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## *Accounts*

# Crystal Engineering of Multidimensional Copper(I) and Silver(I) Coordination Supermolecules and Polymers with Functions

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(Received February 27, 1997)

Considerable progress has been made in recent years in controlling the assembly and orientations of individual molecules to create specific aggregates. It is the aim of this review to give an account of the latest developments in our groups with regard to construction of functional crystal metal complex supermolecules from self-assembly of copper(I) and silver(I) coordination compounds by intermolecular interactions as well as coordination bonds. Several approaches to such self-organization process have been highlighted. Spontaneous organization of hydrogen bonding and host–guest interactions in 3-cyano-6-methyl-2(1*H*)-pyridinone system result in the formation of three-dimensional channel structures and multi-fold interpenetrated diamondoid architectures by modification of hydrogen-bonding mode and distances. Control of effective aromatic stackings between polymeric chains assembles simple phenazine and benzothiadiazole building blocks into well-organized, multidimensional honeycomb and graphite structures. Manipulation of strong interchain S···S contacts in sulfur-rich tetrathiafulvalene derivative system creates a unique bookshelf type frameworks. Employment of multi-coordination sites of the ligands in pyrazine, dithienylethene and dithiaparacyclophane systems generates a number of novel infinite-sheet and -chain metal polymers with the potential to serve as functional supramolecular devices.

Polymers are macromolecules built up by the linking together of large numbers of much smaller molecules. The word "polymer" itself is derived from the Greek roots "meros", meaning parts, and "poly", meaning many. We can usually distinguish organic polymers such as natural proteins and nucleic acids, which are extremely important constituents of all organisms, and inorganic polymers, which form the major part of the earth's crust. Each types is composed of a large number of chemically related subunits (organic and inorganic molecules) joined by covalent bonds. The elements involved in such polymers are usually limited to C, H, N, O, P, S, Al, and Si. The second half of the this century has witnessed a productive interplay between organic chemistry and inorganic chemistry. Recent developments in the study of coordination chemistry have produced numerous coordination polymers by selecting the coordination geometry of metals and the chemical structure of organic ligands. Unlike organic or inorganic polymers, the coordination polymers include transition metal complexes in their constituents and involve much wider ranges of metal and non-metal elements, Table 1. The building blocks are linked together by coordination bonds and non-covalent interactions in nature, which generates self-assembled one, two and three-dimensional metal complexes with specific network topologies,[1]

Table 1. Features of Organic and Coordination Polymers

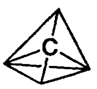
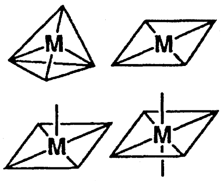
| | Organic | Coordination |
|---|---|---|
| Element | C, N, O<br>P, S, Si | ca. 60 elements |
| Bond angle and distance | Limitation | Diversity |
| Bond nature | Covalent | Coordination |
| Crystal | Flexible | Rigid |
| Charge | Neutral | Localized |
| Solubility | High–low | Low–insoluble |
| Structure of elements | A few<br>–C≡<br>=C=<br>>C=<br> | Several<br>–M– –M<<br> |

Fig. 1.

A great deal of the structural information available has demonstrated the importance of carefully choosing linking

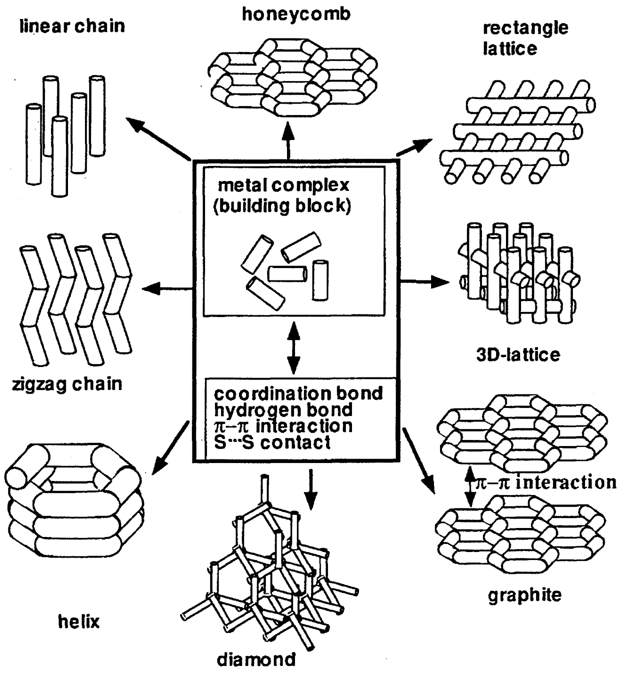


Fig. 1. Metal complex supermolecules and polymers.

ligands for rational design of the system. One of the simplest approaches is to use a bifunctional rod-like diatomic anion such as $CN^-$ and bidentate *N*,*N*′-donor linking groups such as pyridine- or pyrazine-based ligands with a preference for binding metals at each end in a linear fashion, together with a metal center with a preference for a tetrahedral arrangement of ligands.[2—4] The individual frameworks of these polymeric complexes vary significantly, ranging from a honeycomb structure containing hexagonal channels to a helical arrangement, interpenetrating diamondoid networks, infinite interwoven, and interpenetrating molecular ladders and bricks. These sophisticated transition metal coordination polymers have been the subject of intensive research in the last few years, and major advances have been made in both their theoretical descriptions and their application as new materials.[1—4]

Metal complex crystal engineering, which relies primarily upon exploitation of noncovalent interactions to spontaneously link transition metal-based subunits, provides an alternative method for the design of supramolecular self-assembly. Our group has been concentrating on the copper(I) and silver(I) polymers with an aim to design novel and functional metal complex supermolecules by noncovalent interactions as well as coordination bonds. Pearson has classified the copper(I) and silver(I) ions as extremely soft acids favoring coordination to soft bases such as S and unsaturated N-containing ligands.[5] Copper(I) and silver(I) complexes with these soft ligands give rise to an interesting array of stereochemistries and geometric configurations with the coordination numbers of two to five all occurring.[6] The most common stereochemistries for both ions are the linear two-coordinate and the tetrahedral four-coordinate geometries with some distortions of the environment, particularly in the presence of chelating type ligands. Under suitable conditions, these simple coordination compounds with the presence of two rod-like or four sticky sites can be used as building blocks to form the self-assembly of predictable supramolecular aggregates.[7] In the light of this principle, this account will focus on the most recent novel polymeric copper(I) and silver(I) complexes, which combine the covalent bond forming capability of the metal ion with the ligand capable of forming non-covalent interactions such as hydrogen bonding, aromatic stacking, and S···S contacts to construct crystal metal complex supermolecules with functions. The major organic ligands involved in the present study are listed in Fig. 2.

## Hydrogen Bonded System

The hydrogen bond is encountered among compounds with the most polar M–H bonds, that is, it is the relatively weak secondary interaction between a hydrogen atom bound to an electronegative atom and another atom that is also generally electronegative and has one or more lone pairs enabling it to act as a base. While selective and directional hydrogen bonding has been noted as a most powerful organizing force in organic molecular assembly and the vast majority of publications and reviews has been devoted to the self-organization of organic molecules into one-, two-,

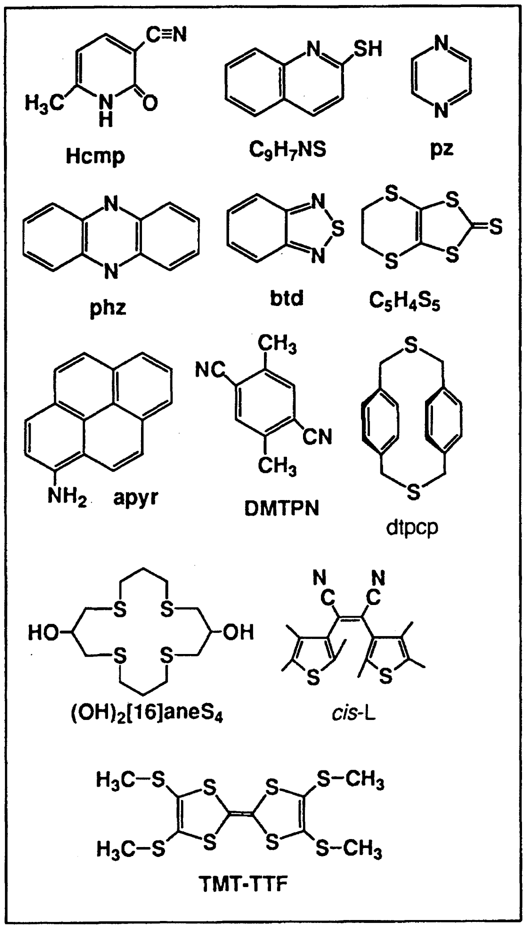


Fig. 2. Important organic ligands involving in this review.

or three-dimensional hydrogen-bonded architectures,[8] such development in crystal engineering of coordination supermolecules is rather slow.[9] We have isolated several hydrogen-bonded copper(I) coordination polymers in which the hydrogen bonding network is either based on the interactions between the tetrahedral counter anions such as $ClO_4^-$ and the uncoordinated NH or OH moieties of the ligands, or between an uncoordinated group and a hydrogen-bonding site of the ligand itself.

**3D-Complex with Aromatic Stacking.** When quinoline-2-thione reacts with $[Cu(MeCN)_4]ClO_4$ in tetrahydrofuran, it gives red plate crystals of $[Cu(C_9H_7NS)_2]ClO_4$.[10] There are two types of metal ions in the structure, each of which involves an infinite linear-chain of $(CuS_2)_\infty$. The aromatic stackings of the neighboring chains lead to an eclipsed conjugated system and the hydrogen bonds between the uncoordinated NH sites of the thione and the $ClO_4^-$ anions give a three-dimensional structure with the average distance of 2.84(1) Å for O···H–N bonds (Fig. 3). Thus, the perchlorate anion not only serves as a counter anion of copper(I), but also acts as a bridge linking adjacent two polymeric chains. A similar example is found in a copper(I) complex of *N*,*N*′-dimethylthiourea, $[Cu(dmtu)_2NO_3]$, in which the coordinated nitrate anion acts as a bridge linking two alternately stacked polymeric $CuS_4$ chains with O···H–N distances of 2.76 and 2.91 Å.[11]

**3D-Complex with Channel Framework.** Although crystal structure is generally thought to be rigid, the supramolecular structures of coordination copper(I) compounds of 3-cyano-6-methyl-2(1*H*)-pyridinone (Hcmp) can be rationally designed by changing the hydrogen-bonding mode and distances.[12,13] The ligand possesses both a coordination group (CN) and a hydrogen-bonding site (O···H–N). The reactions of copper(I) salt with Hcmp in acetone have isolated four coordination polymers $[Cu(Hcmp)_4]X$, where $X = ClO_4^-$, $BF_4^-$, $PF_6^-$ and $CF_3SO_3^-$. Although each structure contains a three-dimensional framework of tetrahedral $CuN_4$ centers linked by intermolecular hydrogen bonds through pyridone N and O atoms in a head-to-tail mode, different patterns of hydrogen-bonding give rise to two different types of frameworks.[12] In the perchlorate and the tetrafluroborate complexes each Hcmp molecule is hydrogen-bonded to two adjacent Hcmp groups and this results in each $[Cu(Hcmp)_4]X$ entity being connected to eight others, Fig. 4(a). A square channel framework is generated with a relatively small size of cavities (Cu···Cu distance = ca. 12.1 Å) filled with guest anions, Fig. 4(b). The hydrogen bond distances of O···H–N are 2.876 and 2.845 Å for the perchlorate and tetrafluroborate, respectively, consistent with the size of the cavity to accommodate the smaller anions. When the small anion is changed to the drastically larger $PF_6^-$ and $CF_3SO_3^-$ the cavities in the square channel lattice for the perchlorate and tetrafluroborate cannot be effectively adapted for large guest ions only by elongating the hydrogen bond distances. If the stoichiometry is to remain the same, one way for the system to respond and avoid this destabilizing repulsion is to rearrange the hydrogen-bonding mode. As a consequence, each Hcmp molecule in the hexaflurophosphate and the trifluoromethanesulfonate complexes is hydrogen-bonded to only one neighboring Hcmp group, Fig. 4(c), and this gives a superdiamond network (Fig. 4(e)) with larger open cavities (Cu···Cu distance = ca. 13.3 Å), that just fit the large anions, Fig. 4(d). The space filling models of the latter type are illustrated in Fig. 5. On the other hand, because of incorporation of acetone into the metal coordination atmosphere in $[Cu_2(Hcmp)_4(Me_2CO)_2](BF_4)_2$, each copper atom only coordinates to two Hcmp moieties in the dimeric unit. The hydrogen-bonding of Hcmp leads to a one-dimensional infinite chain structure.[13] If the system does not involve hydrogen-bonding, a completely different stoichiometry and frameworks arise. The pentanuclear copper(I) cluster with deprotonated $cmp^-$, $[Cu_5(cmp)_4]ClO_4$, was obtained by the

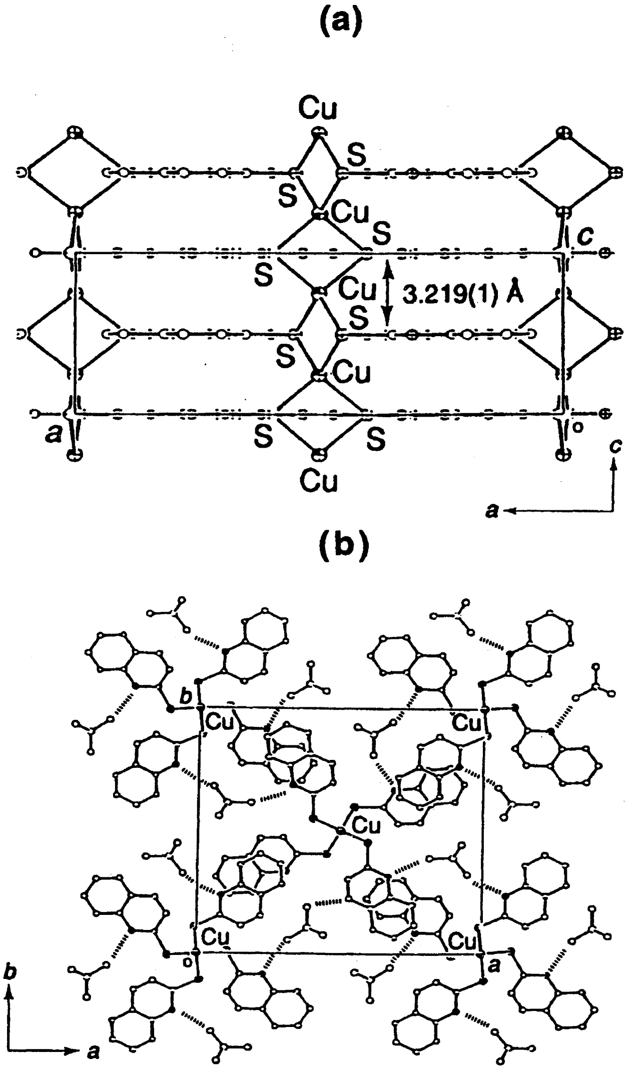


Fig. 3. (a) Crystal structure of $[Cu(C_9H_7NS)_2]ClO_4$ without counter anions, projected down the *b* axis. The ligand sits on the mirror plane. (b) Projection of the stacks of the coordinated ligands of $[Cu(C_9H_7NS)_2]ClO_4$ along the *c* axis. The broken lines indicate the sites of hydrogen bonding between the perchlorate anion and the NH moiety of the ligand.

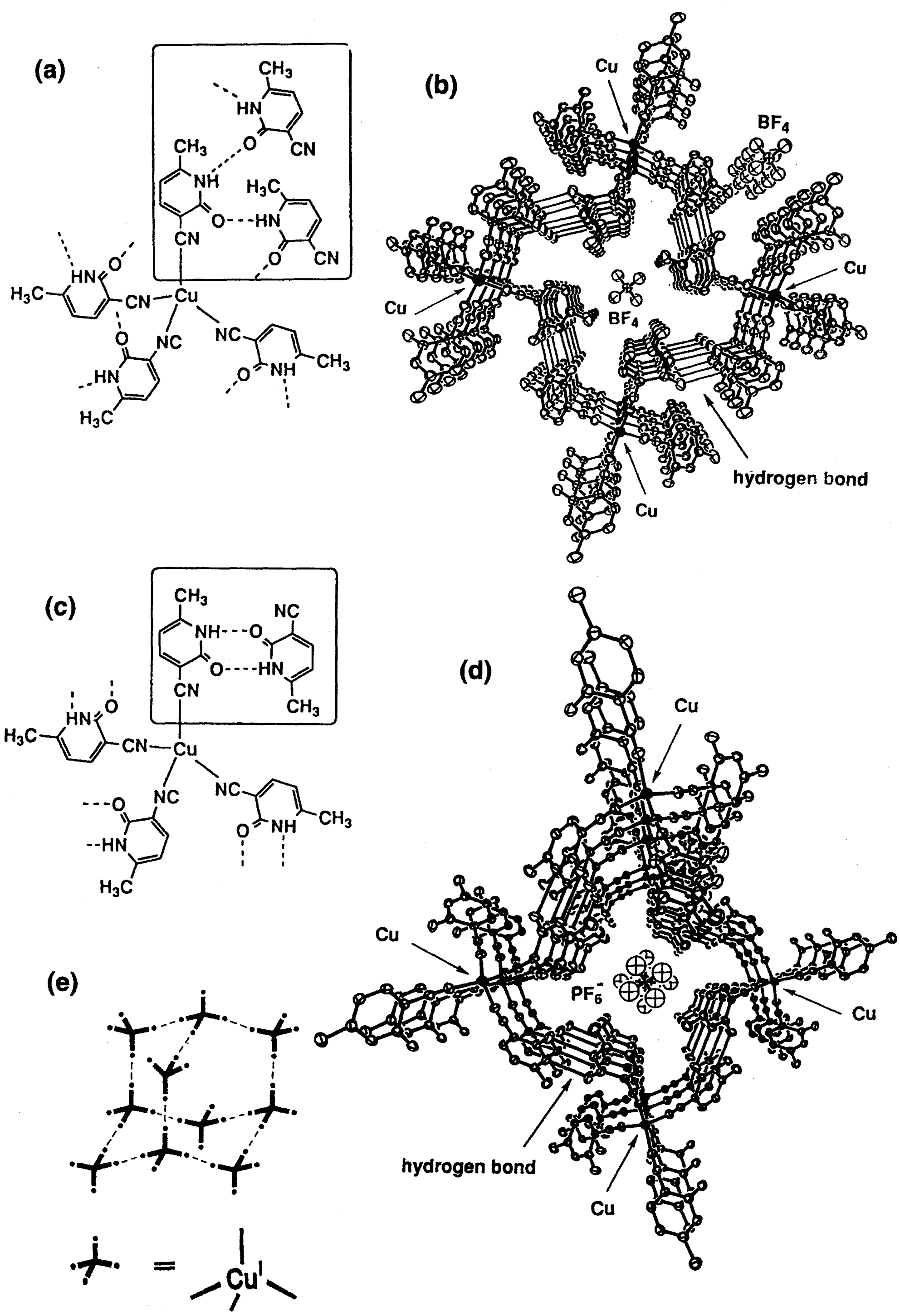


Fig. 4. (a) Schematic molecular structure and (b) packing diagram of $[Cu(Hcmp)_4]ClO_4$ with open square channels. (c) Schematic molecular structure and (d) packing diagram with (e) diamondoid framework in $[Cu(Hcmp)_4]PF_6$.

reaction of copper(I) salts with Hcmp in a protic solvent such as methanol, Fig. 6(a). In the complex, each $cmp^-$ monoanion employs all its three functional groups bridging three rather than two copper atoms, forming a supramolecular channel architecture containing a $Cu_4$ cluster,[13] Fig. 6(b). This finding suggests that the hydrogen-bonding interactions have decisive influence on crystal engineering of coordination polymers. Modification of the hydrogen-bonding mode and distances, as well as the direction of H-bonding sites, can effectively facilitate transition of one framework to the other.

**1D-Mixed Valence Complex.** While most commonly encountered hydrogen-bonded organic or inorganic molecules are based on $Y \cdots H{-}X$ (X and $Y = O$, N) interactions, there are few examples with $Cl \cdots H{-}X$ hydrogen bonds.[14] We have recently isolated a mixed-valence copper complex $[CuCl(bpy)_2]_2[CuCl_2]_2(C_6O_6H_4)$ by reaction of copper(I) chloride with tetrahydroxybenzoquinone

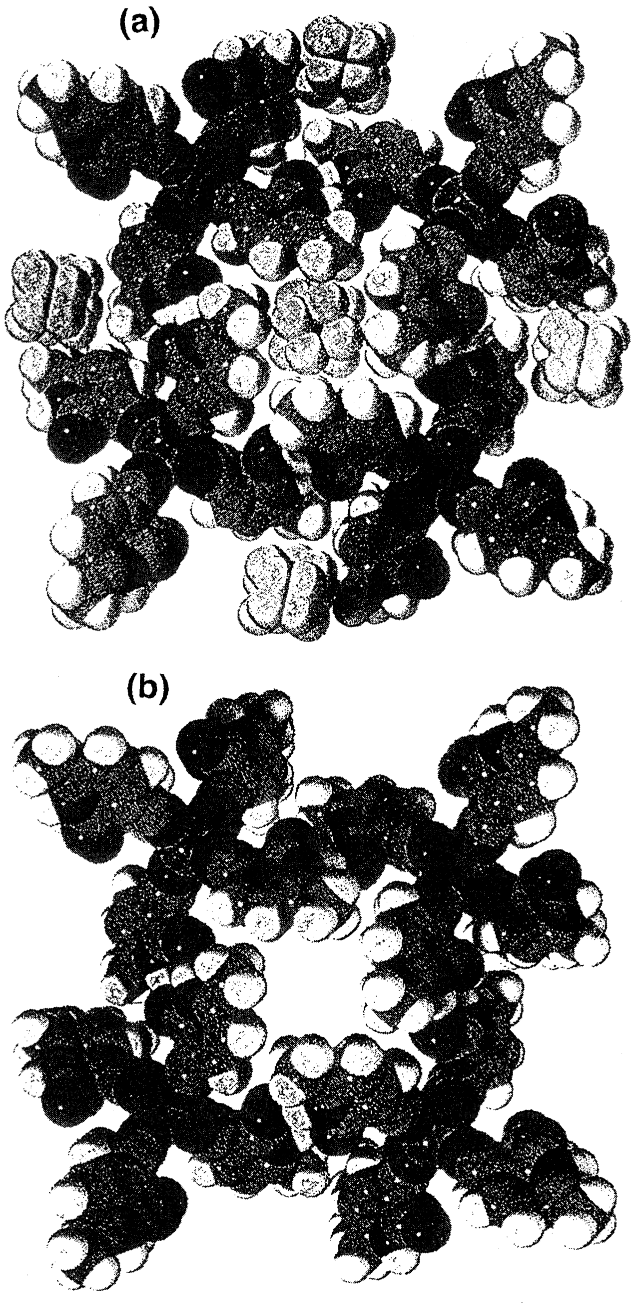


Fig. 5. (a) Space filling models of $[Cu(Hcmp)_4]PF_6$ and (b) the cation $[Cu(Hcmp)_4]^+$.

$(C_6O_6H_4)$ and 2,2′-bipyridine (bpy).[15] In this complex each $C_6O_6H_4$ molecule is located midway between the two $[Cu^ICl_2]^-$ anions and two $[Cu^{II}Cl(bpy)_2]^+$ cations and is approximately symmetrically hydrogen-bonded to four chlorine atoms with its four hydroxyl groups. The average bond distance of Cl···H (2.486 Å) is significantly shorter than their combined contact radii [H(1.20)+Cl(1.75) = 2.95 Å][16] indicating that a strong intermolecular interactions exist. Furthermore, the two quinone oxygens of each tetrahydroxybenzoquinone group and their symmetry equivalents act favorably as proton acceptors symmetrically linked to two bpy hydrogens of the two adjacent $[Cu^{II}(bpy)_2Cl]^+$ ions through O···H–C interactions. The total result of this connection gives rise to an infinite chain arrangement of $Cu^ICl_2$ and $Cu^{II}(bpy)_2Cl$ ions linked by $C_6O_6H_4$ groups with intermolecular Cl···H–O and O···H–C hydrogen-bondings interactions, Fig. 7. Thus, a good match between hydrogen bond donors and acceptors both in number and spatial arrangement is the key point in successful synthesis of such extended structures.

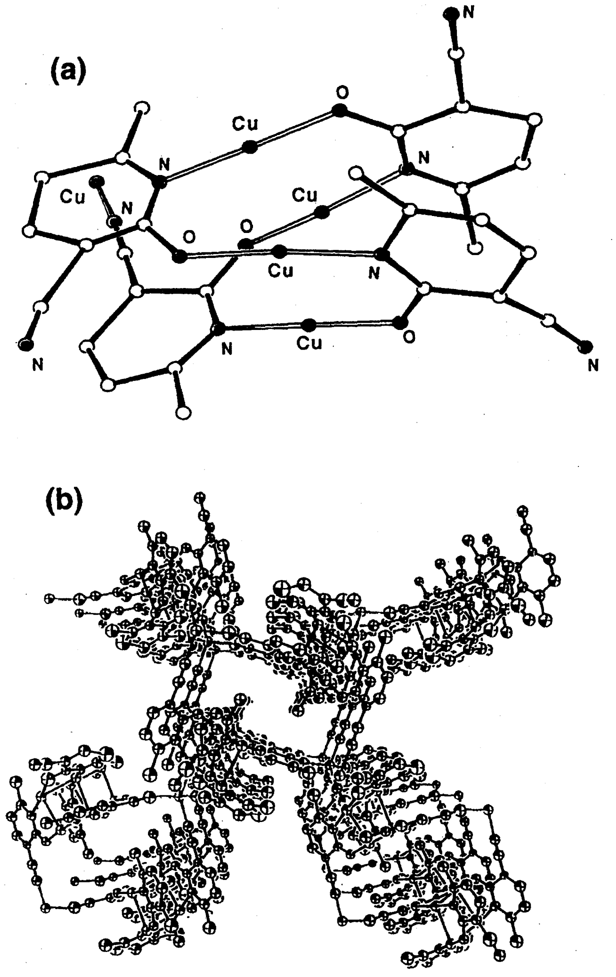


Fig. 6. The supramolecular rectangular channel framework in $[Cu_5(cmp)_4]ClO_4$ formed by tridentate coordination of $cmp^-$ monoanion.

Hydrogen bonding in copper(I) and silver(I) complexes does not always lead to polymeric frameworks; in some rare cases it couples two monomers into a dimeric structure. The examples include a silver(I) complex[17] with pyrazole derivative ligand, $[Ag_2(Hbpypz)_4](ClO_4)_2 \cdot 2(CH_3)_2CO$, where Hbpypz = 3,5-bis(2-pyridyl)pyrazole. There are two crystallographically independent monomeric units in a lattice linked by intramolecular hydrogen bonds between the free pyridine nitrogen atom of one monomeric unit and the N–hydrogen of a pyrazole belonging to another monomeric moiety with N···N distance of ca. 2.87 Å.

## π–π Interaction System

**Phenazine Stacking.** Aromatic ring stacking is one of the intermolecular noncovalent interactions between ligands

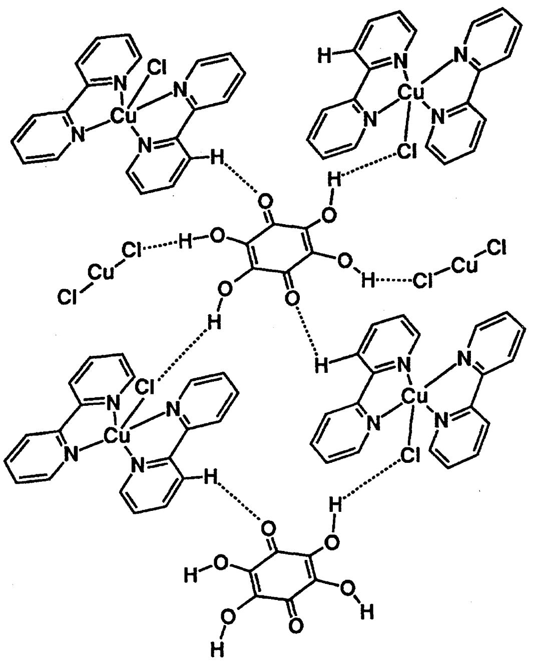


Fig. 7. Hydrogen-bonded networks in the mixed valence copper complex, $[Cu^{II}(bpy)_2Cl][Cu^{I}Cl_2]\ (C_6O_6H_4)_{0.5}$.

in complexes which may enhance the stability of the complex in solution and in the solid state as well.[18] The extreme of the short interplanar distance of aromatic moiety in copper(I) and silver(I) coordination polymers is close to 3.26 or 3.28 Å, but most are in the range of 3.4 to 3.7 Å, similar to that of layers of graphite,[7] Table 2. Some copper(I) polymers with stacks of aromatic ligands display specific properties such as low-energy optically allowed intermolecular electronic transitions (charge-transfer bands), which might have practical applications in future.[19] Phenazine (phz) is a very versatile ligand in the assembly of metal complexes by π–π stacking interactions. We have structurally characterized a number of polymeric copper(I) and silver(I) complexes of phenazine, in which phz can not only act as a building block bridging metal ions through its two nitrogen atoms but also exhibits variety of aromatic stackings.[20—22] Interchain and intersheet π–π interactions frequently appear in the phz complexes with copper(I) halides, $[Cu_2(\mu\text{-}X)_2(phz)]$, which results in a one-dimensional chain (X = I) or in two-dimensional sheet (X = Cl or Br) structures composed of phz-linked $(CuX)_2$ moieties,[21] Fig. 8(a,b). The interplane distances range from 3.36 to 3.46 Å. Similar interchain aromatic stackings are also present in $[Ag(phz)]ClO_4$.[20] This type of interaction can even generate an infinite columnar stack of phz, as found in $[Cu(NO_3)(phz)]$,[22] and a three-dimensional framework, as in $[Ag_2(NO_3)_2(phz)]$, in which six-membered rings of silvers and strong π–π interactions (3.34 Å) of phz further stabilize the structure.[20]

**Intercalation.** Intercalation of metal-free phenazine or pyrene molecules into metal-coordinated phz stacks is yet another form of observed π–π interactions as found in $[Cu_2(phz)_3(MeOH)_2](PF_6)_2\cdot(phz)$[20] and $[Cu(phz)(MeCN)]_2(PF_6)_2\cdot(pyrene)$,[22] Fig. 8(c,e). In the former complex, the metal-free phz and the dicopper cation $[Cu_2(phz)_3(MeOH)_2]^{2+}$ are alternately stacked along the *c*-axis with the nearest separation of 3.42 Å between the planes, whereas in the latter a pyrene molecule is intercalated into every other phz stack with the interplane distance of 3.37 Å, forming an infinite columnar stack. A similar example is found in copper(I) complex of 2,5-dimethylterephthalonitrile,[23] $[Cu(DMTPN)_2]X(thf)\cdot$ (DMTPN), where $X = BF_4^-$ or $ClO_4^-$, in which each copper atom is tetrahedrally coordinated to four nitrogen atoms of four cyano groups of different DMTPN and a π–π stacking column of alternate coordinated and uncoordinated ligands run through the threefold interpenetrated diamondoid frameworks along the [101] direction, Fig. 8(d).

Table 2. Stacks of Aromatic Moieties Found in Copper(I) and Silver(I) Coordination Polymers

| Compounds | Stacking aromatic molecules | Interplane distances (Å) | Ref. |
|---|---|---|---|
| $[Cu_2(phz)_3(MeOH)_2](PF_6)_2\cdot(phz)$ | Phenazine | 3.42 | 20 |
| $[Cu(phz)_2(H_2O)]ClO_4$ | Phenazine | 3.46 | 20 |
| $[Ag(phz)]ClO_4$ | Phenazine | 3.36 | 20 |
| $[Ag_2(NO_3)_2(phz)]$ | Phenazine | 3.34 | 20 |
| $[Cu_2(\mu-X)_2(phz)]$, X = Cl, Br, or I | Phenazine | 3.36, 3.40, 3.46 | 21 |
| $[Cu(NO_3)(phz)]$ | Phenazine | 3.47 | 22 |
| $[Cu(acr)_2(NO_3)]_2(H_2O)\cdot(phz)$ | Acridine | 3.39, 3.41 | 22 |
| $[Cu_2(PFO_3)(phz)]$ | Phenazine | 3.31, 3.43 | 22 |
| $[Cu(phz)(MeCN)]_2(PF_6)_2\cdot pyrene$ | Phenazine, pyrene | 3.37, 3.47 | 22 |
| $[Cu(DMTPN)_2]ClO_4(thf)\cdot DMTPN$ | 2,5-Dimethylterephthalonitrile | 3.37, 3.51 | 23 |
| $[Cu(apyr)_3]ClO_4$ | 1-Aminopyrene | 3.40, 3.43, 3.46, 3.52 | 25 |
| $[Cu_3(CN)_3(biq)_2]$ | 2,2-Biquinoline | 3.28, 3.35 | 7 |
| $[Cu(CN)(dmphen)]$ | 2,9-Dimethyl-1,10-Phenanthroline | 3.26 | 7 |

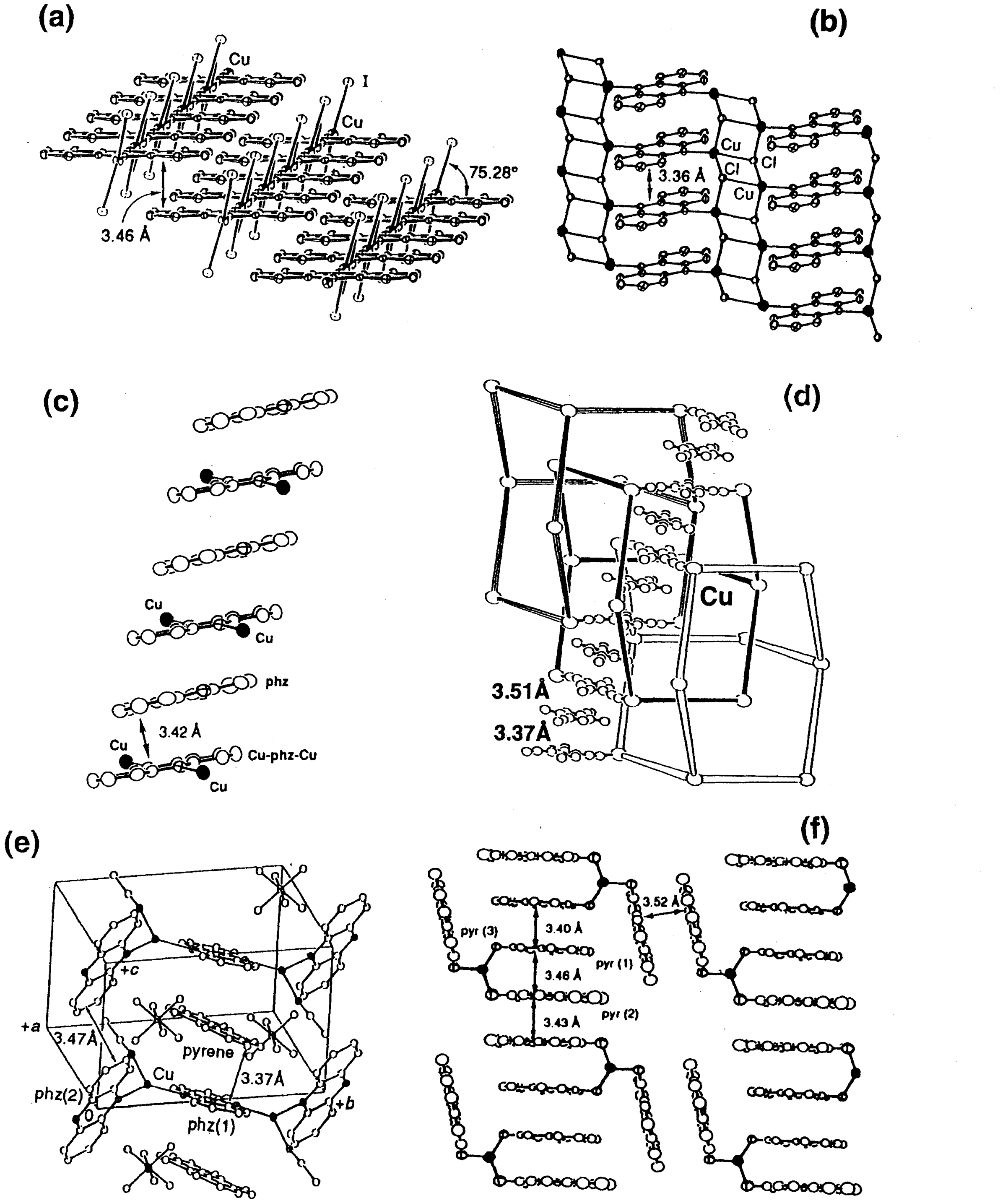


Fig. 8. Different types of π–π stackings: (a) $[Cu_2(\mu\text{-}I)_2(phz)]$ and (b) $Cu_2(\mu\text{-}Cl)_2(phz)]$ (interchain and intersheet π–π stackings), (c) $[Cu_2(phz)_3(MeOH)_2](PF_6)_2\cdot(phz)$ and (d) $[Cu(DMTPN)_2]X(thf)\cdot(DMTPN)$ (intercalation of metal-free aromatic rings into metal-coordinated ring stacks), (e) $[Cu(phz)(MeCN)]_2(PF_6)_2\cdot(pyrene)$ and (f) $[Cu(apyr)_3]ClO_4\cdot MeOH$ (coexistence of a π–π stackings).

The example of coexistence of a π–π stacking system in phz complexes is rather limited, but it is observed in $[Cu(phz)(MeCN)]_2(PF_6)_2(pyrene)$. In this complex there are two columnar stacks: One by intercalation of metal-free phenazine molecules into metal-coordinated phz stacks and the other by the coordinated phz moieties solely, though the overlap is only restricted to the terminal C–C region. These two columns are inclined from each other by 59.4°, Fig. 8(e).

**Charge-Transfer Band.** A large number of copper(I) complexes exhibit intense absorption bands in the visible region, which is ascribed to metal-to-ligand charge-transfer transitions. For example, copper(I) complexes with unsaturated compounds such as pyridine and 2,2′-bipyridine exhibit charge-transfer bands from metal to the ligands.[24] In the solid state, free phz shows a single absorption with high intensity at 372 nm; upon complexation with copper(I) atom, this CT band shifts to ca. 420—560 nm.[20—22] This significant red shift is attributed to the stabilization of the phz π* orbitals caused by double coordination to copper(I) ion.[22] In these complexes, an additional band is observed at ca. 700 nm; this is considered to be a characteristic of copper(I) coordination polymers with phz, Fig. 9.

**Pyrene Stacking.** Obviously, aromatic ring stacking is a general approach to stabilize and synthesize metal complex assemblies. Like phenazine, many other organic molecules with aromatic rings, such as 3,5-bis(2-pyridyl)pyrazole and pyrene, also show π–π interactions in their metal complexes.[14,23] Without π–π interactions, aromatic amines such as naphthylamine and aminophenanthrene rarely form stable monodentate coordination compounds with copper(I) ions. On the contrary, in copper(I) complex of 1-aminopyrene,[25] [Cu(apyr)$_3$]ClO$_4$·MeOH, each copper atom is coordinated by three amine nitrogens in a distorted trigonal geometry and π–π interactions cross-link two columns of aromatic stacks, forming a reasonably stable two-dimensional structure, Fig. 8(f). The average interplanar spacing of 3.43 Å is shorter than that of the free pyrene (3.52 Å).

## S···S Contact System

**Organic Conductive Materials.** Since the initial discoveries that tetrathiafulvalenes (TTF) formed a stable radical cation (in 1970)[26] and that its complex with an electronic acceptor, tetracyanoquinodimethane, TTF·TCNQ, exhibited semiconductivity (in 1973),[27] there has been increasing world attention paied to synthesis of organic metals or synthetic metals based on TTF and its derivatives. Organic superconductivity was first reported in 1980 for tetramethyltetraselenafulvalene hexafluorophosphate, (TMTSF)$_2$PF$_6$, which was found to be superconducting at 0.9 K at 12 kbar.[28] The two-dimensional superconductor ϰ-(BEDT–TTF)$_2$[Cu(NCS)$_2$], where BEDT = bis(ethylenedithio)tetrathiafulvalene, reported in 1988 showed a $T_c$ value of about 10 K.[29] In this complex, BEDT–TTF layers, which are connected only through the S···S contacts, are separated by insulating layers of the polymer anions Cu(NCS)$_2$. During the search for new organic conductive and superconductive materials, we have asked the question: As TTF is a sulfur-rich organic molecule, if metal ions are directly coordinated to TTF and its derivatives, would it be possible to use TTF as a building block to generate supramolecular and macromolecular system by the covalent bonds as well as by S···S contacts?[30] If such system can be designed, its prospect for applications will be promising.[31] Copper atoms play an important role in superconducting copper oxide ceramics with high $T_c$,[32] and the speculation that copper ions coordinated to TTF might create a new molecular system having fascinating conductivity and superconductivity has prompted us to prepare and characterize systematically a series of TTF–copper coordination compounds. In general, the S···S contacts considered to be effective in sulfur-rich conductive compounds refer to those having interplanar S···S separations at 3.35—3.75 Å, close to the sum of two sulfur atom van der Waals radii (3.60 Å), Table 3. A shorter distance has been found in TTF[Pt(dmit)$_2$]$_3$, where the very short S···S contact of 3.23 Å results from a steric effect due to the Pt–Pt bonded dimmer structure.[33]

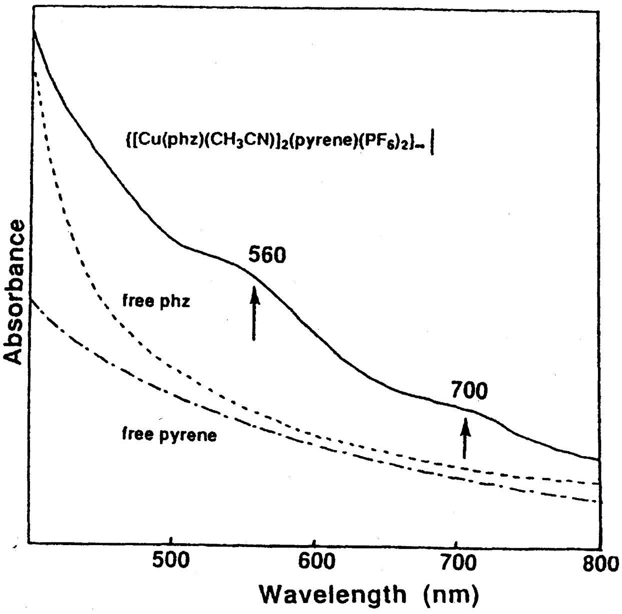


Fig. 9. The Electronic spectra of the free phz, free pyrene and [Cu(phz)(CH$_3$CN)$_2$]$_2$(PF$_6$)$_2$·(pyrene).

**TTF Derivative Complexes with Bookshelf Structure.** The first series of TTF derivatives we have undertaken is tetrakis(methylthio)tetrathiafulvalene (TMT–TTF). When TMT–TTF reacts with copper(I) halide it gives three polymeric complexes with the empirical formula, [Cu$_2$(μ-X)$_2$(TMT–TTF)] (X = Cl$^-$, Br$^-$, I$^-$).[30] All three complexes involve coordination of TMT–TTF directly to copper(I) atom with reasonable bond distances and angles. Each TMT–TTF acts as a tetradentate ligand linking two metal centers forming

Table 3. S···S Contacts in Copper(I) and Silver(I) Coordination Polymers with TTF Derivatives

| Compounds | S···S Distances Å | Ref. |
|---|---|---|
| [Cu$_2$(μ-Cl)$_2$(TMT–TTF)] | 3.53 | 30 |
| [Cu$_2$(μ-Br)$_2$(TMT–TTF)] | 3.63 | 30 |
| [Cu$_2$(μ-I)$_2$(TMT–TTF)] | 3.68 | 30 |
| [Ag(O$_3$SCF$_3$)(TMT–TTF)] | 4.00 | 34 |
| [(CuCl)$_2$TTC$_2$–TTF] | 3.74 | 36(a) |
| [(CuBr)$_2$TTC$_2$–TTF] | 3.577, 3.610 | 36(a) |
| [Cu(TTC$_2$–TTF)]ClO$_4$ | 4.00 | 36(b) |
| [(CuI)$_2$TTC$_2$–TTF] | 3.717, 3.743 | 36(a) |
| [AgNO$_3$(C$_5$H$_4$S$_5$)$_2$] | 3.41, 3.77, 3.84 | 38 |
| [Cu$_4$I$_4$(C$_5$H$_4$S$_5$)$_4$] | 3.257, 3.576<br>3.615, 3.623 | 39 |
| [Ag(O$_3$SCF$_3$)(C$_5$H$_4$S$_5$)] | 3.262, 3.392<br>3.530, 3.589 | 40 |
| [Ag(ClO$_4$)(C$_5$H$_4$S$_5$)] | 3.284, 3.317<br>3.390, 3.440 | 40 |

rhomboid and zigzag or helical structures to give chain and bookshelf structures, respectively, Fig. 9. These polymeric complexes are further associated by a strong S···S contacts of TMT–TTF fragments constituting one-, two-, or three-dimensional networks, Figs. 10 and 11. The S···S contact distances range from 3.53 to 3.75 Å, Table 3. Both structural data and IR spectra indicate the presence of neutral TMT–TTF rather than organic radical cation in the coordination polymers, and as a result, they do not show visible conductivity at room temperature. Reaction of silver(I) trifluoromethanesulfonate with TMT–TTF yielded orange polynuclear silver(I) complex, $[\mathrm{Ag(O_3SCF_3)(TMT\text{–}TTF)}]$, in which each silver(I) ion is six-coordinated by four sulfur atoms from two bridging TMT–TTF groups and two oxygen atoms of the bidentate $\mathrm{O_3SCF_3}$ anions and this results in a two interwoven polymeric chain structure.[34] The closest S···S distance of 4.00 Å between the two chains found in the silver complex is remarkably greater than those in the corresponding copper(I) system, which precludes any strong S···S contacts present.

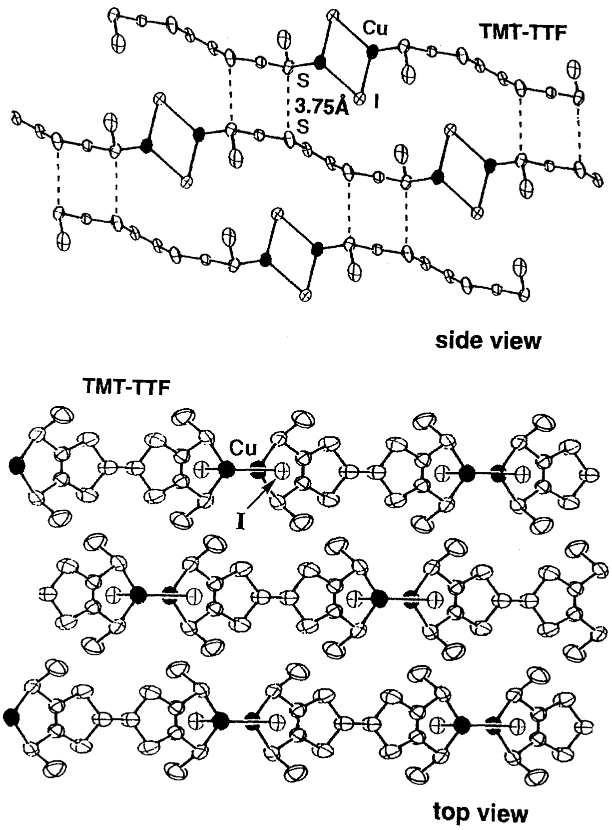


Fig. 11. (a) Side and (b) top views of molecular packing of $[\mathrm{(CuI)_2(TMT\text{–}TTF)}]$. Doted lines represent S···S contacts.

Tetrakis(ethylthio)tetrathiafulvalene ($\mathrm{TTC_2\text{–}TTF}$), which has a central TTF ($\mathrm{C_6S_4}$) $\pi$ system and a side ethylthio chain, is a single-component organic semiconductor with low conductivity ($\sigma_{\mathrm{RT}} \approx 10^{-10}\ \mathrm{S\,cm^{-1}}$).[35] With copper(I) halide, it forms neutral 2 : 1 (metal/ligand) complexes of $[\mathrm{(CuX)_2TTC_2\text{–}TTF}]$ (Fig. 12).[36,37] As in the TMT–TTF system each metal ion is coordinated in a distorted tetrahedral geometry to two bridging halide ions and two sulfur atoms from $\mathrm{TTC_2\text{–}TTF}$ which in turn links two copper atoms forming polymeric chain or helix. The shortest S···S distances between the neighboring chains are 3.74, 3.60, and 3.73 Å for the chloride, bromide, and iodide, respectively. In order to decrease the repulsion between the ethyl groups in neighboring chains all the ethyl groups in one polymeric chain take the same orientation, while the ethyl groups in its two adjacent chains orientate to the opposite direction so that these chains can pack closely to reach the shortest possible S···S contacts. This affords a unique bookshelf type structures.

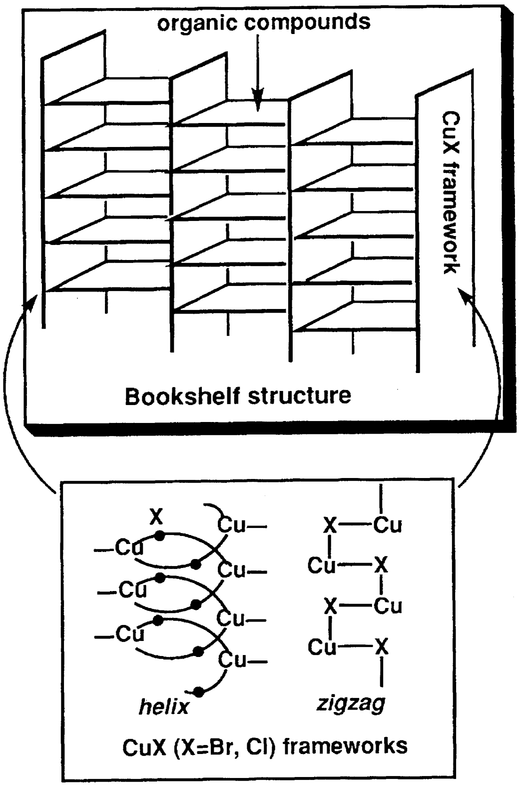


Fig. 10. Schematic diagram of bookshelf structure.

**$\mathbf{C_5H_4S_5}$ Complexes.** The sulfur-rich ligand 4,5-ethylenedithio-1,3-dithiole-2-thione ($\mathrm{C_5H_4S_5}$) can also form novel silver(I)[38] and copper(I)[39] coordination polymers. In $[\mathrm{AgNO_3(C_5H_4S_5)_2}]$ each $\mathrm{C_5H_4S_5}$ displays a bidentate fashion through both thiocabonyl sulfur and thioether sulfur bridging two silver atoms, giving an infinite chain, Fig. 13. The shortest S···S contact of 3.41 Å indicates a strong interaction present between two nearby chains, which leads to a two-dimensional network. In $[\mathrm{Cu_4I_4(C_5H_4S_5)_4}]$ the stepped $\mathrm{Cu_4I_4}$ clusters are bridged by two $\mathrm{C_5H_4S_5}$ ligands and the resultant polymeric chains are further assembled by short interchain S···S contacts (3.257 Å) to form a three-dimensional network. Silver ions in $[\mathrm{Ag(CF_3SO_3)(C_5H_4S_5)}]$ are bridged both by $\mathrm{C_5H_4S_5}$ and $\mathrm{CF_3SO_3}$ to give a two-dimensional structure with S···S contacts containing the shortest distance of 3.262 Å.[40] The $\mathrm{Ag(C_5H_4S_5)_3}$ moieties in $\{[\mathrm{Ag(C_5H_4S_5)_3]ClO_4{\cdot}CH_3CN}\}_2$ are assembled by S···S contacts of 3.284(4)—3.569(2) Å to form a one-dimensional chain structure.

**Conductivity.** Halogen doping of conjugated electron donors has been shown to be an effective strategy for the synthesis of electrically conductive material. Most copper(I) and silver(I) complexes with TTF (or its derivatives) are insulators ($\sigma < 10^{-12}$ S cm$^{-1}$), but their iodine-doped products usually show conductivity or semiconductivity.[30,34,36—39] One of the common features of the conducting process is that the constituent molecules are in a mixed-valence (or partial-oxidation) state, and therefore, a partial oxidation of the ligands can be assumed to have occurred in the above system. A detailed understanding of the conductivity observed in these partially oxidized polymers will only be possible if the structural data are available. The search for new coordination polymers with multidimensionally expanded TTF derivatives is still active and challenging. However, these polymers and their $I_2$-doped conducting products still await practical applications. Problems awaiting solution in this respect include how single crystals of the products are obtained with suitable size for physical measurements, and how electron-filling control of the polymers is efficiently achieved.

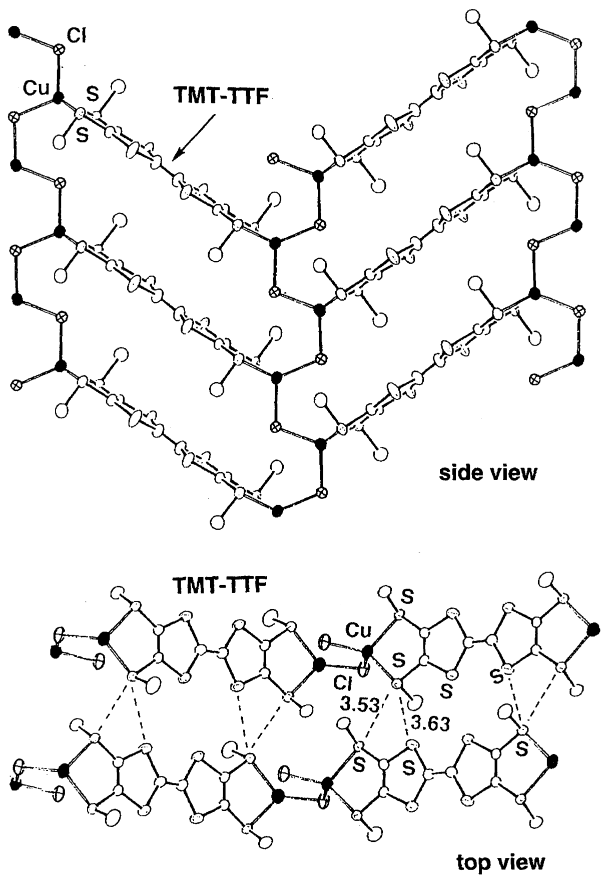


Fig. 12. (a) Side and (b) top views of molecular packing of [$(CuCl)_2$(TMT–TTF)] with bookshelf structure. Doted lines represent S···S contacts.

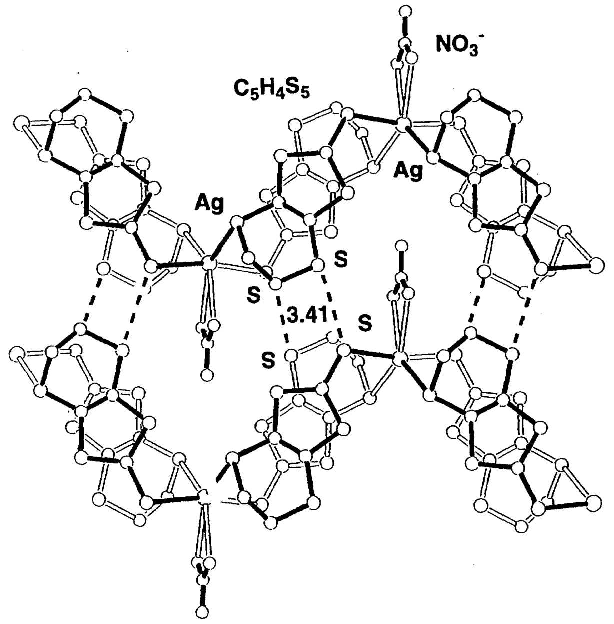


Fig. 13. Molecular packing of [$(Cu(NO_3)C_5H_4S_5)_2$]. Doted lines represent S···S contacts.

## Honeycomb, Graphite, and Helical Structures

**Honeycomb and Graphite Structures.** A variety of choices in linking ligands, together with the different transition-metal coordination geometries exhibited, makes coordination polymer chemistry a fruitful research field. Unique structures such as honeycomb, graphite, infinite chain, single helix, and two- or three-dimensional networks, have been characterized in an impressive number of polynuclear copper(I) and silver(I) complexes with 2,1,3-benzothiadiazole or pyrazine. 2,1,3-Benzothiadiazole (btd) is considered to be a potential ligand for construction of honeycomb and graphite complexes.[41] In [$Cu_2(ClO_4)(btd)_3$]$ClO_4$·2thf, each copper atom is coordinated to one oxygen of the perchlorate and three nitrogens of different btd molecules and the structure is composed of a honeycomb framework [$Cu_6(btd)_6$]$^{6+}$ based on six-membered rings of coppers interconnected by the ligands, Fig. 14. The 2-D sheet rings composed of the six copper atoms are still maintained in [$Cu(HPO_3F)(btd)$], even though $HPO_3F$ anions also take part in the interconnecting of the ring. The most remarkable feature in the polymer with nitrate, [$Cu(NO_3)(btd)$], is that the six-membered rings of coppers interconnected by btd and the bidentate bridging $NO_3^-$ are in a chair form. This leads to stacking of btd molecules within and between the 2-D sheets and formation of a layered structure similar to that of graphite,[41] Fig. 15. The shortest interplanar spacing of btds within and between the sheets are 3.30 and 3.39 Å, respectively, similar to that between the layers composed of six-membered rings of carbons in graphite, Fig. 16. One more remarkable feature in this complex is its electrical conductivity, with $\sigma = 10^{-6.3}$ S cm$^{-1}$. It is interesting to see that the similar silver(I) complex, [$Ag(btd)$]$ClO_4$, does not have honeycomb or graphite structure, but has an infinite chain of Ag atoms interconnected by btd groups. The preference of silver(I) ion for a two-coordination linear geometry rather than three- or four-coordination geometries might be responsible for this discrepancy.

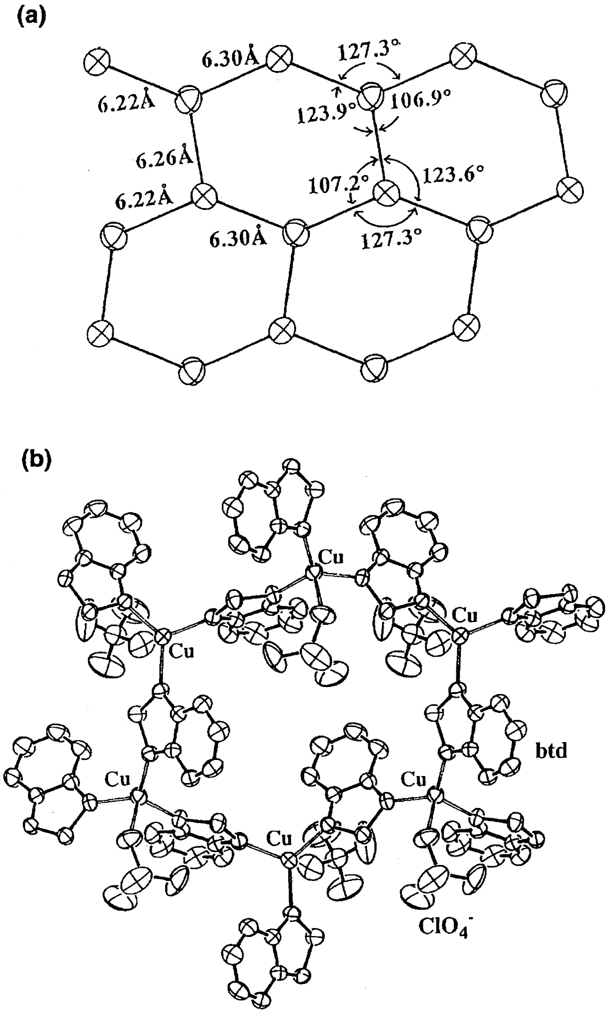


Fig. 14. (a) 2D Honeycomb structure of $[Cu_2(ClO_4)(btd)_3]$-$(ClO_4)$, where only copper centers are presented, and (b) the six-membered ring of coppers connected by btd molecules.

Pyrazine (pz) and substituted pyrazines have long been known to act as *exo*-bidentate ligands to linearly bridge metal ions, generating oligomeric and polymeric metal complexes with infinite chain and pleated sheet structures, double and triple interpenetrating frameworks and interwoven honeycomb architecture,[42] Fig. 17. Kitagawa et al. have explored ways to modify the substituents to tailor the copper/pyrazine polymer structures, such as mode of polymerization, dimensionality and frameworks.[43—46] The complex $[Cu(pz)_{3/2}(CH_3CN)](PF_6)\cdot 0.5Me_2CO$ contains a chair-form of hexanuclear copper units bridged by pz, which constituents an infinite two-dimensional sheet spreading out along the *ab* plane (Fig. 18),[44] while the ternary pz complex $[Cu_2(\mu$-3-methylpyridazine$)_2(pz)_3](ClO_4)_2$ contains three- and four-coordinate tetranuclear copper units which are sequentially linked by pyrazines, affording a zigzag cation chain.[46]

In the substituted pyrazine system, the polymerization modes are greatly affected by the substituents.[43] While $[Cu_2(Me_4pz)_3](ClO_4)_2$ gives a zigzag chain,[44] $[Cu_2(2,6\text{-}Me_2pz)_3](ClO_4)_2(Me_2CO)_2$ shows planar sheets composed of $Cu_6$ hexagons. Our findings reveal that the basic unit of these polymers can be considered as one-dimensional zigzag chains. The interchain connection, which causes the poly-

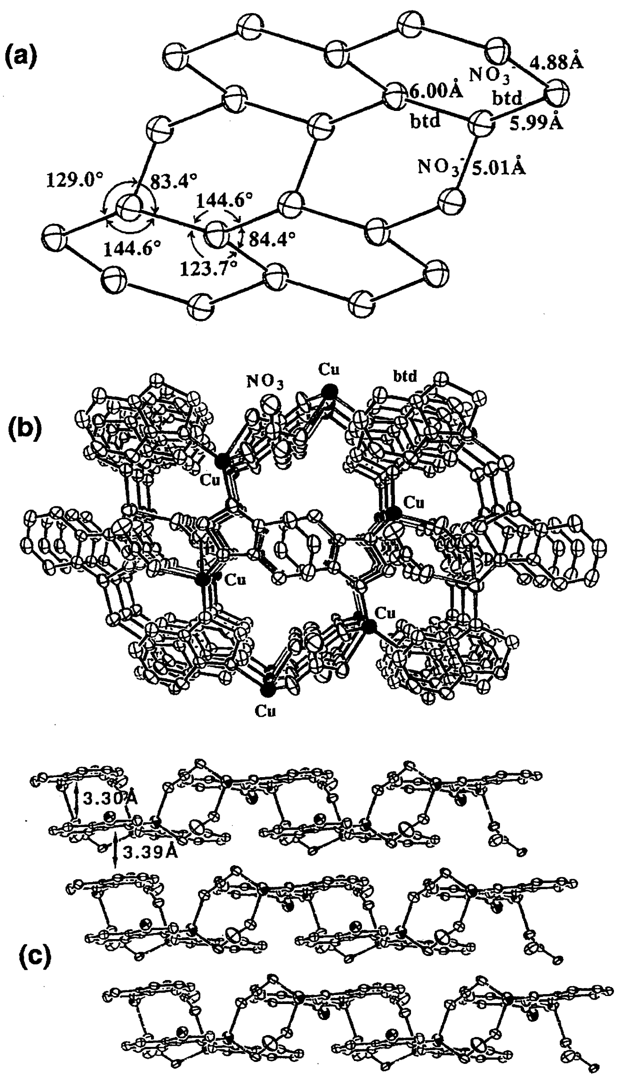


Fig. 15. (a) 2D Honeycomb structure of $[Cu(NO_3)(btd)]$, where only copper centers are presented, and (b) top and (c) side views of the graphite-like packing arrangement.

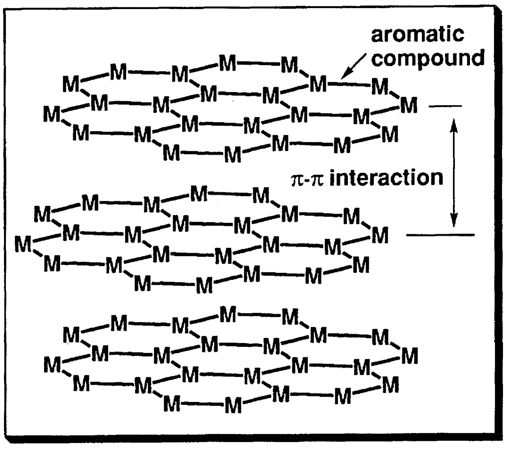


Fig. 16. Schematic diagrams of graphite structure.

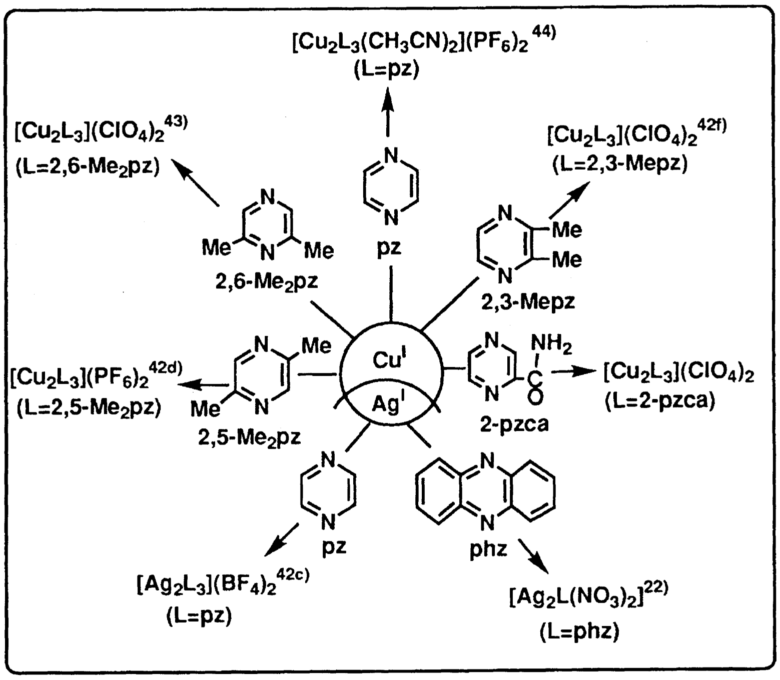


Fig. 17. Cu(I) and Ag(I) complexes of pyrazine and the derivatives with honeycomb structure.

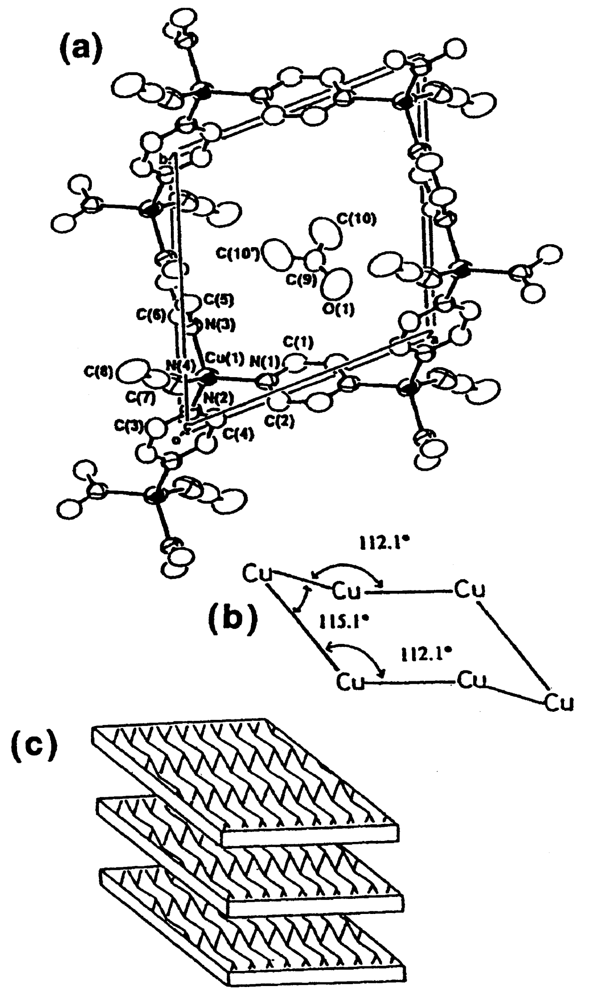


Fig. 18. (a) Structure of $[Cu_2(pz)_{2/3}(CH_3CN)](PF_6)\cdot 0.5\ Me_2CO$, (b) hexagonal motif, and (c) layered structure.

merization mode to vary, largely depends on the spatial factor of the pyrazine molecules, such as size and orientation of the substituents.[7]

**Helical Structure.** Recently we have studied copper(I) coordination polymers with the tridentate ligand, pyrazinecarboxamide (pzca).[47] Reaction of an acetone solution of the copper(I) metal salt with 2-pzca yielded deep red brick complexes $[Cu_2(pzca)_3](ClO_4)_2(Me_2CO)_2$ and $[Cu(pzca)(Me_2CO)_{0.5}](BF_4)$. We have found that it is possible to use this simple molecular building block to generate an unusual hexagonal circular array of ligand-bridged Cu(I) ions. Depending upon whether the counter ion is perchlorate or tetrafluroborate, these arrays assemble respectively as a honeycomb structure or as a helical array. The most remarkable feature of the tetrafluroborate is that the infinite helices generate a three-dimensionally extended hexagonal array of Cu atoms with a large cavity where the counter anions, $BF_4^-$, are placed (Fig. 19). Organic and inorganic polymers existing in helical structures are of great practical and theoretical interest.[48] Most of previously reported single and double helical polynuclear copper(I) and silver(I) complexes based on oligopyridine or oligophenanthroline ligands are generated by the complexation of two ligands twisted around the tetrahedral metal ions lying on the helical axis. However, in $[Cu(pzca)(Me_2CO)_{0.5}](BF_4)$, the primary coordination involves pzca groups tridentately bridging two copper atom, and the helical structure is further stabilized by secondary interaction between Cu atoms and the bridging acetone as the continuous strand, Fig. 20. It demonstrates that assembled helical structures of copper(I) complexes with tridentate oligopyrazine ligands, rather than bidentate oligopyridine or oligophenanthroline ligands, can also be achieved by introducing a suitable spacer group like acetone between the metal-binding sites to match the metal ion stereochemical

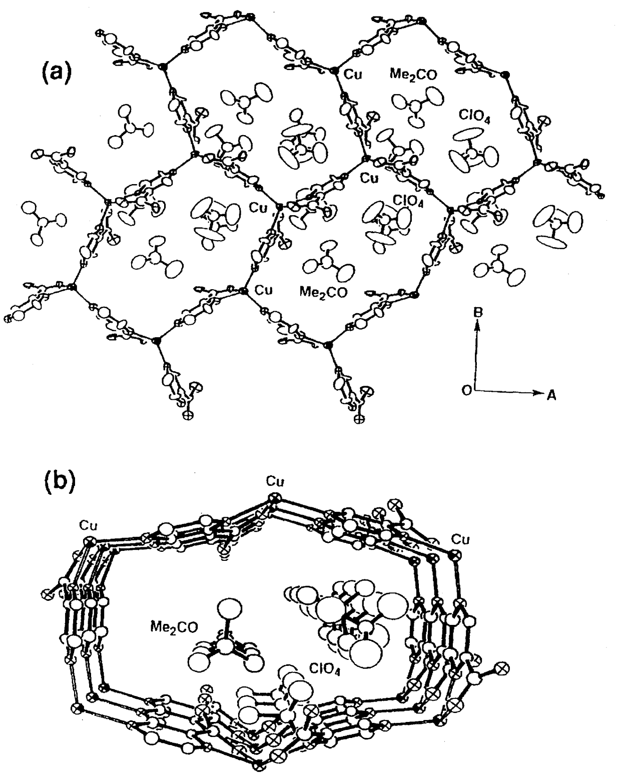
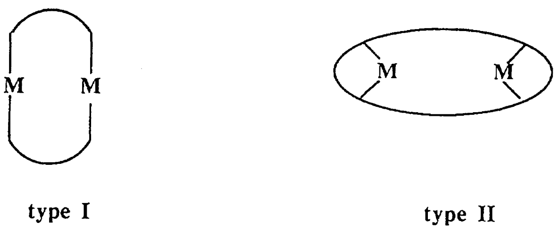


Fig. 19. (a) 2D Honeycomb structure of $[Cu_2(pzca)_3](ClO_4)_2(Me_2CO)_2$ and (b) the overlapped honeycomb array generating hexagonal channels to accommodate $ClO_4^-$ ions and acetone molecules.

preference.[48] The conditions for self-assembly of Cu(I)/pzca derived from the detailed study of the complex might be able to be applied to different systems for the successful synthesis of many other helical coordination compounds.

## Macrocyclic and Photochromic Ligand System

**Double Ring Complex.** Studies on the ion trap have been developed and form an important subdivision of host–guest chemistry which involves two structural types of host molecules, a cyclic and macrocyclic.[49] Many cyclic multidentate organic ligands, such as cryptants, crown ethers, cyclophanes, and other coronands have been synthesized; formation of metal complexes with these polytidentate ligands is well established. In terms of trapping transition metal ions two types of macrocyclics have appeared, in type I metal ions, are involved as ring members and in type II, donor groups are involved as a ring member to which metal ions are coordinated as a pendant (Chart 1).



type I type II

Chart 1.

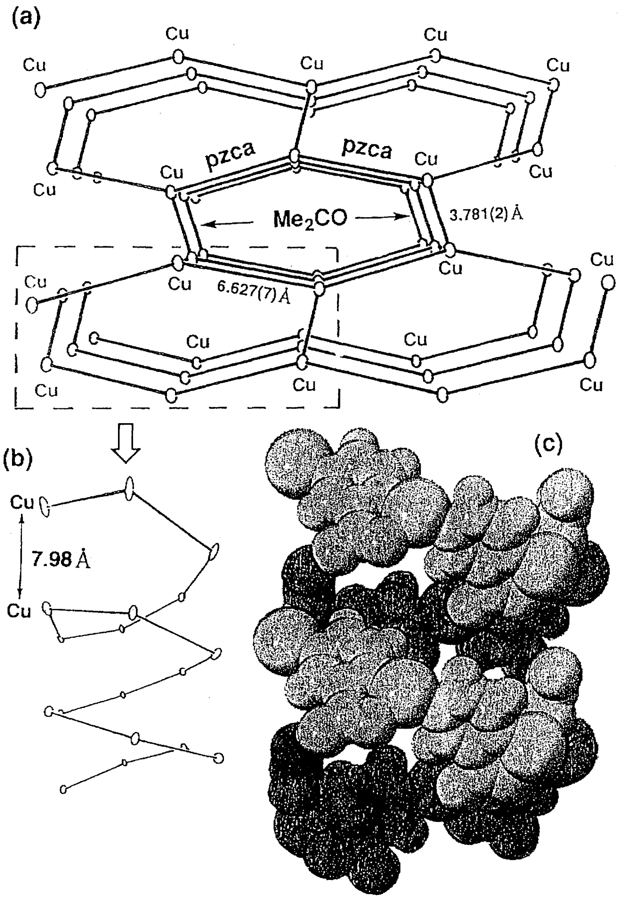


Fig. 20. (a) Overlapped hexagonal cyclic array and (b) the helical cyclic array in $[Cu(pzca)(Me_2CO)_{0.5}](BF_4)$, where only copper centers are presented. (c) Space filling model of $[Cu(pzca)(Me_2CO)_{0.5}]^+$. $BF_4^-$ ions are deleted for clarity.

The dinuclear macrocyclic system of copper(I) and silver(I) with 1,6-bis(diphenylphosphino)hexane (dpph) has been characterized by Kitagawa et al.[50] In $[M_2(\mu\text{-}X)_2(dpph)_2]$ ($X = ClO_4^-$, $NO_3^-$, $PF_2O_2^-$, or $CH_3CO_2^-$), two diphosphines and two metal ions form a 18-membered macrocycle (type I) which traps two anions each bridging two metal centers. Thus each structure has two rings sharing two metal atoms: the outer larger one is composed two bridging diphosphines while the inner ring contains two bridging anions, Fig. 21.

**Control of Dimensionality.** Macrocyclic thioether com-

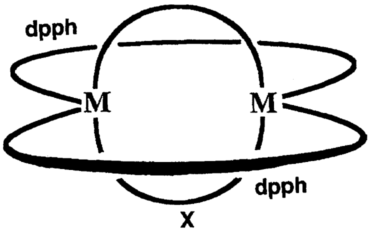


Fig. 21. $[M_2(dpph)_2(\mu\text{-}X)_2]$ with double rings (dpph = bis(diphenylphosphino)hexane; $X = ClO_4^-$, $NO_3^-$, $PF_2O_2^-$, or $CH_3CO_2^-$).

plexes of copper(I) and copper(II) have been the subject of much interest for a long time as simple models for blue copper proteins. By contrast, the investigation of the corresponding silver(I) complexes has developed only recently.[51] We have successfully examined silver(I) and copper(II) complexes with 1,5,9,13-tetrathiacyclohexadecane-3,11-diol but failed in isolating the stable corresponding copper(I) complex.[52] In the mononuclear copper(II) complex $[Cu\{(OH)_2[16]aneS_4\}][ClO_4]_2$, the crown thioether traps the metal ion in the center of the 16-menbered ring (type II) by coordination of four thioether donors to the copper atom, even though the macrocycle itself is strongly pleated and twisted. By contrast, the *exo* conformation mode of the macrocycle has been found in the silver(I) complex, $[Ag\{(OH)_2[16]aneS_4\}]NO_3$; in this the thioether adopts a much flattened conformation with an opened 16-membered cavity filled with $NO_3^-$ and a three-dimensional tetrahedral polymeric network is created (Fig. 22). This is obviously attributable in part to the metal-ion size in respect to the cavity size of the macrocycle. On the other hand, formation of two silver complexes with a polymeric tetrahedral network also results from the strong tendency of Ag(I) ion to achieve a tetrahedral coordination sphere rather than square planar, which can not be obtained simply by distortion or rearrangement of the macrocycle. The study reveals that the conformation of the ligand and the dimensionality of its complexes in crown thioether system are also controlled by the counter anion as well as the metal ions. This conclusion is in line with the results in the copper(I) and silver(I) complexes of 2,11-dithia[3,3]paracyclophane.[53] Although this thia-bridged cyclophane acts as a rod-like ligand linking two metal atoms in all compounds studied, if a second bridging ligand such as a halide ion exists, it gives a wide arrange of coordination polymers from one-dimensional infinite chains observed in $[Cu_2Br_2(dtpcp)(MeCN)_2]$ to two-dimensional sheets in $[Cu_2I_2(dtpcp)(MeCN)_2]\cdot thf$, or three-dimensional frameworks found in $[Ag(dtpcp)(NO_3)]$, Fig. 23(a,b,c).

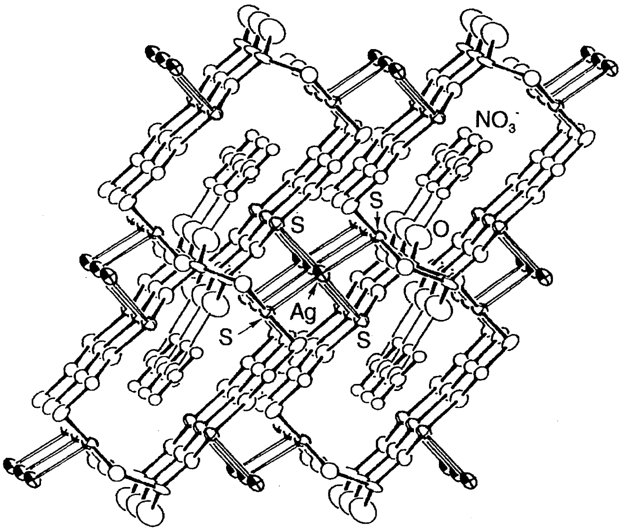


Fig. 22. Molecular arrangements of three-dimensional silver(I) complex, $[Ag\{(OH)_2[16]aneS_4\}]NO_3$.

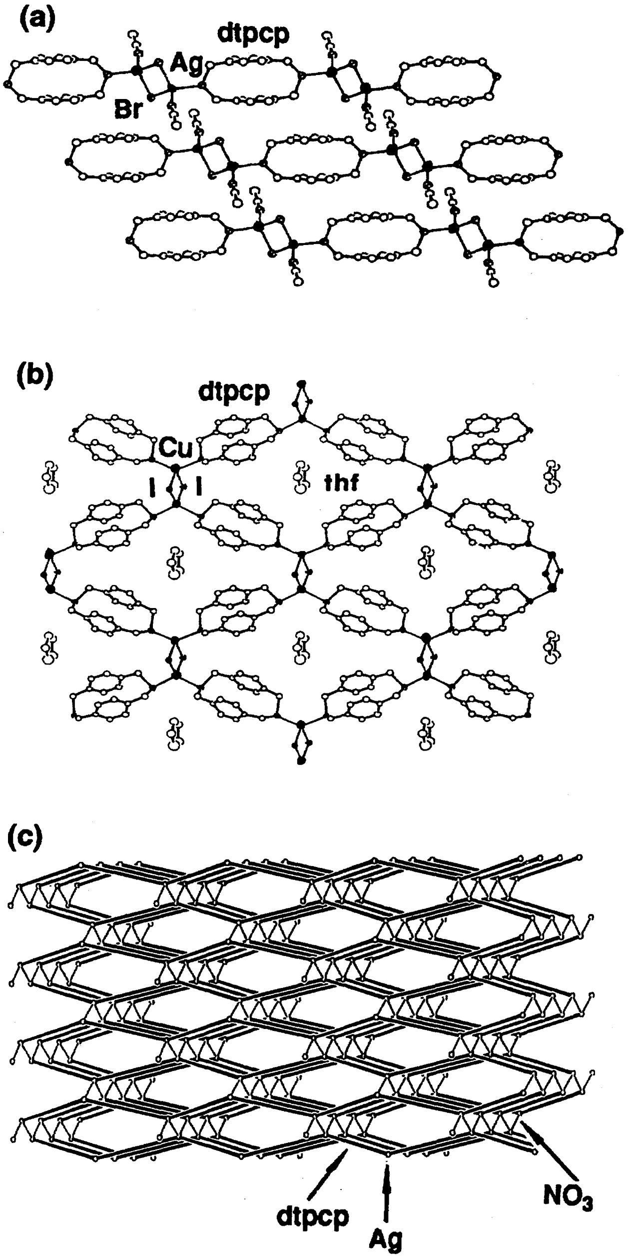


Fig. 23. (a) Molecular arrangements of 1D-$[Cu_2Br_2(dtpcp)(MeCN)_2]$, (b) 2D-$[Cu_2I_2(dtpcp)(MeCN)_2]\cdot thf$, and (c) 3D-$[Ag(dtpcp)(NO_3)]$.

**Light-Induced Crystal Oscillation.** Study of photochromic compounds, which undergo thermally irreversible and fatigue-resistant photochromic reactions, is one of the key points in the current revival of interest in designing of light-triggered molecular and supramolecular devices.[54] Reaction of copper(I) salt with photochromatic ligand *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (*cis*-L) in acetone produced a photoreactive polynuclear copper(I) complex $[Cu(\textit{cis}\text{-}L)_2]ClO_4$ in which each metal center is coordinated with one CN group of the four dithienylethene molecules.[55] Each *cis*-L in turn bridges two copper atom with two cyano groups, leading to an infinite chain of metal cations, as shown in Fig. 24(a). The complex has been found

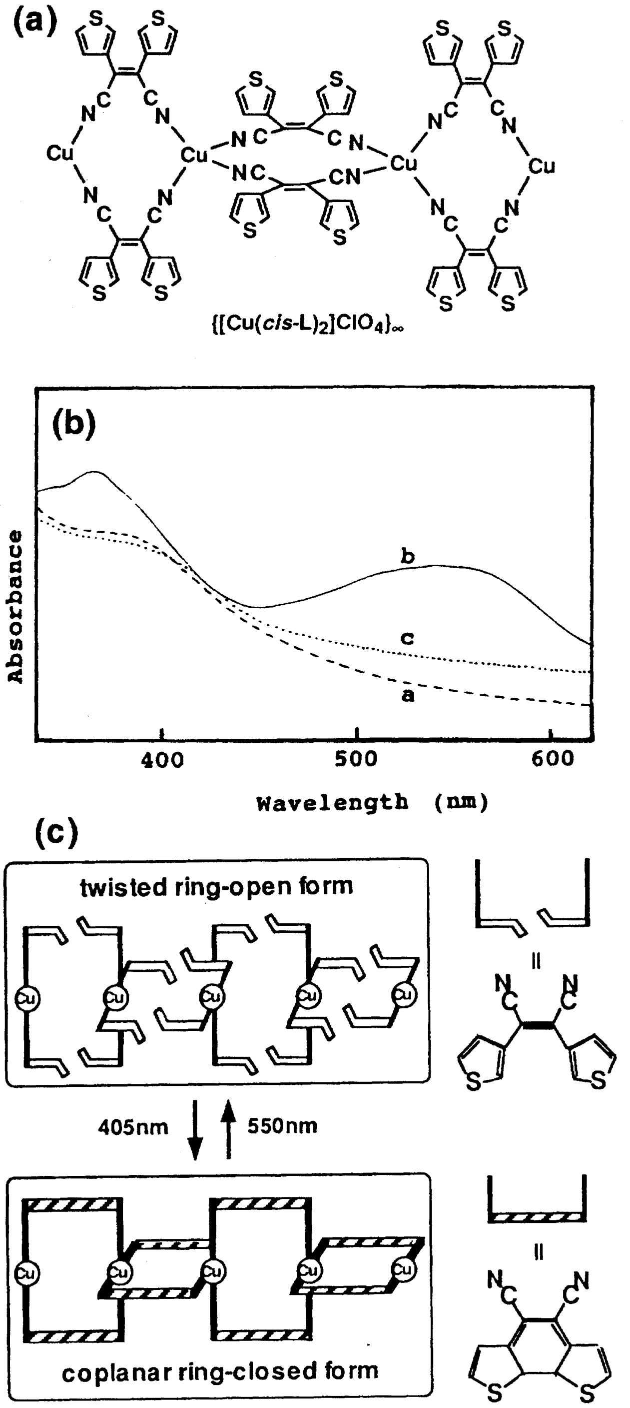


Fig. 24. (a) Schematic figure showing one-dimensional array of [Cu(*cis*-L)$_2$]ClO$_4$. (b) Absorption spectra of the complex as KBr disc: **a**, before irradiation; **b**, in the photostationary state under irradiation with 405 nm light; **c**, irradiation of **b** with 550 nm light. (c) Schematic view of reversible light-induced cyclization/ring-opening process.

in crystalline state to exhibit the reversible photoinduced cyclization/ring-opening process. During the cyclization reaction of *cis*-L, the two thiophene rings twisted with dihedral angle of 48.3° approach each other and the ethene double bond is converted into a single bond. The most important feature of the compound is that this is the first example of copper(I) coordination polymers with photochromic ligand to show a light-induced crystal oscillation, Fig. 24(b).

In conclusion, the rational design of metal-containing polymers by self-assembly of metal complexes has been one of the most exciting and challenging subjects in solid-state coordination chemistry. This paper reviews many of our current developments in the search for new supramolecular and macromolecular coordination compounds by the incorporation of a copper(I) or silver(I) ion into unsaturated N-containing ligands and sulfur-rich organic molecular system. We have demonstrated that the development of multifunctional ligands which can give organized supermolecules upon complexation to two or more metals is a key feature in crystal engineering. We have found that an important step toward the rational design of such systems is the controlled linking of simple building blocks. Thus, apart from consideration of the fragments, there are many other elements to be taken into account concerning the linkage: The preference of the metal ion for specific stereochemistry, intermolecular interactions such as hydrogen-bonding, π–π stackings, and S···S contacts, host–guest interactions, as well as complementarity of solvents and anions. We expect that with the development of the methodology based on these results, the synthesis is possible of more complex multidimensional compounds which will have important implications for the construction of new functional solid inorganic materials.

The authors are indebted to professor Susumu Kitagawa of Tokyo Metropolitan University for his outstanding contributions to the studies on copper(I) and silver(I) coordination polymers described in this paper. This work was partially supported by a Grant-in-Aid for Science Research from the Ministry of Education, Science, Sports and Culture. The authors are also grateful to Kinki University for financial support.

## References

1) a) "Transitional Metals in Supramolecular Chemistry," ed by L. Fabbrizzi and A. Poggi, Kluwer Academic Publishers, The Netherlands (1994); b) A. Müller, H. Reuter, and S. Dillinger, *Angew. Chem., Int. Ed. Engl.*, **34**, 2328 (1995).

2) a) B. F. Abraham, B. F. Hoskins, J. Liu, and R. Robson, *J. Am. Chem. Soc.*, **113**, 3045 (1991); b) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, **112**, 1546 (1990); c) T. Soma, H. Yuge, and T. Iwamoto, *Angew. Chem., Int. Ed. Engl.*, **33**, 1665 (1994); d) I. Dance, P. Dean, and K. Fisher, *Angew. Chem., Int. Ed. Engl.*, **34**, 314 (1995).

3) a) L. R. MacGillivray, S. Subramanian, and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, **1994**, 1325; b) M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi, and K. Ogura, *J. Am. Chem. Soc.*, **117**, 7287 (1995); c) O. M. Yaghi and G. Li, *Angew. Chem., Int. Ed. Engl.*, **34**, 207 (1995); d) L. Carlucci, G. Ciani, D. M. Proserpio, and A. Sironi, *J. Chem. Soc., Chem. Commun.*, **1994**, 2755; e) O. J. Gelling, F. van Bolhuis, and B. L. Feringa, *J. Chem. Soc., Chem. Commun.*, **1991**, 917; f) T. M. Garrett, U. Koert, J.-M. Lehn, A.

Rigault, D. Meyer, and J. Fisher, *J. Chem. Soc.*, *Chem. Commun.*, **1990**, 557; g) M. Fujita and K. Ogura, *Bull. Chem. Soc. Jpn.*, **69**, 1471 (1996).

4) a) L. Carlucci, G. Ciani, D. M. Proserpio, and A. Sironi, *J. Am. Chem. Soc.*, **117**, 4562 (1995); b) T. Otieno, S. J. Rettig, R. C. Thompson, and J. Trotter, *Inorg. Chem.*, **32** 1607 (1993).

5) R. G. Pearson, *J. Chem. Educ.*, **45**, 643 (1968).

6) a) B. J. Hathaway, in "Comprehensive Coordination Chemistry," ed by G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford (1987), Vol. 5, pp. 533—774; b) R. J. Lancashire, in "Comprehensive Coordination Chemistry," ed by G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon, Oxford (1987), Vol. 5, pp. 775—859.

7) S. Kitagawa and M. Munakata, "Trends in Inorganic Chemistry," (1993), p.3.

8) a) O. Ermer, *Adv. Mater.*, **3**, 608 (1991); b) G. R. Desiraju, "Crystal Engineering, The Design of Organic Solids," Elsevier, Amsterdam (1989); c) J. D. Wright, "Molecular Crystals," 2nd ed, Cambridge University Press, Cambridge (1994).

9) a) S. B. Copp, S. Subramanian, and M. J. Zaworotko, *J. Am. Chem. Soc.*, **114**, 8719 (1992); b) O. M. Yaghi, G. Li, and T. L. Groy, *J. Chem. Soc.*, *Dalton Trans.*, **1995**, 727; c) M. Mitsmi, J. Toyoda, and K. Nakasuji, *Inorg. Chem.*, **34**, 3367 (1995); d) K. Endo, T. Sawaki, M. Koyanagi, K. Kobayashi, and H. Masuda, *J. Am. Chem. Soc.*, **117**, 8341 (1995).

10) S. Kitagawa, S. Kawata, Y. Nozaka, and M. Munakata, *J. Chem. Soc.*, *Dalton Trans.*, **1993**, 1399.

11) E. Dubler and W. Bensch, *Inorg. Chim. Acta*, **125**, 37 (1986).

12) M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa, and M. Maekawa, *J. Am. Chem. Soc.*, **118**, 3117 (1996).

13) L. P. Wu, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, and M. Munakata, *J. Chem. Soc.*, *Dalton Trans.*, **1996**, 2031.

14) a) S. L. James, G. Verspui, A. L. Spek, and G. van Koten, *J. Chem. Soc.*, *Chem. Commun.*, **1996**, 1309; b) C.-W. Chan, D. M. P. Mingos, A. J. P. White, and D. J. Williams, *J. Chem. Soc.*, *Chem. Commun.*, **1996**, 81; c) D. S. Reddy, Y. E. Ovchinnikov, O. V. Shishkin, Y. T. Struchkov, and G. R. Desiraju, *J. Am. Chem. Soc.*, **118**, 4085 (1996).

15) M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Yamamoto, M. Maekawa, and K. Moriwaki, *Inorg. Chim. Acta*, in press.

16) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

17) M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa, M. Maekawa, S. Kawata, and S. Kitagawa, *J. Chem. Soc.*, *Dalton Trans.*, **1995**, 4099.

18) S. H. Kim and R. B. Martin, *J. Am. Chem. Soc.*, **106**, 1707 (1984).

19) G. Ferraudi and S. Muralidihavan, *Coord. Chem. Rev.*, **36**, 46 (1981).

20) M. Munakata, S. Kitagawa, N. Ujimaru, M. Nakamura, M. Maekawa, and H. Matsuda, *Inorg. Chem.*, **32**, 826 (1993).

21) M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Honda, and S. Kitagawa, *J. Chem. Soc.*, *Dalton Trans.*, **1994**, 2771.

22) T. Kuroda-Sowa, M. Munakata, H. Matsuda, S. Akiyama, and M. Maekawa, *J. Chem. Soc.*, *Dalton Trans.*, **1995**, 2201.

23) T. Kuroda-Sowa, M. Yamamoto, M. Munakata, M. Seto, and M. Maekawa, *Chem. Lett.*, **1996**, 349.

24) M. Munakata, S. Kitagawa, S. Kosome, and A. Asahara, *Inorg. Chem.*, **25**, 2622 (1986); S. Kitagawa, M. Munakata, and A. Higashie, *Inorg. Chim. Acta*, **59**, 219 (1982).

25) M. Munakata, J. Dai, M. Maekawa, T. Kuroda-Sowa, and J. Fukui, *J. Chem. Soc.*, *Chem. Commun.*, **1994**, 2331.

26) F. Wudl, G. M. Smith, and E. J. Hufnagel, *J. Chem. Soc.*, *Chem. Commun.*, **1970**, 1453.

27) J. P. Ferraris, D. O. Cowan, V. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).

28) a) D. Jerome, A. Mazand, M. Ribault, and K. Bechgaard, *J. Phys. Lett.*, **41**, L95 (1980); b) K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, and N. Thorup, *Solid State Commun.*, **33**, 1119 (1980).

29) H. Urayama, H. Yamochi, G. Saito, K. Nozawa, K. Oshima, A. Kawamoto, and J. Tanaka, *Chem. Lett.*, **1988**, 55.

30) M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Hirota, and S. Kitagawa, *Inorg. Chem.*, **34**, 2705 (1995).

31) T. Jørgensen, T. K. Hansen, and J. Becher, *Chem. Soc. Rev.*, **1994**, 41.

32) F. K. Adrian and D. O. Cowan, *Chem. Eng.*, **1992**, 24.

33) M. Bousseau, L. Valade, J.-P. Legros, P. Cassoux, M. Gardauskas, and L. V. Interrante, *J. Am. Chem. Soc.*, **108**, 1908 (1986).

34) M. Munakata, L. P. Wu, X. Gan, T. Kuroda-Sowa, and Y. Suenaga, *Mol. Cryst. Lig. Cryst.*, **284**, 319 (1996).

35) K. Imaeda, T. Enoki, Z. Shi, P. Wu, N. Okada, H. Yamochi, G. Saito, and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, **60**, 3163 (1987).

36) a) X. Gan, M. Munakata, T. Kuroda-Sowa, M. Maekawa, and Y. Misaki, *Polyhedron*, **14**, 1343 (1995); b) X. Gan, M. Munakata, T. Kuroda-Sowa, M. Maekawa, and M. Yamamoto, *Polyhedron*, **14**, 1647 (1995).

37) X. Gan, M. Munakata, T. Kuroda-Sowa, and M. Maekawa, *Bull. Chem. Soc. Jpn.*, **67**, 3009 (1994).

38) J. Dai, M. Munakata, T. Kuroda-Sowa, Y. Suenaga, L. P. Wu, and M. Yamamoto, *Inorg. Chim. Acta*, **255**, 163 (1997).

39) J. Dai, M. Munakata, L. P. Wu, T. Kuroda-Sowa, and Y. Suenaga, *Inorg. Chim. Acta*, in press.

40) J. J. Dai, T. Kuroda-Sowa, M. Munakata, M. Maekawa, Y. Suenaga, and Y. Ohno, *J. Chem. Soc.*, *Dalton Trans.*, in press.

41) M. Munakata, T. Kuroda-Sowa, M. Maekawa, M. Nakamura, S. Akiyama, and S. Kitagawa, *Inorg. Chem.*, **33**, 1284 (1994).

42) a) O.-S. Jung and C. G. Pierpont, *J. Am. Chem. Soc.*, **116**, 2229 (1994); b) T. Soma, H. Yuge, and T. Iwamoto, *Angew. Chem.*, *Int. Ed. Engl.*, **33**, 1665 (1994); c) L. Carlucci, G. Ciani, D. M. Proserpio, and A. Sironi, *J. Am. Chem. Soc.*, **117**, 4562 (1995); d) T. Otieno, S. J. Rettig, R. C. Thompson, and J. Trotter, *Inorg. Chem.*, **32**, 1607 (1993); e) L. R. MacGillivray, S. Subramanian, and M. J. Zaworotko, *J. Chem. Soc.*, *Chem. Commun.*, **1994**, 1325; f) M. M. Turnbull, G. Pon, and R. D. Willett, *Polyhedron*, **10**, 1835 (1991).

43) S. Kitagawa, S. Kawata, M. Kondo, Y. Nozaka, and M. Munakata, *Bull. Chem. Soc. Jpn.*, **66**, 3387 (1993).

44) S. Kitagawa, M. Munakata, and T. Tanimura, *Inorg. Chem.*, **31**, 1714 (1992).

45) S. Kawata, S. Kitagawa, M. Kondo, I. Furuchi, and M. Munakata, *Angew. Chem.*, *Int. Ed. Engl.*, **33**, 1759 (1994).

46) S. Kitagawa, M. Munakata, and T. Tanimura, *Chem. Lett.*, **1991**, 623.

47) M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, K. Moriwaki, and S. Kitagawa, submitted for publication.

48) a) J.-M. Lehn, "Supramolecular Chemistry," VCH, Weinheim (1995); b) N. Ohta, H. Masuda, and O. Yamauchi, *Angew. Chem.*, *Int. Ed. Engl.*, **35**, 531 (1996); c) O. J. Gelling, F. van Bolhuis, and B. L. Feringa, *J. Chem. Soc.*, *Chem. Commun.*, **1991**, 917; d) C. Piguet, G. Bernardinelli, B. Bocquet, A. Quattropani, and A. F. Williams, *J. Am. Chem. Soc.*, **114**, 7440

(1992); e) S. Rüttimann, C. Piguet, G. Bernardinelli, B. Bocquet, and A. F. Williams, *J. Am. Chem. Soc.*, **114**, 4230 (1992).

49) a) R. A. Bell, G. G. Christoph, F. R. Fronczek, and R. E. March, *Science*, **190**, 151 (1975); b) B. Dietrich, J. Guilhem, J.-M. Lehn, C. Pascard, and E. Sonveaux, *Helv. Chim. Acta*, **67**, 91 (1984); c) F. Voegtle, I. Lueer, V. Balzani, and N. Armaroli, *Angew. Chem., Int. Ed. Engl.*, **30**, 1333 (1991).

50) S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa, and M. Munakata, *Inorg. Chem.*, **34**, 1455 (1995).

51) a) S. R. Cooper and S. C. Rawle, *Struct. Bonding (Berlin)*, **72**, 1 (1990); b) A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, **35**, 1 (1990); c) S. R. Cooper, *Acc. Chem. Res.*, **21**, 141 (1988); d) G. Wu, W. Jiang, J. D. Lamb, J. S. Bradshaw, and R. M. Izatt, *J. Am. Chem. Soc.*, **113**, 6538 (1991).

52) M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa, and M. Maekawa, *J. Chem. Soc., Dalton Trans.*, **1995**, 3215.

53) M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, and S. Nakagawa, *J. Chem. Soc., Dalton Trans.*, **1996**, 1525.

54) a) S. L. Gilat, S. H. Kawai, and J.-M. Lehn, *Chem. Eur. J.*, **1**, 275 (1995); b) S. H. Kawai, S. L. Gilat, R. Ponsinet, and J.-M. Lehn, *Chem. Eur. J.*, **1**, 285 (1995).

55) M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, and K. Furuichi, *J. Am. Chem. Soc.*, **118**, 3305 (1996).

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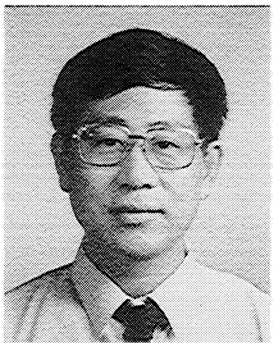

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