)](H_2O)_2]_n$. These motifs are linked by hydrogen bond to form a sheet structure. Figure 4 shows a pillared layer structure, where phenazine molecules are incorporated regularly between the two sheets. The two nitrogen atoms of phenazine are utilized to form hydrogen bond with apically coordinated water molecules. Another layer is obtained from hydrogen bond link of monomeric motifs, $[M(C_6X_2O_4)_2(H_2O)]$. Similarly, phenazine molecules are regularly clathrated between the layers[42], which is well illustrated in Figure 4.

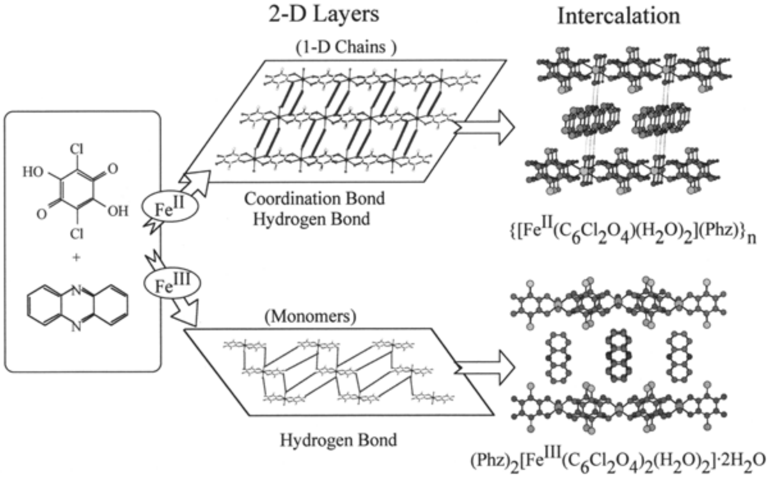


FIGURE 4

Pillared-layer structures constructed by coordination bond

A series of 3D coordination polymers with pillared-layer structure based on tricadmium carboxylates are synthesized by reaction of cadmium(II) perchlorate and 4-pyridinecarboxaldehyde in the presence of various guest molecules at hydro(solvo)thermal condition.[43] The structures of $[Cd6(isonicotinate)_{10}(H_2O)_2]$ in Figure 5 shows layer structure. Three

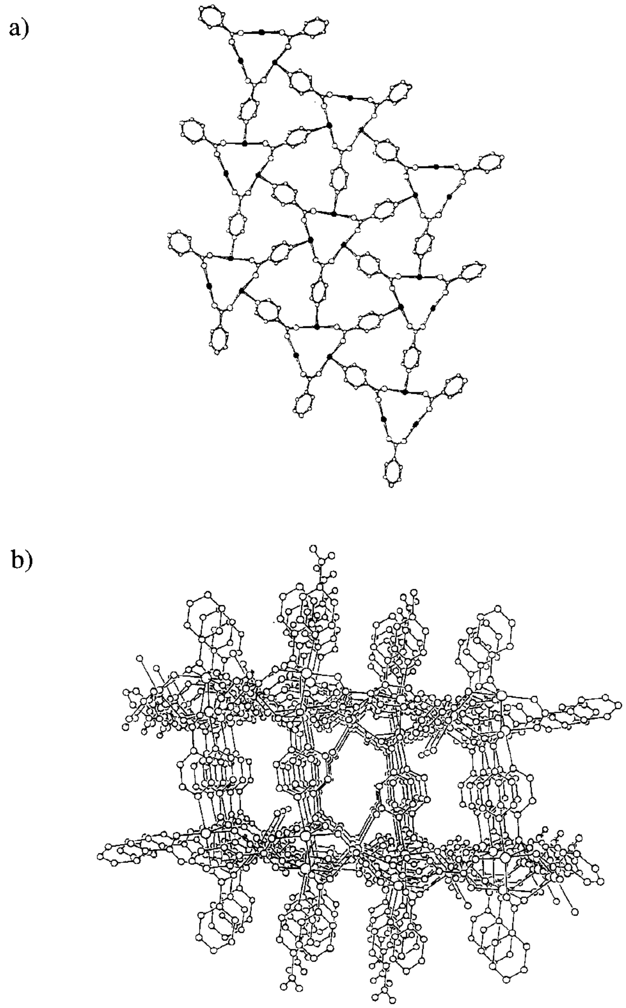


FIGURE 5

cadmium centers are bridged by the carboxylates to form a 2D infinite layer, and the other pyridine carboxylate bridges these sheets to form 3D pillared-layer structure.

This is a typical instance of pillared layer structures created from only one multifunctional ligand. In this context, the framework is characteristic of ligand. This synthesis is owed to a sort of serendipity. Therefore, modification of a pillared layer structure, such as pillar length, with the common framework maintained would face with great difficulties.

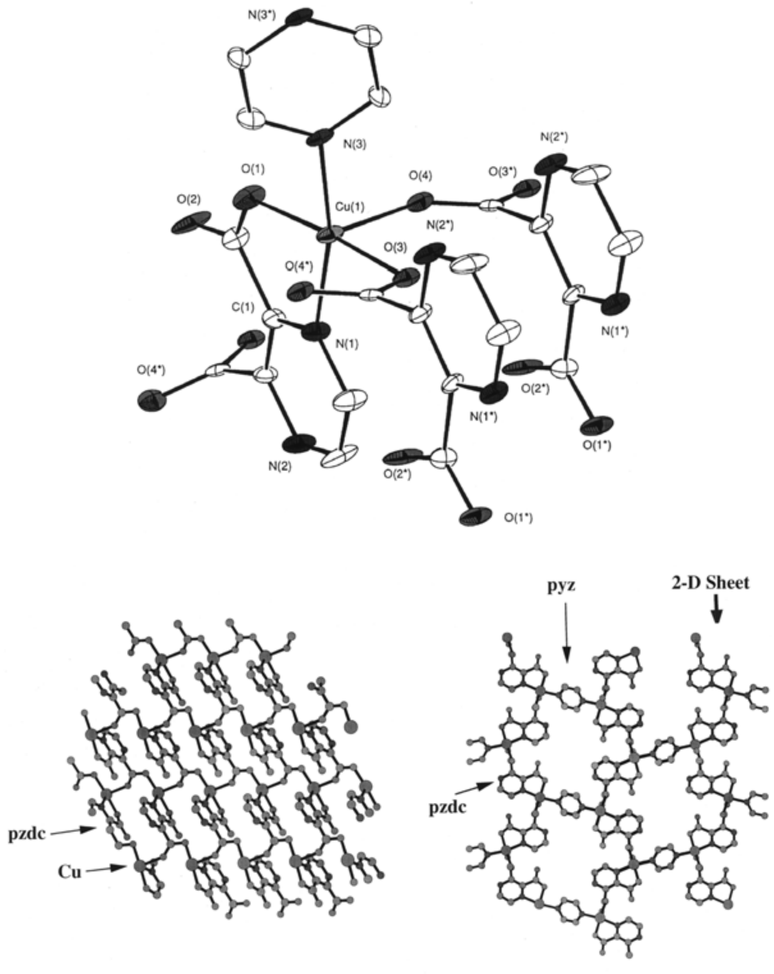
PILLARED-LAYER STRUCTURES FOR RATIONAL SYNTHESIS

$[Cu_2(pzdc)_3(L)]$ (pzdc=pyrazine-2,3-dicarboxylate; L = pyrazine(pyz), 4,4′-bipyrizine(bpy), 4-pyridylisonicotinamide(pia))

It has been demonstrated that the pillared-layer structure is effective for the systematic construction of 3D networks with large channels.[21] Although this type of network has been investigated in the hydrogen-bonded assembly[44] of organic molecules, the nature of the micropores in the absence of included guest molecules is far from robustness of framework.

In comparison, coordination networks can afford more stable structures. Very recently a new method for synthesis of stable pillared-layer structures has been developed by using coordination networks. In this system a series of channels with various shapes and functionalities could be created.[45] A common layer is constructed from copper ion and pyrazine-2,3- dicarboxylate (pzdc), and then pillar ligands interlink the layers to form $\{[Cu2(pzdc)2(pyrazine)]\cdot 2H_2O\}_n$ (**1**). The crystal structure of complex **1** is shown in Figure 6. Ligation of the three oxygen atoms of the carboxylate groupes, one nitrogen atom of pzdc, and one nitrogen atom of the pillar ligand form a distorted square pyramidal geometry around the Cu(II) atom. This module consists of a 2D sheet of $[Cu(pzdc)]_n$ and ligands that bridge each sheet as pillars. A pzdc molecules links the three Cu(II) atoms; one nitrogen atom from pzdc and one oxygen atom from the carboxylate group chelate with the Cu(II) atom while each oxygen atom of the other carboxylate group forms a monodentate ligand with two Cu(II) atoms. As a result, an extended neutral 2D sheet forms in the ac-plane (Figure 6a). The sheet has a puckered structure with a thickness of about 7.5 Å. This sheet has no proper cavities, preventing mutual interpenetration.

Coordination of the pyz ligands to the Cu(II) atoms provides a pillared-layer structure, in which each 2D sheet is separated by about 4 Å



b) View of the 2-D Sheet **c) View of the 3-D Structure**

FIGURE 6

(Figure 6c). Hereafter, we define the distance of the pore size as a value which is obtained by considering Van der Waals radii. Regulated arrangement of the pillar ligands along the a-axis with spacing of 11 Å creates extended channels along the c-axis with dimensions of about 4 × 6 Å. The size and chemical properties of the channel depend on various kinds of pillar ligands used, thus expected to be controllable. This new framework prompted us to construct coordination compounds with interesting channel properties in which sizes and chemical environments could be varied. For this purpose, two pillar ligands, 4,4′-bpy (bpy) and pyridylisonicotinamide (pia) were chosen; the former provides a large pore size, while the latter creates a large channel with specific hydrogen bonding site for guest molecules. These two complexes, $\{[Cu_2(pzdc)_2(bpy)\cdot 3H_2O]\}_n$ **2** and $\{[Cu_2(pzdc)_2(pia)]\cdot 5H_2O\}_n$ **3**, were successfully synthesized by using procedure similar to that of **1**, and obtained as microcrystals. The formation of similar pillared-layer networks was confirmed by elemental analyses and XRPD patterns. The XRPD pattern is shown in Figure 7. The shifts of the (0 n 0) reflections demonstrate the elongated b-axes of **2** (29.0 Å) and 3 (32.6 Å) compared with that of **1** (19.849Å). These observations are in agreement with the expected elongation of the corresponding pillar ligands (Figure 8). From these results the channel dimensions of **2** and **3** are estimated to be about 8 × 6 Å and 11 × 6 Å, respectively.

The utilization of these microchannels requires robust nature of the frameworks. For this purpose, three dimensionally linked coordination framework is prerequisite. Therefore, pillared-layer coordination polymers are most relevant. In order to judge whether or not the framework is robust, there are two experimental requirements, both of which are simultaneously to be satisfied: (1) Thermogravimetric analysis (TG). When guest molecules are removed at a certain temperature range, no weight loss should be observed. However, we cannot say that a framework is robust only on the basis of TG results because deformation of the framework often affords no TG change. Therefore, the following measurement is necessary. (2) Powder X-ray analysis (XRPD pattern). If the structure is robust, XRPD pattern of the polymer with no guests should be sharp enough and essentially the same as that of with guests. A typical example which attains the two requirements is $[Co_2(4,4'\text{-bpy})_3(NO_3)_2]$, so called Tongue-and-Groove structure (Figure 9).[46] This compound gives stable and robust structure. A XRPD analysis has been done carefully, indicating no structural change. This is not a pillared-layer structure but a double layer, whose structure is tightly constructed by interlocking with interdigitation of the double layers. Single crystal X-ray diffraction for isostructural compound demonstrated that lattice constants a, b and c, are all unaltered up to 110 °C ever without guest molecules.[47]

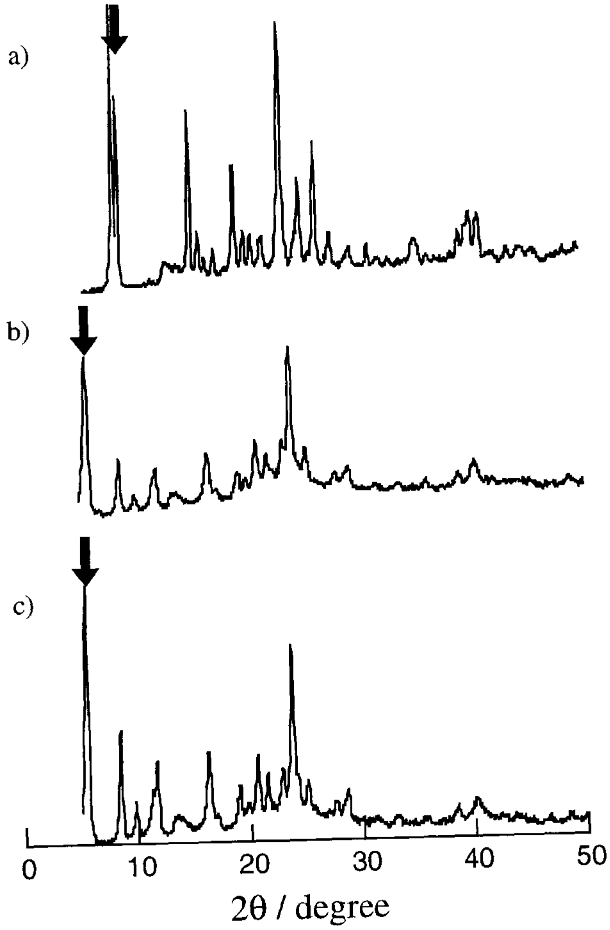


FIGURE 7

For compounds **1–3** no chemical decomposition was observed between 100 °C and 260 °C in thermogravimetric analysis. In addition, by measuring the XRPD pattern at 100 °C under reduced pressure, the porous network is proved to be retained in this phase, indicating that the porosity is retained in the absence of the included guest molecules.

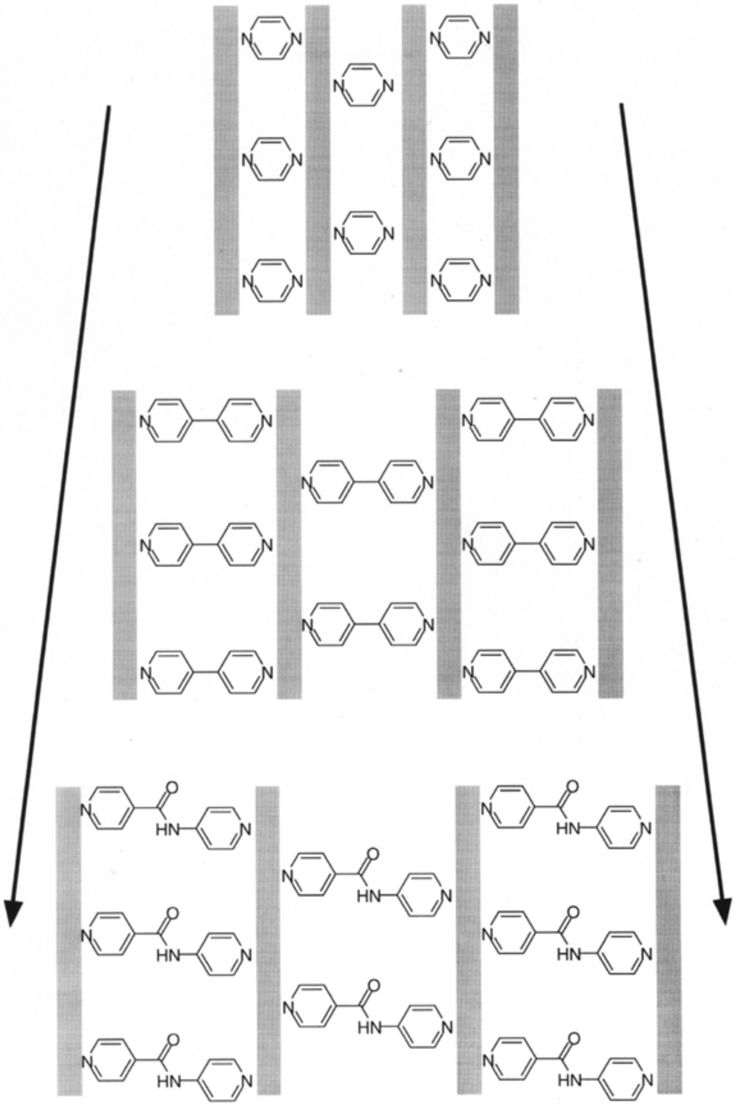


FIGURE 8

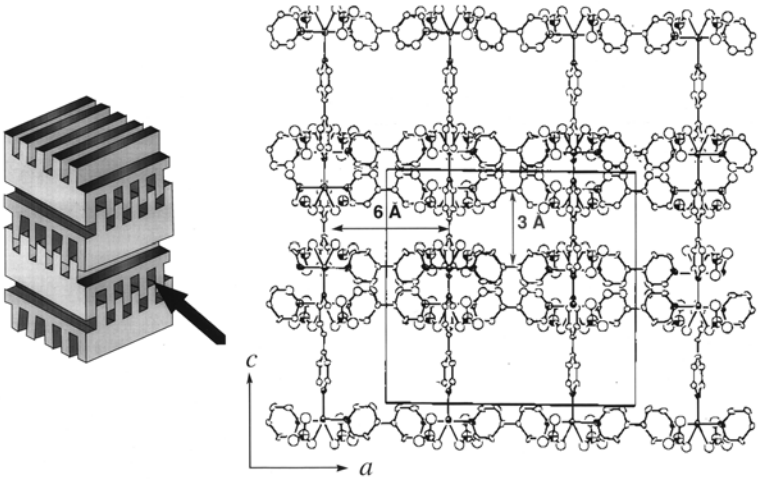


FIGURE 9

$[Cu(4,4'\text{-bpy})(SiF_6)]$

Although a number of porous coordination polymers have been hitherto synthesized, still lacking are examples of coordination polymers providing useful channels which are so robust that the coordination framework is stably maintained even under a wide pressure region at ambient temperature. In addition, since nature dislikes vacuum, aim at preparation of a large channel faces with difficulties; (1) counter anions often occupy channel, (2) an interpenetrating network is readily formed, and (3) a channel network is broken down on removal of guest molecules. Therefore, development of the rational synthesis to overcome the three difficulties is the most significant for creation of useful porous materials. Generally, when water or other solvent molecules coordinate to metal ions, resulting networks are essentially low dimensional and often afford no channels. In order to prepare a higher dimensional framework, increase in the number of coordination sites, which are available for linking ligands, is important. In octahedral metal complexes, water or counter anions tend to coordinate the metal atom, resulting in the reduction of coordination sites for linking ligands. If we can set the coordination environment such that solvent molecules and counter anions

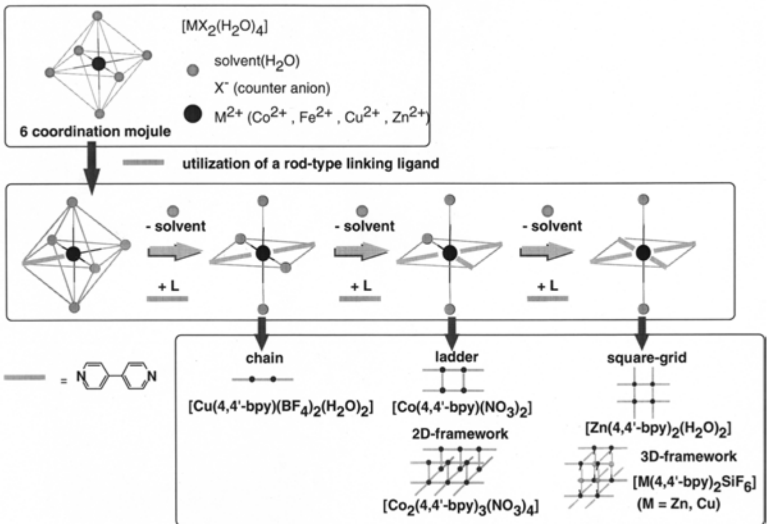


FIGURE 10

dissociate in an octahedral metal ion, all the six sites could be used for 3D frameworks. This is illustrated in Figure 10 by use of 4,4′-bipyridine. If the two sites are available, a linear chain of [Cu(4,4′-bpy)(BF_4)(H_2O)][48] forms. In the case of three sites, 1D ladder, [Co(4,4′-bpy)(NO_3)$_2$][49], or 2D sheet, [Co_2(4,4′-bpy)$_3$(NO_3)$_4$][50], are obtained. A square grid of [Zn(4,4′-bpy)$_2$(H_2O)$_2$][51] tends to form with interpenetration. The 3D [Zn(4,4′-bpy)$_2$(SiF_6)][52] was successfully obtained only under the critical anhydrous condition. We chose Cu(II) ion and SiF_6 dianion as the building blocks for construction of a 3D porous coordination polymer. The Cu(II) ion (d^9) is liable to undergoes Jahn-Teller distortion, affording weak coordination sites in the axial positions and consequently, the dianionic SiF_6 can coordinate to the Cu(II) ion more easily than water or other solvent. Since the SiF_6 dianion can link the copper units sitting in the nearest-neighbor square-grid layers, the resulting 3D framework is expected to be robust and free from the occupation of channels by free counter anions. X-ray analysis of **4**·8H20 clearly demonstrates the 3D network based on a square grid of [Cu(4,4′-bpy)$_2$]n and a pillar anion of SiF_6.[53] Figure 11 shows the coordination environment of the Cu(II) ion. Four pyridine nitrogen atoms of 4,4′-bpy are coordinated to the Cu(II) ion. Association of two F atoms of the SiF_6 anions provides a (4+2) environment. Bridging the Cu(II) ions by 4,4′-bpy affords a 2D network of square grids. The layers are linked with SiF_6 anions by coordination bond to give a 3D structure without interpenetration. This network provides channels with dimensions of ca. 8 Å × 8 Å along the c-axis and ca. 8 Å × 4 Å along the a- and b-axes, as shown in Figures 12(a) and 12(b), respectively. The channel is filled with eight crystallization H_2O molecules per Cu(II) ion. In this crystal, there are two kinds of H_2O molecules. One coordinates directly to F atoms of SiF_6 dianion by hydrogen bonds, and the other is linked by former H_2O molecules by hydrogen bonds, resulting in an 8-membered ring. These rings are located in SiF_6 layers and not $Cu(4,4'\text{-bpy})_2$ layers, because of the preference of hydrophilic environment. The similar network has been obtained for Zn(II), the compound $[Zn(4,4'\text{-bpy})2(SiF_6)]_n$,[52] was synthesized from dimethyl formamide/dioxane solution media. On the other hand, it has been previously reported that $\{[Zn(4,4'\text{-bpy})_2(H_2O)_2]SiF_6\}_n$,[54] which affords interpenetration of 2D $[Zn(4,4'\text{-bpy})_2(H_2O)_2]_n$ sheets, resulting in no channels, was isolated from an aqueous media containing $ZnSiF_6$ and 4,4′-bpy. Similarly, the reaction of $ZnSiF_6$ with 4,4′-azopyridine, whose length is longer than 4,4′-bpy, in $EtOH/CH_2Cl_2$ media yields the similar interpenetration network, $\{[Zn(4,4'\text{-bpy})_2(H_2O)_2]SiF_6H_2O\}_n$.[55] The framework in Zn(II) is sensitive to the solvent used, in particular water. This propensity is well illustrated in Figure 10.

Porous Properties of Pillared Layer Complexes

In order to examine the porous functionality of these synthetic materials, their methane adsorption capabilities were measured. Gas adsorption activity is one of the most attractive properties of porous materials such as zeolites. Generally, porous nature has been examine by nitrogen or argon as a probe under low pressure at their liquefied temperature. At low temperature, frameworks could happen to be retained even though they collapse at ambient temperature without guest molecules. For practical use, the examination of porous nature at high pressure and ambient temperature is necessary. Figure 13 reveals the results of the adsorption

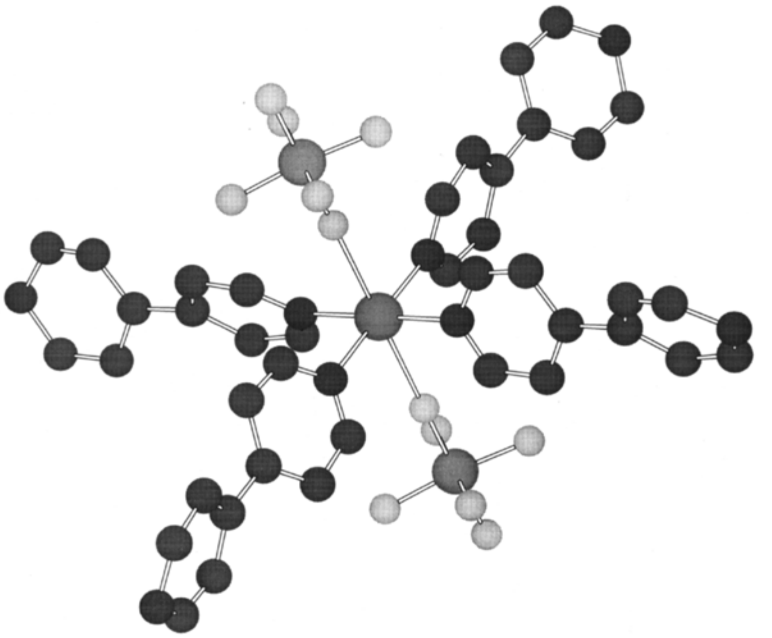
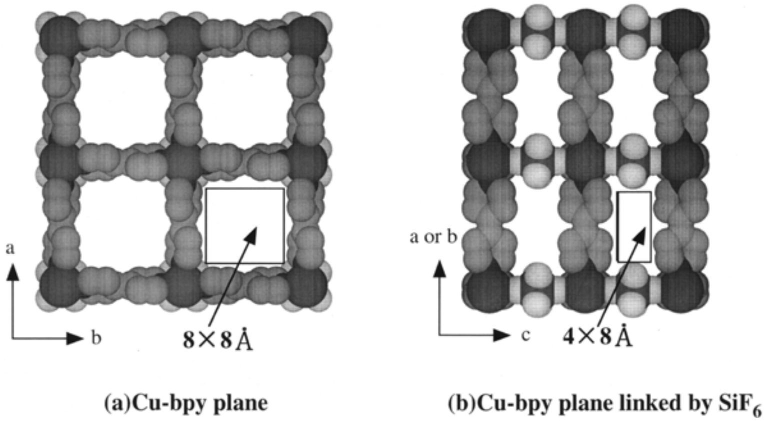


FIGURE 11



(a)Cu-bpy plane

(b)Cu-bpy plane linked by SiF_6

FIGURE 12

activity experiments of anhydrous complexes **1, 2** and **3**, obtained by drying under vacuum with methane in the range 1 to 31 atm. A rapid increase in the amount of adsorbed gas is shown by an increase in pressure of up to 5 atm, which represents the diffusion of the methane into the channels. These isotherms are of type I according to IUPAC classification.[56] The increased methane adsorption activity for **2** and **3** compared to **1** corresponds to the larger channel sizes of these complexes. This activity is comparable to that of zeolites.

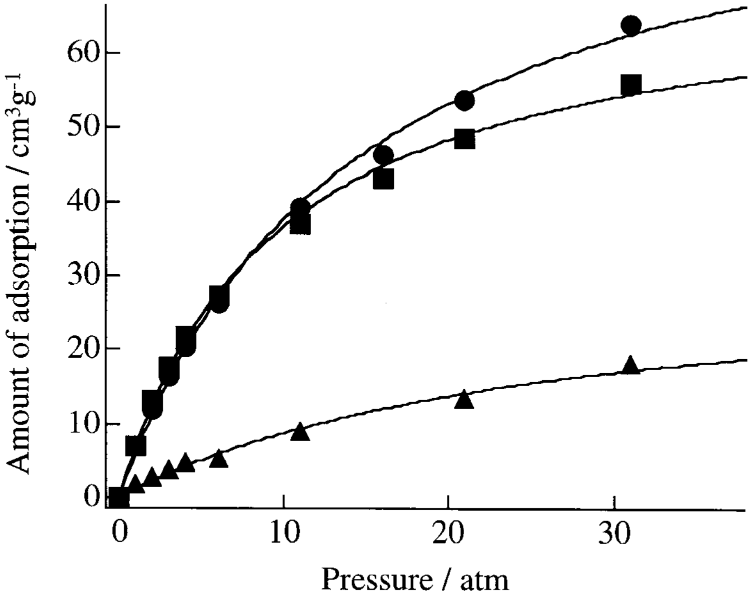


FIGURE 13

In compound **4**, the surface area, pore size distribution and micropore volume were calculated from argon gas adsorption at 873 K measured with a volumetric adsorption apparatus according to the BET equation and Horvath-Kawazoe (HK) method,[57] respectively. The differential pore volume plot, represented by the HK method, shows only one sharp peak at ca 7.8 Å as shown in Figure 14. This result reveals that this complex provides the same square pore (8 Å × 8 Å) as the result of the X-ray

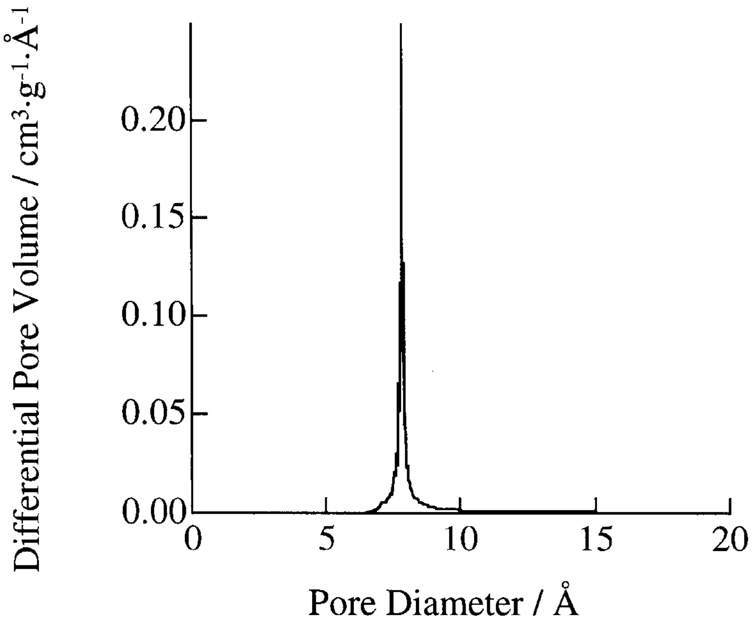


FIGURE 14

analysis. The argon molecules cannot pass through the rectangular pore (8 Å × 4 Å) at 87.3 K because of the larger diameter of argon. The micropore volume and specific surface area on the basis of argon adsorption is calculated to be 0.56 mLg^{-1} and 1337 m^2g^{-1}.

The methane adsorption experiment was also carried out on zeolite 5A, which has the highest known methane adsorption capacity. Figure 15 shows the isotherms for methane adsorption in the pressure range between 0 and 36 atm at 298 K. Desorption/re-adsorption experiments for 4 trace the same isotherm, indicating that the channel structures are retained throughout this process. At 36 atm, the density of methane adsorbed in 4 for micropore volume is 0.21 gmL^{-1}. The methane density of the compressed gas (0.16 gml^{-1}) at 300 K and 280 atm is almost the same as that of 4 at 298 K and 36 atm, indicative of a concentration effect from strong micropore filling in the channelling cavities.

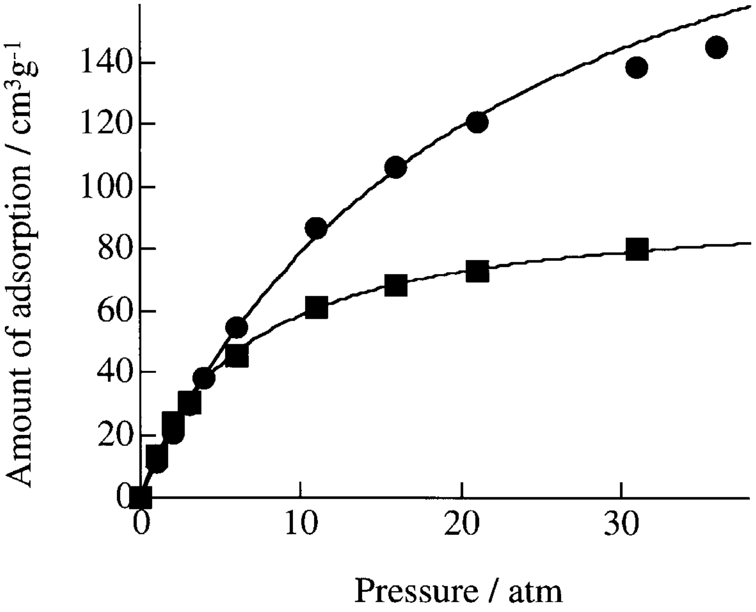


FIGURE 15

The high-pressure adsorption of supercritical methane in the micropore field has been studied with the following extended Dubinin-Radushkevich (DR) equation:[58–59]

$$[\ln(W_L/W)]^{1/2} = (RT/bE_0)(\ln P_{0q} - \ln P) \qquad (1)$$

Here the parameters, W, bE_0, P_{0q} are the amount of adsorption at a pressure P, the adsorption energy, and the saturated vapor pressure of the quasi-vaporized supercritical methane, respectively. The large inherent micropore volume, W_L, of 10.0 $mmolg^{-1}$ is obtained from the Langmuir plot. This isotherm is well explained by this DR equation. The methane adsorption quantity at high pressure (ca. 6.5 $mmolg^{-1}$ at 36 atm) is much larger than that of zeolite 5A (ca. 3.7 $mmolg^{-1}$ at 36 atm). The obtained parameters, bE_0 ($kJmol^{-1}$) and P_{0q} (atm), are 8 and 284, respectively. The value of bE_0 is a typical one about a physical adsorption of methane into microporous materials. Table II summarizes all the parameters to estimate porous properties for pillared layer type complexes as far as we concern.[60] In conclusion, this material has the highest adsorption ability of any reported porous coordination polymer and opens up a new dimension for the study of adsorbents of inorganic-organic hybrid materials based on coordination polymers.

TABLE II

		W[cc/g]	*bE0[kJ/mol]*	*P0q[atm]*	*suface area*
1	$[Cu_2(pzdc)_2(pyr)]_n$	34.3	7.4	348	571^a
2	$[Cu_2(pzdc)_2(bpy)]_n$	71.2	8.4	168	845^a
3	$[Cu_2(pzdc)_2(pia)]_n$	91.4	8.4	251	–
4	$[CuSiF_6(bpy)_2]_n$	225.4	7.8	249	1337

a. reference 60 (J. Phys. Chem. 2000, 104, 8940).

FUTURE PROSPECT

Large Channel

To perform the host-guest chemistry using porous coordination polymers, large channel size enough to include various guest molecules is indispensable. Particularly, catalytic action is one of our goals, the dimension about 20 Å × 20 Å channel is desired to ensure enough space to carry out reaction and to diffuse reactant and product molecules effectively in the channel. However, when we try to construct larger channel using long bridging ligands, an interpenetrated structure preferentially forms and results in small channel and poor porosity. This problem prevents us to construct large channel. Recently a large square grid network without interpenetration is synthesized by reaction of $Ni(NO_3)$ and 4,4′-biprydylbiphenyl in MeOH and o-xylene.[61] It was shown that large grid sheet structure without interpenetration could be built by using appropriate template molecules, together with stronger layer-layer interaction. To construct large channel without interpenetration would be one of key view point in this field.

Pillar Functionalities

Molecules forming a channel surface, which could interact with guest molecules, are very important for controlling inclusion properties because the confined guest molecules intimately interact not only with themselves but also the surface molecules and/or ions. For example, the channel of coordination polymer (**1, 2** and **4**) containing pyridine affords hydrophobic space while that of pyridylnicotineamide provides hydrogen bonding donor (NH) and acceptor (C=O). These two porous polymers would show different inclusion property for non-polar polar molecules or molecules with hydrogen bond capability. Therefore, modification of porous host surface with multifunctional molecules would produce a novel porous coordination polymer, which reveals selective formation of specific assembly of guest molecules, activating of guests, and so on. Moreover introducing of coordinatively unsaturated metal sites into channels enables us to expect highly reactive system.

In order to control not only channel size and shape but also chemical properties, rationally designed and realized porous frameworks are very important, therefore pillared layer compounds discussed in this article are promising for the next generation system.[62]

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