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Accounts

Functional Micropore Chemistry of Crystalline Metal Complex-Assembled Compounds

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Syntheses of new porous frameworks with specific pore size and type are of considerable interest for the appearance of zeolite-like functionalities. It is useful to take advantage of metal complex-assembled compounds because of designable frameworks, high microporosity, and flexible frameworks based on a variety of coordination geometries of metal centers and multifunctionality of bridging organic parts. Many recent reports show that the synthesis procedures are developing from serendipitious to rational level. Therefore, the micropore chemistry of metal complex-based assemblages is directed toward not only new frameworks but also functionalities such as gas and small molecule adsorption, ion exchange, heterogeneous catalysis, photo-chemical and -physical properties. For chemical and physical functionalities robustness of a framework is required even in the absence of guest molecules in the cavity. The stability is largely dependent on the structural dimensionality of the assemblages. A wide variety of structures of metal complex-based assemblages are listed and recent findings in this functional chemistry are described.

A great deal of interest in transition metal complex-assemblages has recently been devoted to the development of rational synthetic routes to novel two- and three-dimensional crystal frameworks, due to their potential applications in many areas. The molecule-based crystal is characteristic of the assemblage, dissimilar to inorganic assemblage, and types of the solid structures range from naturally-occurring mineral to artificial novel ones. This is ascribed to a variety of coordination geometries of building blocks.[1,2] The coordination number varies from two to seven coordinate depending on the transition metal element and the oxidation state. The number less than 4 is found in the group 10 and 11 element compounds, in particular, two-coordinate form is characteristic of group 11 metal(I) compounds. The number 6 widely occurs in the transition metal compounds of groups 4 to 9. In addition to the metal complex geometry, functionality of an organic ligand as a connector is essential for the formation of network structures and therefore the multibonding capacity regarding coordination, hydrogen bondings, and attractive π-stacking is necessary to designing and tuning crystal structures.

In this review, we focus our interest mainly on coordination polymers. The spatial dimensionality is an important factor to understand polymer structures and crystal lattices. The dimensionality is defined as the spatial structure of polymer backbone built by coordination bonds (Fig. 1). The pendant types are not mentioned in this review. Figure 2 exhibits the distribution and occurrence of low-dimensional structures. One- and two-dimensional complexes cover most of the polymers. There are two ways to realize high dimensionality by cross-linking of low-dimensional polymer motifs,

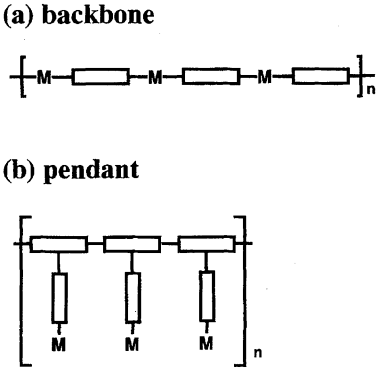

Fig. 1. Types of coordination polymers regarding role of metal ions. (a) Metal ions are incorporated in backbone, and (b) metal complex units are attached to the backbone as pendants.

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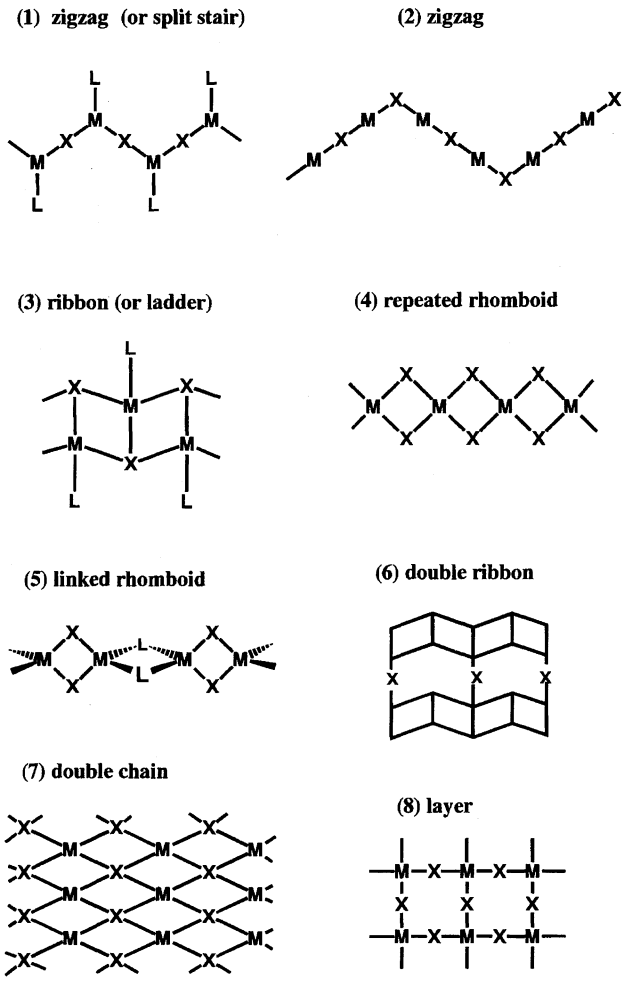

Fig. 2. One-((1)–(5)) and two-((6)–(8)) dimensional polymer frameworks.

respectively. One is to use coordination bonds, by which transition metal ions in chains or sheets are linked. In this case, at least two multi-coordination sites of ligands are used. The other is to utilize attractive interactions such as hydrogen bonding and aromatic stacking. In this context, functionality in bonding of the ligands is a very important factor. There are many linking ligands used for polymers. Halide, CN^-, and SCN^- anions are representative of simple ones, while carboxylates and diazines are organic-type ligands. The ligands which appear in this manuscript are listed in Fig. 3 with their linking abilities. The concept of crystal engineering[2—9] has in recent years provided numerous examples of rationally designed, from one- to three-dimensional, polymeric structures. Of particular potential interest in inclusion chemistry are two- and three-dimensional coordination polymers, which can be designed to have very specific pore sizes and types. These compounds can form porous structures with channels that are potentially tunable by choosing unit sizes or functionalities of building block.

In the following paragraphs, we survey open inorganic and organic frameworks and then various open metal-organic frameworks constructed by molecular building block approaches. Most of the compounds are associated with structural beauty such as artificial metalo-organic compounds. Some of the compounds show zeolite-like attributes,[10] and others reveal optical, electric and magnetic properties. The functional chemistry of microporous metal-organic materials will begin to emerge in a few years.

Microporous inorganic compounds, zeolites, as well as aluminum phosphates and its derivatives, are used extensively in separation science, in heterogeneous catalysis, in nonlinear optics and electro devices, and in ship in bottle synthesis.[10—14] Three-dimensional porous structures of zeolites are tightly held after removals of the crystalline water solvents included within the pores. Most of the traditional and advanced applications for zeolites are based on the ability of these open crystalline structures to selectively incorporate and exchange both charged and neutral species within the void spaces and interconnecting channels on a molecular scale. Depending on the type of connection between tetrahedral building blocks, linear or pseudo-linear channels are formed with diameters ranging from 4.2 to 7.4 Å. In other structural types, cages are formed with diameters of 6.4 to 12 Å and window sizes from 2.3 Å (6-ring) to 13 Å (18-ring).

Organic molecules provide polymeric structures by covalent bonds, however, there is a significant barrier in crystallization. Recently, many researchers have taken advantage of hydrogen-bonded networks to restrict relative orientation of molecules, capable of crystallization.[5,6,15—23] The compounds, H_4adb and tdtp, form hydrogen-bonded network, whose cavities are capable of crystalline-phase guest-addition, -removal, and exchange, are demonstrated.[17,24] Antracene-bisresorcinol compound, H_4adb, forms molecular sheets, **1**, consisting of hydrogen-bonded homopolymeric chains of resorcinol together with anthracene stack columns having a face-to-face distance of 12—13 Å; large supramolecular cavities left are occupied by two solvent molecules as guests via hydrogen bonding.[8] Crystallization of tdtp generates porous inclusion compounds, **2**, in which each tdtp is held in position by 16 intermolecular hydrogen bonds, thereby creating a three-dimensional network so robust that it remains ordered even when most of the guests are removed.[17]

I. Porous Coordination Compounds

The building-block approach has been utilized for the rational assembly of coordination compounds. In the case of coordination polymers, many researchers have proposed a strategy in the design of new porous crystal phases, which are assembled from suitable metal centers and organic molecules of different nature and size. A family of metal-bridging building blocks containing 4-pyridyl donors has often been used. For instance, the rod-like type 2-connector, 4,4′-bpy, affords a wide variety of assembled structures with transition metal ions; these are summarized schematically in Fig. 4.

The first basic polymeric structure in 4,4′-bpy complexes is one-dimensional infinite chains. Zig-zag chain structures are found in $\{[Cu(2,2'\text{-bpy})(4,4'\text{-bpy})(ClO_4)_2]\}$ (**3**),[25,26] $[\{Cu(tta)(4,4'\text{-bpy})]\}$ (**4**),[27] $\{[Cu(4,4'\text{-bpy})(CH_3CN)_2]\cdot BF_4\}$ (**5**),[28] $\{[Cu_2(NO_3)_2((C_6H_5)_3P)_2(4,4'$-

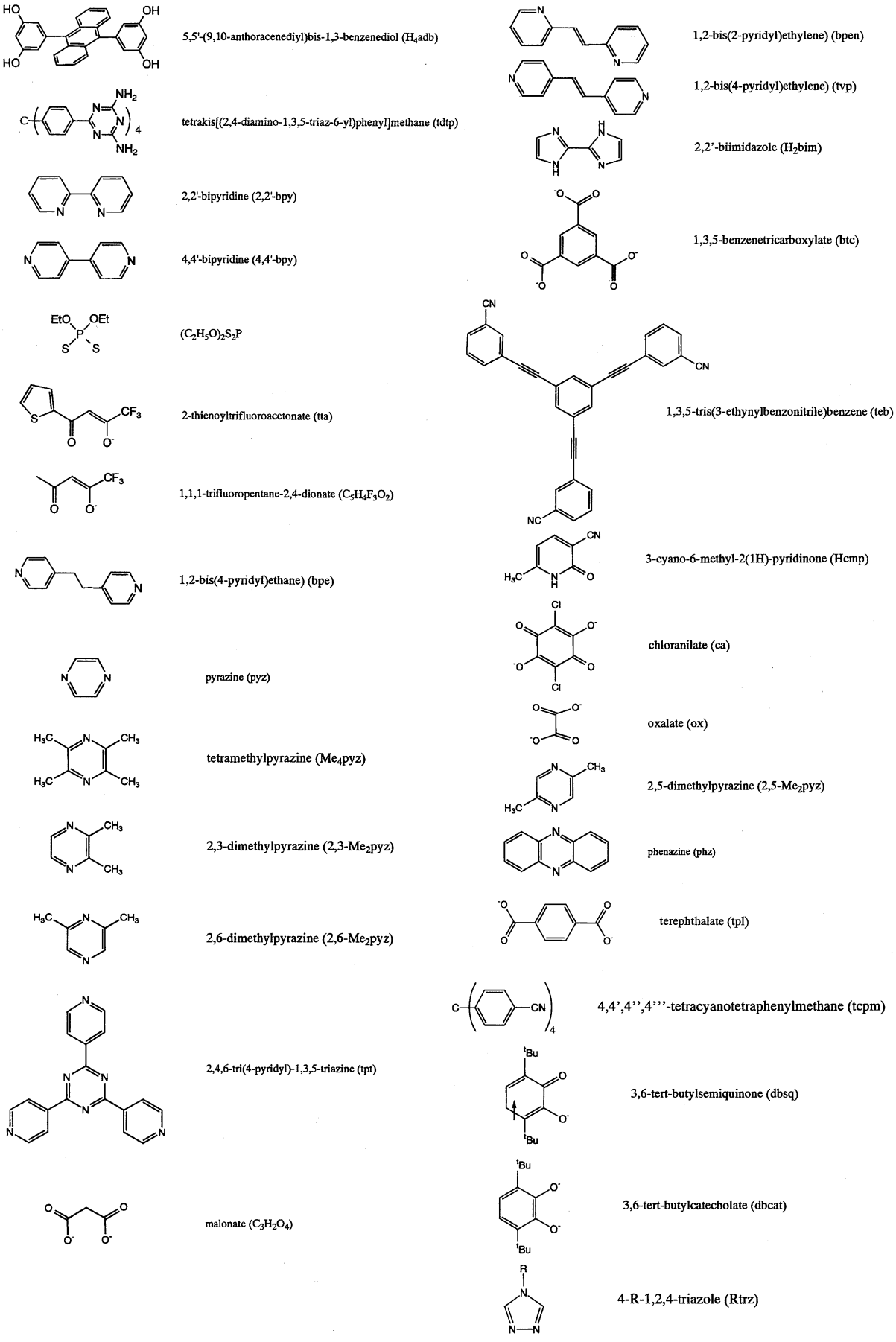

Fig. 3. Linking ligands mentioned in this article. Abbreviations are used in the text.

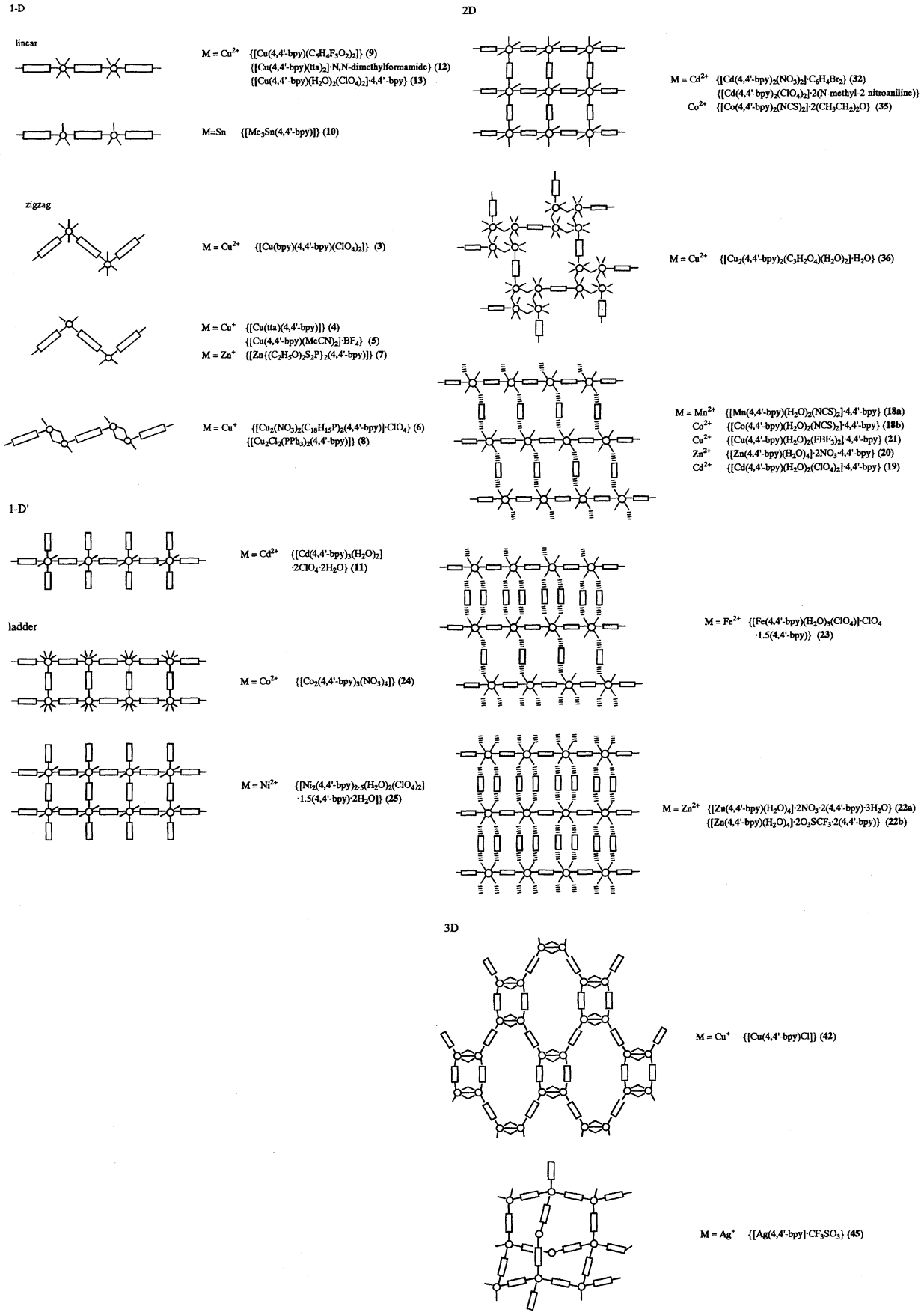

Fig. 4. Schematic structures of coordination polymers of 4,4′-bpy. Open circle and rectangle shape show metal ion and 4,4′-bpy, respectively. Bold and dashed lines denote coordinate bond and hydrogen bond, respectively.

bpy)]} (**6**),[29] {[Zn((C$_2$H$_5$O)$_2$S$_2$P)$_2$(4,4′-bpy)]} (**7**),[30] and {[(Cu$_2$Cl$_2$)(PPh$_3$)$_2$(4,4′-bpy)]} (**8**).[31] Straight chain structures are also obtained for {[Cu(4,4′-bpy)(C$_5$H$_4$F$_3$O$_2$)]} (**9**),[32] {[(CH$_3$)$_3$Sn(4,4′-bpy)]} (**10**),[33] {[Cd(4,4′-bpy)$_3$(H$_2$O)$_2$]·2ClO$_4$·2H$_2$O} (**11**),[34] {[Cu(4,4′-bpy)(tta)$_2$]·*N*,*N*-dimethylformamide} (**12**),[35] and {[Cu(4,4′-bpy)(H$_2$O)$_2$(ClO$_4$)$_2$]·4,4′-bpy} (**13**).[36] From one-dimensional chains, composite compounds with polyoxomolybdates form, such as {[Cu(4,4′-bpy)$_4$]·Mo$_8$O$_{26}$} (**14**), {[Ni(H$_2$O)$_2$(4,4′-bpy)$_2$]$_2$·Mo$_8$O$_{26}$} (**15**), and {[[Cu(4,4′-bpy)]$_4$·Mo$_{15}$O$_{47}$]·8H$_2$O]} (**16**),[37] Cubane-like molecules, [M(CO)$_3$(μ_3-OH)]$_4$ (M = Mn and Re),[38] are linked with 1,3-diaminopropane, hexamethylenetetraamine and 4,4′-bpy (**17**), respectively, by hydrogen-bonds to afford cavity spaces, which contain solvent molecules.

I-1. Cavities. Microporous cavities are generated by linking straight chains with a repeating unit {M–(4,4′-bpy)–M}. The first group of the compounds shows a structure linked by hydrogen bonds between metal-free 4,4′-bpy and coordinated water molecules; {[M(NCS)$_2$(H$_2$O)$_2$(4,4′-bpy)]·4,4′-bpy} (**18**) (M = Mn[39] and Co[40]), {[Cd(4,4′-bpy)(H$_2$O)$_2$(ClO$_4$)$_2$]·4,4′-bpy} (**19**),[34] {[Zn(4,4′-bpy)(H$_2$O)$_4$]·4,4′-bpy} (**20**),[41] and {[Cu(H$_2$O)$_2$(4,4′-bpy)(BF$_4$)$_2$]·4,4′-bpy} (**21**)[42] show that the metal atoms are linked by M–(4,4′-bpy)–M and M–OH$_2$···(4,4′-bpy)···H$_2$O–M assemblies, involving coordinated and hydrogen bonded 4,4′-bpy, respectively, to form two-dimensional rectangular grid sheets. The rectangular cavity of **21** has a dimension of 11.08×14.95 Å, accommodating two anions from neighboring sheets.[42] Another type of network, {[Zn(4,4′-bpy)(H$_2$O)$_4$]·2(4,4′-bpy)}$^{2+}$ (**22**) and {[Fe(4,4′-bpy)(H$_2$O)$_3$(ClO$_4$)]·ClO$_4$·1.5(4,4′-bpy)} (**23**), is obtained by hydrogen bond cross-linkage of [M(4,4′-bpy)] which generates two-dimensional layers of rhombic meshes of the dimensions of 11.29—11.44 Å and 15.08—15.78 Å for coordination and hydrogen bond parts, respectively.[41]

The coordination bond bridge of 4,4′-bpy between linear chains also occurs in [Co$_2$(4,4′-bpy)$_3$(NO$_3$)$_4$] (**24**), which shows a ladder structure of square cavities with dimensions of 11.4×11.4 Å.[43] The cavities clathrating CH$_3$CN or CHCl$_3$ form microchannels in the crystal, providing columns of chloroform molecules running through the cavities. The large cavity can be generated by using *anti*-1,2-bis(4-pyridyl)ethane (*anti*-bpe).[44] Under the presence of ferrocene was obtained another supramolecular isomer, which comprises bilayer of linear chains formed by two *anti* ligands that bridge Co(II) moieties. The bilayers contain channels filled with CH$_3$CN. {[Ni(4,4′-bpy)$_{2.5}$(H$_2$O)$_2$(ClO$_4$)$_2$]·1.5(4,4′-bpy)·2H$_2$O} (**25**) has a non-interpenetrated railroadlike network,[45] an analog of a ladder structure, with cavities of 11×11 Å dimensions, where hydrogen-bonded hydrated anions and 4,4′-bpy guest molecules are included. The railroad-like chains give sheet structures by using π–π interactions of the terminal 4,4′-bpy, resulting in the formation of a one-dimensional channel having 11×11 Å dimensions. The partially dehydrated solid shows anion exchange from ClO$_4^-$ to PF$_6^-$ when the sample was immersed in an aqueous NaPF$_6$ solution.

Substituents of the linking ligand are relevant in controlling the crystal structures. Pyz is a simple two-connector ligand for low-dimensional compounds. The substituents well illustrate the control of crystal structures. For instance, many infinite chain copper(II) compounds have been synthesized.[46—52] Recently, several copper(I) coordination polymers have been isolated and characterized by X-ray crystallography. Interestingly, the geometries of the copper atoms and the dimensionality of polymer modes affect the microporous structure of the solids.[1] Me$_4$pyz provides a linear chain structure (**26**),[53] while a two-dimensional structure (**27**) is built from hexagonal motifs of Cu$_6$(2,3-Me$_2$pyz)$_6$.[47] Polymer frameworks can be controlled by the pyrazine substituents. Two types of hexagonal arrays are constituted from planar and chair-like Cu$_6$ motifs, respectively.[53,54] {[Cu$_2$(pyz)$_3$(CH$_3$CN)$_2$]·2PF$_6$·C$_3$H$_6$O} (**28**) has a cationic infinite two-dimensional sheet with a chair-type cyclohexane-like Cu$_6$ motif (Fig. 5). The Cu–Cu distance of the two copper atoms linked by pyz is ca. 6.8 Å, and the mutually-confronted two pyrazines on the sides of the hexagon are parallel to each other, providing a large cavity of hexanuclear copper atoms. Interestingly, as in Fig. 5 an acetone molecule is included in each cavity, while the counteranions, PF$_6^-$, are placed above the sides of the cavity. The cationic and anionic layers are alternatively arranged. The distance between the nearest-neighbor cationic sheets, interrupted by the PF$_6^-$ anions, is more than 8 Å. 2,6-Me$_2$pyz affords an array of planar Cu$_6$ hexagons of {[Cu$_2$(2,6-Me$_2$pyz)$_3$]·2ClO$_4$·2C$_3$H$_6$O}

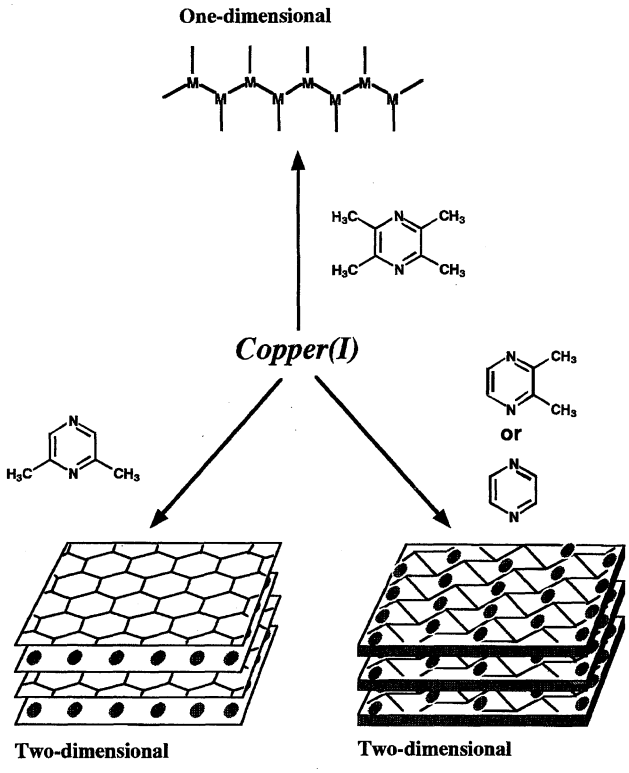

Fig. 5. Effect of substituent of pyrazine on crystal framework. The bold lines in the figures denote pyrazine molecules. The circles show acetone molecules.

(**29**) as shown in Fig. 5.[1] The copper atom has a Y-shaped form with three nitrogen atoms, but the environment is different because of the two non-identical nitrogen donors of 2,6-Me_2pyz. The Cu_6 motif is constructed by the alternating arrangement of the two different copper moieties. The distances between the two copper atoms linked by a 2,6-Me_2pyz range from 6.710(2) to 6.743(2) Å. The two mutually-confronted pyrazines on the sides of the hexagon are sitting out of the plane and are parallel to each other, providing a large cavity of hexanuclear copper atoms. As in Fig. 5, acetone molecules are not included in the cavities but placed over cavities, dissimilar to the case of **28**, while the counter anions, ClO_4^-, are placed above the sides. Thus the crystal structure is described as an alternation of acetone-perchlorate layers and flat copper(I) polymer layers. The distance between the neighboring copper layers is ca. 6.5 Å.

Coordination polymers having large cavities are $\{[Cu_3(tpt)_4]\cdot 3ClO_4\}$, (**30**)[55] and $\{[Zn(CN)(NO_3)(tpt)_{2/3}]\cdot solv\}$ (solv=3/4$C_2H_2Cl_4$·3/4CH_3OH or 3/2$CHCl_3$·1/3CH_3OH) (**31**).[56] The latter compound has a cavity with the dimension of ca. 23 Å, which accommodates approximately nine $C_2H_2Cl_4$ molecules, together with nine molecules of methanol.

I-2. Channels. A CdN_4O_2 chromophore affords a two-dimensional layer of an edge-sharing, perfectly planar square with a Cd(II) ion and 4,4′-bpy at each corner and side, respectively. The crystal structure is made up of layers stacked on each other with an interplane separation of 6.30, 8.90, and 8.72 Å for $\{[Cd(4,4'\text{-bpy})_2(NO_3)_2]\cdot C_6H_4Br_2\}$ (**32**),[57] $\{[Cd(4,4'\text{-bpy})_2(H_2O)_2]\cdot 4,4'\text{-bpy}\cdot 2(2\text{-nitroaniline})\cdot 2ClO_4\cdot H_2O\}$ (**33**), and $\{[Cd(4,4'\text{-bpy})_2(ClO_4)_2]\cdot 2(N\text{-methyl-2-nitroaniline})\}$ (**34**),[34] respectively. There are channels with dimensions of 11.7×11.7 Å, and *o*-dibromobenzene or 2-nitroaniline are clathrated in each square cavity. $\{[Co(4,4'\text{-bpy})_2(NCS)_2]\cdot 2(C_2H_5)_2O\}$ (**35**)[40] has a two-dimensional network similar to that of the cadmium compounds. However, the Co-4,4′-bpy layers are staggered relative to each other so that the Co atoms in one layer sit above or below the squares formed by the cobalt atoms of the adjacent layers, indicative of the absence of channels. A similar staggered form occurs in $\{[Cu_2(C_3H_2O_4)_2(H_2O)_2(4,4'\text{-bpy})]\cdot H_2O\}$ (**36**),[58] showing no channels.

The bipyridine derivative is readily obtained by inserting a substituent as a spacer. Bpen is a typical ligand; the one-dimensional chain of $\{[M(bpen)]\cdot X\}$ ($M=Cu^I$, $X=PF_6^-$ (**37a**); $M=Ag^I$, $X=ClO_4^-$ (**37b**)) shows a rectangular wire structure (Fig. 6).[59] Tvp ligand affords a compound, $\{[Fe(tvp)_2(NCS)_2]\cdot CH_3OH\}$ (**38**),[60] which consists of two perpendicular, two-dimensional networks. Each sheet made up of edge shared Fe_4 rhombuses stacks in parallel. An equivalent stack of sheets is found in planes perpendicular to the first set, defining large square channels, where solvent molecules are located.

Intermolecular hydrogen bonding provides channel structures. $[Co(Hbim)_3]$ (**39**)[61] has a honeycomb sheet structure of hydrogen-bonded $Co(Hbim)_3$ units, whose stacked structure affords a channel of the cavity diameter of 17 Å.

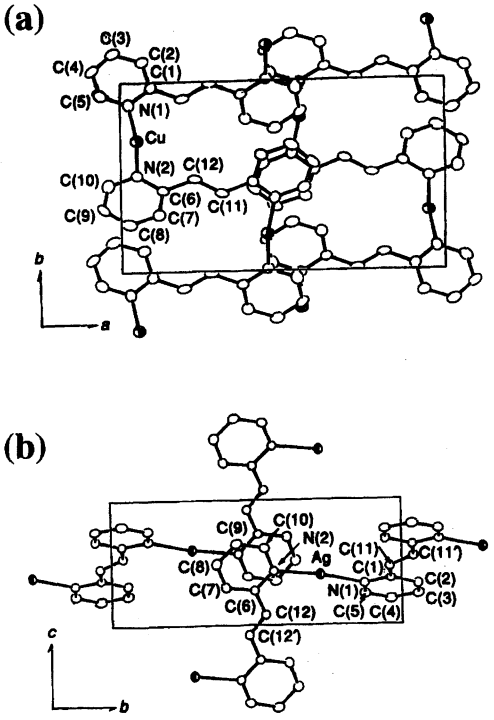

Fig. 6. ORTEP view of portions of polymeric chains of (a) $\{[Cu(bpen)]\cdot PF_6\}$ and (b) $\{[Ag(bpen)]\cdot ClO_6\}$.

The interpenetration gives rise to no or only small channeling structures even for open two-dimensional network. $\{[Re(CO)_3(\mu\text{-}OH)]_4\cdot 2(4,4'\text{-bpy})\}$ (**17**)[38] has open two-dimensional networks of square cavities, however, they are filled by self-inclusion of a second identical but independent network, affording a doubly interwoven carpet like structure. $\{[Zn(4,4'\text{-bpy})_2(H_2O)_2]\cdot 2SiF_6\}$ (**40**),[62] which is the first sheet of square-type grids from 4,4′-bpy, shows that an equivalent stack of sheets is found in planes perpendicular to the first, giving rise to the interpenetration pattern. Interestingly, when the *anhydrous* synthetic condition of this compound was used, $\{[Zn(4,4'\text{-bpy})_2(SiF_6)]\}$ (**41**)[63] was obtained. This has no interpenetration, and thus large square channels of hydrophobic nature with the same dimensions (ca. 11.4×11.4 Å) are generated. The effective size of their pores (8×8 Å) compares well with those of large zeolites. The μ-SiF_6^{2-} ions, which are capable of acting as a linear bridge, form perfectly linear bridges.

$\{[Cu(4,4'\text{-bpy})Cl]\}$ (**42**)[64] shows Cu(I) dimer-based interpenetrating sheets, affording a neutral three-dimensional framework, in which the interpenetrating two-dimensional networks fill up most of the pore space, with channels of only small diameter (ca. 2×4 Å) remaining open. The interpenetration in $\{[Cu(4,4'\text{-bpy})_{1.5}]\cdot 1.5H_2O\cdot NO_3\}$ (**43**)[65] does not fill all the available voids, but leaves a significant portion in the form of two rectangular extended channels (8×6 and 4×5 Å) which are occupied by nitrate anions that are hydrogen-bonded to solvent water molecules. The diamond-like structure is also found in $\{[Cu(4,4'\text{-bpy})_2(PF_6)]\}$ (**44**)[66] and $\{[Ag(4,4'\text{-bpy})_2]\cdot CF_3SO_3\}$ (**45**).[67]

In $\{[Ag(4,4'\text{-bpy})(NO_3)]\}$ (**46**),[68,69] each silver(I) is linked

to two nitrogens of 4,4′-bpy units in a nearly linear coordination to form extended chains. Adjacent chains are cross-linked in an almost perpendicular fashion by Ag–Ag bonds leading to a three-dimensional open network. The overall structure is composed of three networks that interpenetrate to give an open framework having 23×6 Å channels where the nitrate ions reside.

In $\{[Co_2(4,4'\text{-bpy})_3(NO_3)_4]\}$ (**47a**),[70] two one-dimensional chains in the A and B directions are linked by additional 4,4′-bpy bridging as a pillar, as shown in Fig. 7. These basic units assemble with AA BB AA BB pattern along the *c*-axis, where A B and B A schematically show the basic A–B unit. The most characteristic feature of this assembly of the basic units is described as *tongue-and-groove* structure, whose schematic picture is illustrated in Fig. 8. This type of assembly has not yet been observed in the three-dimensional frameworks of 4,4′-bpy bridged coordination polymers. The interplanar distance between A and B in the three-dimensional basic unit A B or B A is about 11.3 Å. The non-linked neighboring planes are separated by ca. 2.6 Å for A–A and B–B, and ca. 6.1 Å for A–B. The relatively large distance between the neighboring A and B planes (ca. 6.1 Å) creates channeling cavities with dimensions ca. 3×6 Å along the *a*-axis, and ca. 3×3 Å along the *b*-axis. These channeling cavities are occupied by lattice water, which shows no significant binding interactions with the crystal framework.

The two polymeric compounds, $\{[V(OH)(C_4O_4)(H_2O)]_2\}$ (**48**) and $\{[\{V(OH)(C_4O_4)\}_2]\cdot 4H_2O\}$ (**49**),[71] are composed of similar macrocyclic units constructed from cationic octahedral vanadium dimers and squarate anions. Both compounds consist of layers stacked on each other, providing rectangular and square channels of dimension, 3.0×6.5 Å and 7.04×7.11 Å, respectively. The latter channels have cyclic water tetramers.

A three-connecting ligand is used for building porous three-dimensional solid. $\{[Co(btc)(py)_2]\cdot 2/3py\}$ (**50**)[9] has extended sheets of btc ligands and Co ions along the *x*–*y* plane, which stack along the *z*-axis to give alternating cobalt-carboxylate and metal-free pyridine layers. $\{[M_3(btc)_2]\cdot 12H_2O\}$ (M = Co (**51a**), Ni (**51b**), and Zn (**52a**))[72] is composed of zig-zag chains of M–btc, which are hydrogen-bonded to yield a tightly held three-dimensional network. The one-dimensional channels are observed with the diameter of 4×5 Å. The compound, $\{[Zn_2(btc)(NO_3)]\cdot H_2O\cdot 5C_2H_5OH\}$ (**53**),[73] possesses a three-dimensional structure with channels of 14 Å section, where ethanol and water molecules reside. $\{[Ag(teb)(CF_3SO_3)]\cdot 2C_6H_6\}$ (**54**)[74] shows three-connected, two-dimensional coordination network, whose cyclic motif is a [12]annulene-like segment. The sheets are stacked in an ···ABCD··· sequence, creating channel structures with 2 molecules of benzene per one ligand teb.

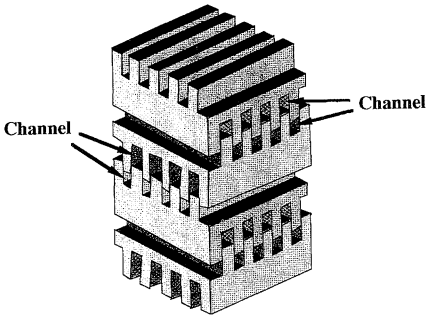

Fig. 8. Tongue-and-groove structure for $\{[M_2(4,4'\text{-bpy})_3(NO_3)_4]\}$ (M = Co, Ni, Zn). Arrow shows a channeling cavity.

Three-dimensional channeling structures are formed by connecting metal cyanide anions, $[M(CN)_n]^{m-}$ ($n=6$, $m=3$, M = Co, Fe, Ru, Os; $n=8$, $m=4$, M = Mo, W) with organotin cations, $(R_3Sn)^{3+}$, and the structures are potentially tunable by changing the building unit sizes.[75,76] In $\{[Fe(CN)_6][Me_3Sn][CoCp_2]\}$ (**55**),[76] the large channels accommodate $CoCp_2$ molecules to afford a stacked column. The Hcmp ligand, which possesses both a coordination and a hydrogen-bonding site, affords square channel frameworks of $\{[Cu(Hcmp)]\cdot X\}$ (X = ClO_4, BF_4, PF_6, and CF_3SO_3) (**56**) constructed from a tetrahedral Cu(I) motif, and the cavity size

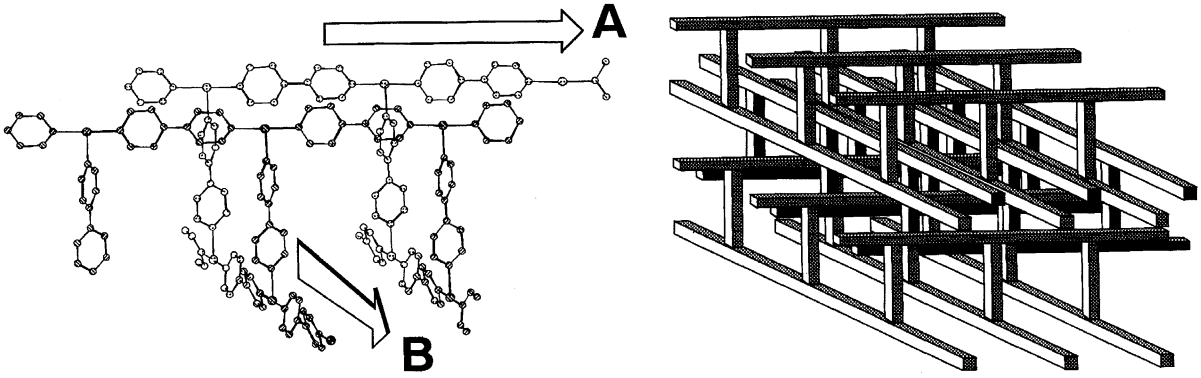

Fig. 7. Formation of the crystal structure of $\{[Co_2(4,4'\text{-bpy})_3(NO_3)_4]\}$. A section of the 3-D basic unit made up of chains A and B is shown on the left, and the result of their assembly on the right.

depends on guest anions.[2,77]

A cyclic compound of vanadium(III), $[V_8(\mu\text{-}OH)_4(\mu\text{-}EtOH)_8(\mu\text{-}CH_3COO)_{12}]$ (**57**), has a 6 Å-diameter of the ring (Fig. 9), which are stacked along the *c*-axis in the crystal lattice to produce a channel passing through the interior hole[78] which is another category for building channel structures.

I-3. Layers. A variety of inorganic layered materials have been prepared.[79,80] These intercalate inorganic or organic molecules as pillars, providing a large family of pillared interlayered solids with a wide spectrum of physicochemical properties and pore dimensions. On the other hand, few are layered coordination polymers with stable common frameworks are few.

Recently, we have prepared crystalline layered coordination polymers having flexible interlayer spaces. A useful synthetic way is to fabricate web-like two-dimensional coordination polymers from one-dimensional chains as warp and additional ligands as woof which bridge the chains. In $\{[Cu(ca)(pyz)]\}$ (**58**), pyrazine is used as woof to build two-dimensional coordination polymers from one-dimensional [Cu(ca)] chains.[81] The crystal structure of **58** has parallel sheets consisting of an infinite square array of copper(II) ions bridged by ca dianions and pyrazine. The sheets are parallel and well separated from each other: The shortest interlayer metal–metal distance is 9.785(2) Å, while within the layer the nearest-neighbor Cu–ca–Cu and Cu–pyz–Cu distances are 7.993(1) and 6.977(2) Å, respectively. On this basis the square lattice parameters can be modified. The distance (*r*) between the two copper atoms for Cu–L–Cu is important for cavities. For instance, the shortest *r* is found for L = ox (5.5 Å) in $\{[Cu_2(ox)_2(pyz)_3]\}$ (**59**)[82] and the longer one is 12 Å for compounds of 4,4′-bpy. This fabrication of two-dimensional polymers from warp- and woof-components has been quite useful for obtaining tetragonal copper lattices, and can be readily expanded to a wide variety of compounds having tetragonal or rhombic lattices. As a hydrogen-bond donor, CH_3OH also serves as the woof in the synthesis of woven polymer.[83–86] $\{[Cu(ca)(CH_3OH)_2]\}$ (**60**) affords the two-dimensional layers in which the straight one-dimensional chains are linked by two hydrogen bonds between the apically coordinated CH_3OH ligand and the oxygen atom of ca^{2-} in the nearest neighbor chain.[81,87] The structure is shown in Fig. 10. The hydrogen-bond link sheet is also found in $\{[Cu(ca)(H_2O)_2]\cdot(H_2O)\}$ (**61**).[87–89] The compound is a good instance of being able to realize lattice structures with the aid of hydrogen bondings. This fabrication of two-dimensional or three-dimensional polymers from warp- and woof-components has been demonstrated to be quite useful to obtain layered structures, and can readily be expanded to a wide variety of compounds having intercalated molecules for solid state chemistry.

New copper(II) intercalation compounds, $\{[Cu(ca)(H_2O)_2]\cdot G\}$ (G = 2,5 – Me_2pyz (**62a** and **62b**) and phz (**63**)) have been synthesized and characterized.[90] **62a** and **62b** have slightly different structures in the stacking and hydrogen bonding distances of Me_2pyz molecules. For all the compounds, the crystal structures consist of one-dimensional $[Cu(ca)(H_2O)_2]$ chains and uncoordinated guest molecules (G) (Fig. 11). Each copper atom for **62** and **63** displays a six-coordinate geometry with the two *bis*-chelating ca^{2-} anions and water molecules, providing an infinite, nearly coplanar linear chain. These chains are linked by hydrogen bonds between the coordinated water and the oxygen atoms of ca^{2-} on the adjacent chain, forming extended layers. The guest molecules are intercalated in between the layers, just like pillars, which are supported with N···H_2O hydrogen bond-

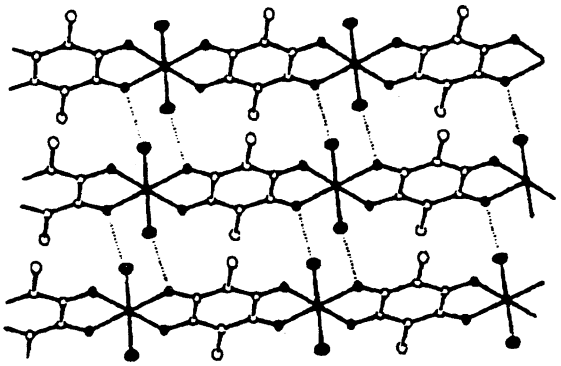

Fig. 10. Two-dimensional sheet structure obtained from coordination bond and hydrogen bond for $\{[Cu(ca)(CH_3OH)_2]\}$. The methyl carbon atoms of CH_3OH are omitted for clarity. The dashed line shows hydrogen bond.

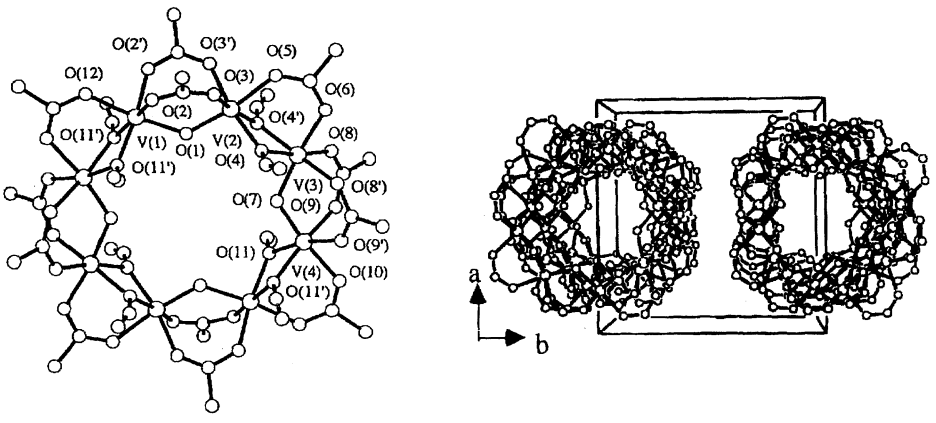

Fig. 9. (a) CHARON drawing of $[V_8(\mu\text{-}OH)_4(\mu\text{-}EtOH)_8(\mu\text{-}CH_3COO)_{12}]$ and (b) view of the channel structure.

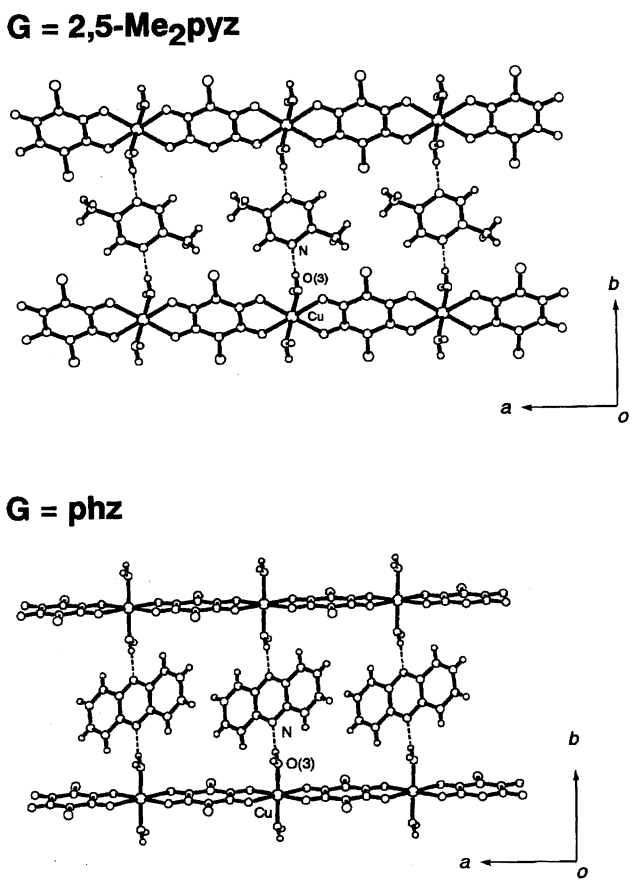

Fig. 11. Intercalation structure of $\{[Cu(ca)(H_2O)_2]\cdot G\}$. The straight chain is constructed from $[Cu(ca)(H_2O)]$motif.

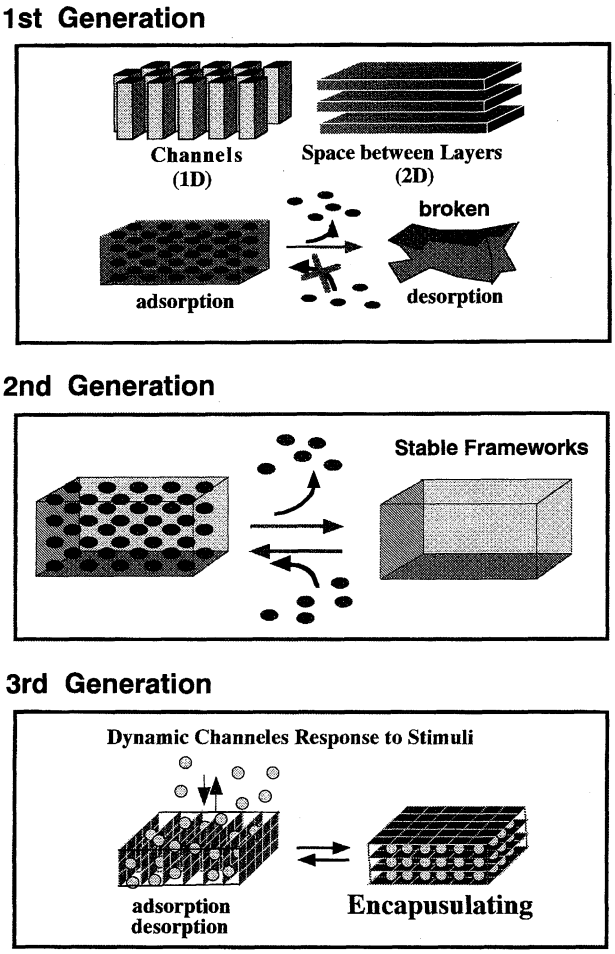

Fig. 12. Classification of crystalline-coordination compounds having porous structures based on the stability and dynamic nature of frameworks.

ing. The guest molecules are stacked on each other with the interplanar distance of ca. 3.2 Å. The distances of O–H- - -N (guest molecules) fall within the range of 2.74—2.80 Å, insensitive to the guest, whereas the inter-layer distances increase in the order: 9.25 Å (**62a**),10.24 Å (**62b**), and 11.03 Å (**63**). The degree in lengthening the distance correlates well with the size of a molecule, indicative of the stability of the two-dimensional sheet structure and the flexibility of the sheet packing.

I-4. Stable Microporous Structure. As mentioned above, there have been a wide variety of assembled-coordination compounds having microporous structures, which usually accommodate guest molecules such as solvent molecules. Unfortunately, most of the inclusion coordination compounds irreversibly lose crystallinity, undergo a phase change, or alter their morphology upon loss of their guests. Therefore, reversible removal and readsorption of guests in solids without collapse of cages or channel structures, while well-known in materials such as zeolites, is a much less common phenomenon in solids of assembled coordination compounds. In this respect microporous solids of assembled coordination compounds are classified in three groups (Fig. 12). (1) The first generation compounds, which show a variety of porous structures, are unstable to the loss of inclusions. (2) The second generation compounds, which possess stable frameworks, reversibly lose and readsorb guest species without undergoing a change in phase or morphology. (3) The third generation compounds exhibit dynamic structures, which change their own frameworks responding to the external stimuli, such as pressure, light, and so on.

In order to build the second generation compounds, a major research effort has focused on three-dimensional metal–organic frameworks. One choice is to use a multidentate organic ligand,[9,72,74] whose functionality could impart rigidity to the structure, consequently allowing the guests to be removed or exchanged without destruction of the porous framework. A scaffolding structure constructed from tetrahedral metal center and rodlike connecting units will afford large size of stable cavities.[4] Another choice is to use interpenetration of two-dimensional sheets with large cavities, where sometimes channels remain in small openings (Fig. 13). The third is to use pillar molecules for two-dimensional sheets, where coordination bonds or ionic interactions occur between the pillar molecule and metal atom in the sheet (Fig. 13).[20,63] Serendipitious findings in the synthesis are also important event in this field. For instance, we have found quite a stable framework, called the "tongue-and-groove" structure, illustrated in Figs. 7 and 8,[70] whose functionality is mentioned below.

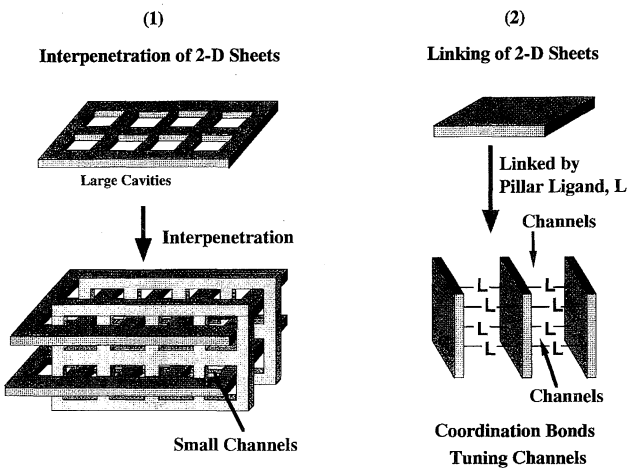

Fig. 13. Strategy for building stable microchannel structures. (1) Formation of interpenetrating structure from two-dimensional framework having *large* cavities. (2) Formation of three-dimensional structure which is constructed from two-dimensional sheets and pillar ligands.

II. Function of Coordination Compounds with Micropores

There have been various self-assembled molecular capsules, which can accommodate molecules of the size from methane to adamantanes. Encapsulation of organic guests was demonstrated by use of discrete molecular compounds.[91,92]

On the other hand, crystalline coordination polymers also provide cavities for encapsulating guest molecules. The large cavity with the dimension of ca. 23 Å has been created in $\{[Zn(CN)(NO_3)(tpt)_{2/3}]\cdot solv\}$ (solv = $3/4C_2H_2Cl_4\cdot 3/4CH_3OH$ or $3/2CHCl_3\cdot 1/3CH_3OH$) (**64**),[56] which accommodates approximately nine $C_2H_2Cl_4$ molecules, together with nine molecules of methanol. The large but sealed-off chambers possess potential functionality not only for trapping all sorts of interesting species but also for conducting unusual pseudosolution chemistry, both photochemical and thermal, in minute pressure cooker vessels.[56] This chemistry is still undeveloped.

II-1. Gas Adsorption. Natural gas is an alternative fuel for transport which presents economic, mechanical and ecological advantages. A great number of vehicles in the world are powered by compressed natural gas (CNG). The high pressure necessary to reach a convenient energy density for CNG system is, however, a serious limitation to its widespread use. During the past decade, a number of studies have shown that the energy density can be increased considerably at moderately high pressure when the gas is adsorbed on microporous solids.[93—96] This has produced an increasing interest in developing a system for adsorbed natural gas. Adsorption in a porous material offers the possibility of storing methane at high density while maintaining moderate physical conditions for the bulk phase, and the search for a suitable material is currently an active area of research.[97] A porous crystal of coordination polymers is a candidate for this purpose because the microporosity (fraction of micropore volume to total volume) could be larger than that of inorganic compound; space taken by the atoms of the microporous compound and the space wasted by poor packing of crystallites could both be potentially minimized. Many researchers are facing the difficulty that the low-dimensional frameworks in the coordination solids are not robust. In this sense, most of coordination solids so far synthesized belong to the first generation compounds (Fig. 12). Therefore, the attention is focused on coordination compounds whose building blocks are held together by stronger bonds to give high-dimensional frameworks.

Very recently, the structural instability has been overcome in crystalline coordination polymers, $\{[M_2(4,4'\text{-bpy})_3(NO_3)_4]\}$ (M = Co (**47a**), Ni (**47b**), and Zn (**47c**))[70] which is the first crystallographically well-characterized system displaying reversible methane-adsorption capability. The unique three-dimensional structure with channeling cavities described above has gas adsorption properties. Figure 14 shows the results of the adsorption activity experiments of the anhydrous sample, obtained by drying under vacuum, with CH_4, N_2, and O_2 at 298 K. The rapid increase in the amount of the adsorbed gases is recognized with increases in the pressure up to 5 atm, indicating that this process is diffusion of the gases into the cavities.[98] No structural decomposition in removal of crystal waters in vacuo was observed by X-ray powder diffraction patterns (Fig. 15). Moreover, the adsorption and desorption experiments of CH_4 trace the same isotherm (Fig. 14), indicating no deformation of the crystal frameworks in this process. The isotherms are found to be type I in the IUPAC classification.[98] About 2.3 mmol of CH_4 and 0.80 mmol of N_2 or O_2 are adsorbed per 1.0 g of the anhydrous sample at 30 atm. Adsorption capabilities of zeolites for several gases (CH_4, N_2, CO_2, Ar, Kr, and Xe)

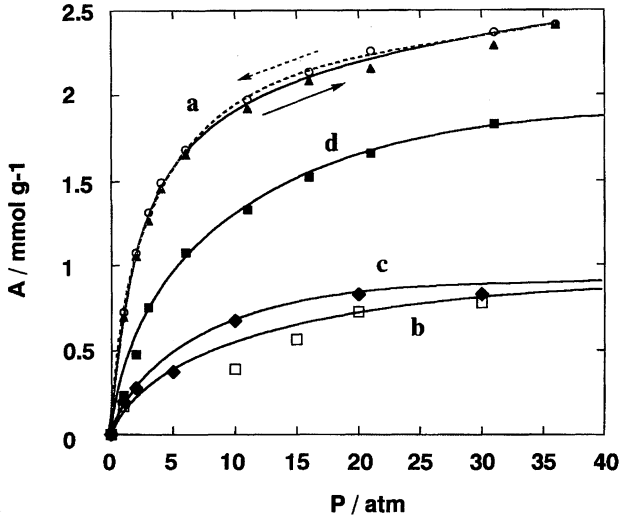

Fig. 14. Isotherms for the adsorption of CH_4 (a), N_2 (b), and O_2 (c) on anhydrous samples, and that for CH_4 of zeolite 13X (d) at 298 K. The symbol "A" indicates absolute adsorption in mmol of adsorbed gas per gram of anhydrous sample. The gas desorption (circles) was carried out directly after gas adsorption (triangles).

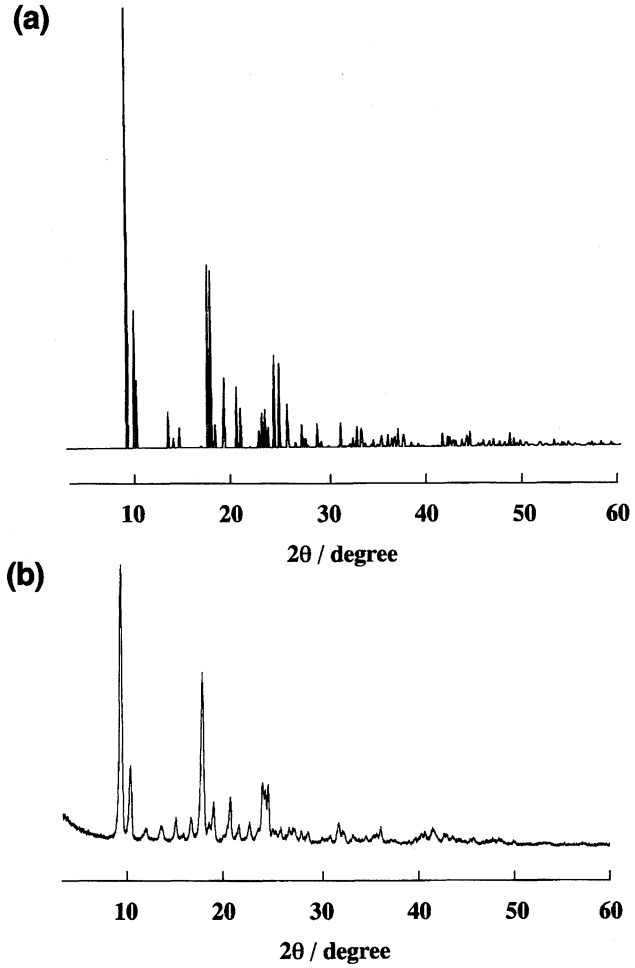

Fig. 15. Simulated (a) and observed (b) X-ray powder diffractions patterns of anhydrous compound **47a** after a cycle of dehydration–hydration at 298 K.

have been reported, indicating that the gas affinity is associated with cavity size.[95,96,99—101] Zeolite 13X and 5A, which afford high affinity for the gases,[95] have channeling dimensions of 7.4×7.4 Å and 4.1×4.1 Å, respectively, similar to those of compounds **47a—c**. In addition to structural dimensions, specific interaction of metal–organic cavity frame with adsorbed molecules could be controllable in the coordination polymers, possibly affording a new type of adsorption properties.

Anhydrous copper(II) terephthalate (**65**) adsorbs gases such as N_2, Ar, O_2, and Xe, which are not adsorbed on the surface but are occluded within the solid.[102] Temperature dependence of the magnetic susceptibility is similar to that of copper acetate, implying that the dimeric copper unit remains in the solid state. The X-ray crystallographic structure has not been determined, yet but the channel structure is considered to be constructed from two-dimensional sheets of the square grids.

II-2. Small Molecules Occlusion. The dehydrated sample, $\{[Zn_3(btc)_2 \cdot H_2O]\}$ (**52a**), upon liberating water ligands from each formula unit, becomes a porous solid with a pore diameter of 4×5 Å,[72] and absorbs ten ammonia molecules and one water molecule per open coordination site on the Zn to afford $\{[Zn_3(btc)_2] \cdot 2H_2O \cdot NH_3\}$ (**52b**). The adsorbed solid may be converted back to $\{[Zn_3(btc)_2] \cdot 12H_2O\}$ (**52c**) by desorption of ammonia at 250 °C and 0.080 pressure for 5 h, followed by the addition of water. The Co and Ni analogues, however, undergo decomposition and/or deformation of the microporous structures. $\{[Zn_2(btc)(NO_3)] \cdot H_2O \cdot 5C_2H_5OH\}$ (**53**) has the framework represented by an extended channel systems with 14 Å cross-section, where mobile ethanol and water guest molecules reside. The compound is highly selective to alcohols.[73] **54** contains 16 molecules of benzene per unit cell in the channels, four of which are disordered.[74] The disordered benzene molecules are desorbed by heat treatment (110 °C for 10 min) and benzene vapor is readsorbed by cooling to room temperature. **50** shows that the crystal lattice thus formed is thermally stable up to 350 °C, even after removal of included pyridine guest molecules and the inclusions can be selectively readsorbed.[9]

II-3. Ion Exchange. When compound **25** is heated at 70 °C, and immersed in an aqueous $NaPF_6$ solution, the ClO_4^- anions are exchanged to PF_6^- anions.[45] In **46** the addition of a slight excess of $NaPF_6$ (aq) to a suspension of crystalline samples in water at room temperature showed that the NO_3^- anions exchange with PF_6^- anions.[68,69] It takes 6 h to yield ca. 95% of exchanged species. Analogous experiments can be done for MoO_4^{2-}, BF_4^-, and SO_4^{2-} anions. Similarly, **43** shows that most of the nitrate anions can be exchanged in aqueous media with BF_4^-, and SO_4^{2-} anions.[65] The three-dimensional framework of $\{[Cu(tcpm)] \cdot BF_4 \cdot xC_6H_5NO_2\}$ (**66**)[4] can exchange anions, since the crystals retain their external faces and edges and their internal transparency when the suspension is treated in solution of NBu_4PF_6 (large excess) in nitrobenzene.

II-4. Heterogeneous Catalysis. A unique character of the network material is observed in **32**.[57] This complex shows i) the selective clathration of *o*-dibromobenzene or *o*-dichlorobenzene from their meta and para isomers, and ii) catalysis for the cyanosilylation of aldehydes. Treatment of benzaldehyde and cyanotrimethylsilane with a CH_2Cl_2 suspension of the powdered complex gave 2-(trimethylsiloxy)phenylacetonitrile in 77%.[57]

In the case of organic network materials, antracene–bisresorcinol compound **1** shows a novel catalysis in the solid state for the acrolein–cyclohexadiene Diels–Alder reaction.[103] The suggested mechanism involves a catalytic cycle composed of adsorption of the reactants in the cavities of polycrystalline host **1**, preorganized intracavity reaction, and desorption of the product. The host also promotes stereoselective intracavity reactions for alkyl acrylates and cyclohexadiene but, in this case, not in a catalytic manner.

II-5. Photochemical Properties. Anionic three-dimensional coordination polymers of oxalato-bridged metal complexes with stoichiometries, $[M^{II}_2(ox)_3]_n^{2n-}$ (M = Mn) and $[M^{I}M^{III}(ox)_3]_n^{2n-}$ (M^{I} = Na and Li; M^{III} = Al and Cr), have been obtained, which contain $[M^{II}(2,2'\text{-bpy})_3]^{2+}$ cations as a template.[104—106] For both types, the formal $[M(ox)_{3/2}]$ subunits, representing 3-connecting points, build up well-

defined three-dimensional 3-connected 10-gon nets (10, 3) with $[M^{II}(2,2'\text{-bpy})_3]^{2+}$ cations occupying the vacancies in the same manner. Some of these compounds afford intriguing photophysical processes, such as light-induced electron transfer and excitation energy transfer in the solid state. In single crystal $\{[Na^{I}Cr^{III}(ox)_3]\cdot[Cr^{III}(2,2'\text{-bpy})_3]\cdot ClO_4\}$ (**67**),[105,106] the absorption spectra show the spin-flip transitions of both $[Cr^{III}(2,2'\text{-bpy})_3]^{3+}$ and the $[Cr^{III}(ox)_3]^{3-}$ chromophores, which are clearly distinguished. Irradiating into the spin-allowed $^4A_2$–$^4T_2$ absorption band of $[Cr(ox)_3]^{3-}$ results in intense luminescence from the ^2E state of $[Cr(2,2'\text{-bpy})_3]^{3+}$ as a result of rapid energy transfer processes. This type of phenomenon could be important for possible applications of these systems in heterogeneous photocatalysis.

The photomechanical polymer $\{[Co(pyz)(3,6\text{-dbsq})(3,6\text{-dbcat})]\}$ (**68**) was characterized.[107] The light-induced transition from $\{[Co^{III}(pyz)(3,6\text{-dbsq})(3,6\text{-dbcat})]\}$ to $\{[Co^{II}(pyz)(3,6\text{-dbsq})_2]\}$ for complex units along the polymer chain would have an associated change of approximately 0.2 Å in Co–N bond length since the ionic radius of the cobalt ion increases from low spin Co(III) to high spin Co(II) (Fig. 16). Propagated along the length of the polymer, the micromechanical change in Co–N bond length would correspond to a change of 0.06 mm per millimeter of polymer length.

II-6. Others. Cooperative spin transition (ST) compounds could be used as molecular switches in new electronic devices because of their bistable nature. The spin crossover phenomenon is the result of an electronic instability driven by external stimuli such as temperature, pressure, and electromagnetic radiation. There have been many ST compounds so far synthesized, most of which are molecular crystals. Polymer crystals are few. One example is **38**, which shows low-spin to high-spin crossover behavior in the temperature range from 100 to 250 K.[60] Linear chain compounds of $\{[Fe(Rtrz)_3]\cdot A_2\cdot nH_2O\}$ (A = anion) (**69**) also show ST phenomena.[108] The ST phenomena reveal sample-dependence, attributed to subtle effects induced by the presence of crystalline defects and molecular inclusions (counter anions or solvent molecules), or both. The role of polymeric structure constituted by coordination bonds is not clear.

III. Scope in the Future

In the 1990's, many porous solids of assembled metal complexes have been studied, most of them clathrating solvent molecules or other guest molecules. As mentioned above, assembled metal complexes show a low-dimensional crystal structure; thus the clathrated guest molecules play important roles in their crystal stability by interconnecting building blocks. In the late 1990's, robustness of crystal frameworks themselves is a principal subject, so three-dimensionally linked structures have been explored. However, stable structures, where building blocks are tightly held together, are inconsistent with those which display reversible inclusion and removal of guest molecules. The robust solids of coordination compounds usually result only in structural beauty, apart from effective use of voids. In other words, design and synthesis of compounds classified in the second generation (Fig. 12) is one of the challenges that must be overcome to achieve the functional properties in this field. Fortunately, just before the 21st century, several porous solids of assembled metal complexes have been created, which possess functionality such as reversible gas and small molecules ad-

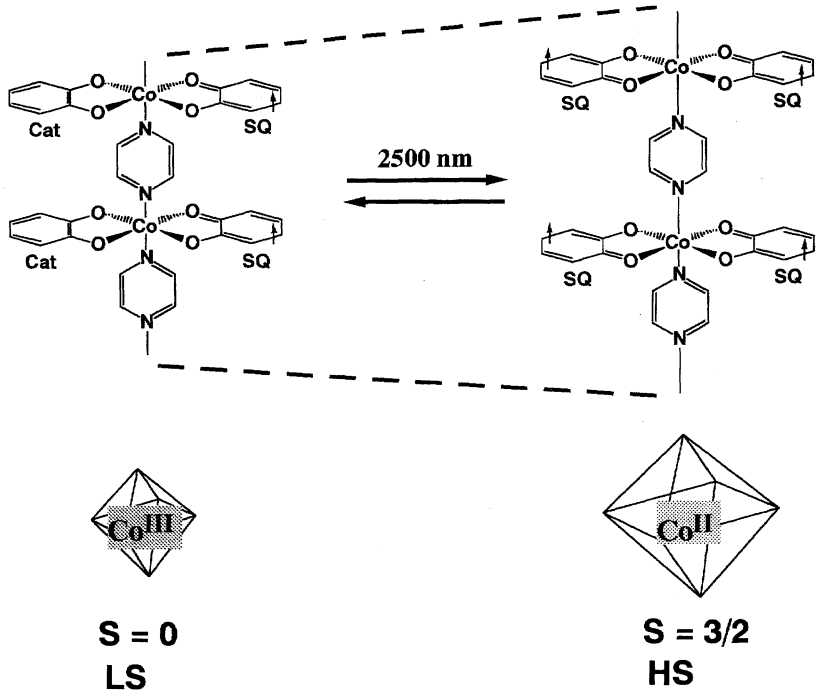

Fig. 16. Photomechanical oscillation compound, $\{[Co^{III}(pyz)(3,6\text{-dbsq})(3,6\text{-dbcat})]\}$. The crystal lengthens when irradiated with light (λ = 2500 nm).

sorption, anion exchange, heterogeneous catalysis, and other physicochemical properties. This functionality for solids of metal complexes is still in embryo. Further improvement of these compounds is required in these areas: (1) high microporosity, (2) chemical affinity of voids, (3) chiral nature of voids, and (4) physical nature of voids. Hereafter the 3rd generation compounds possessing dynamic structures could appear in the near future. This is associated with the form of solids, in particular, thin layer or nano-sized particles. In this context, drastic development and/or revolution of synthesis for assembled metal complexes would be required. Basic functional chemistry of porous coordination compounds would provide us fruitful materials.

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25) i) parenthesis, [ ] denotes ligands or anions, which are directly coordinated to a metal ion, ii) a repeating unit of a polymer is shown in { }.
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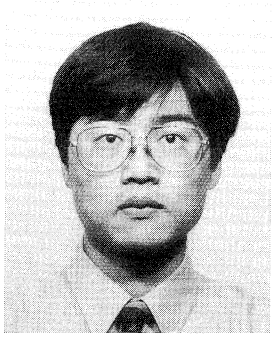

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