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TOWARD THE CONSTRUCTION OF FUNCTIONAL SOLID-STATE SUPRAMOLECULAR METAL COMPLEXES CONTAINING COPPER(I) AND SILVER(I)

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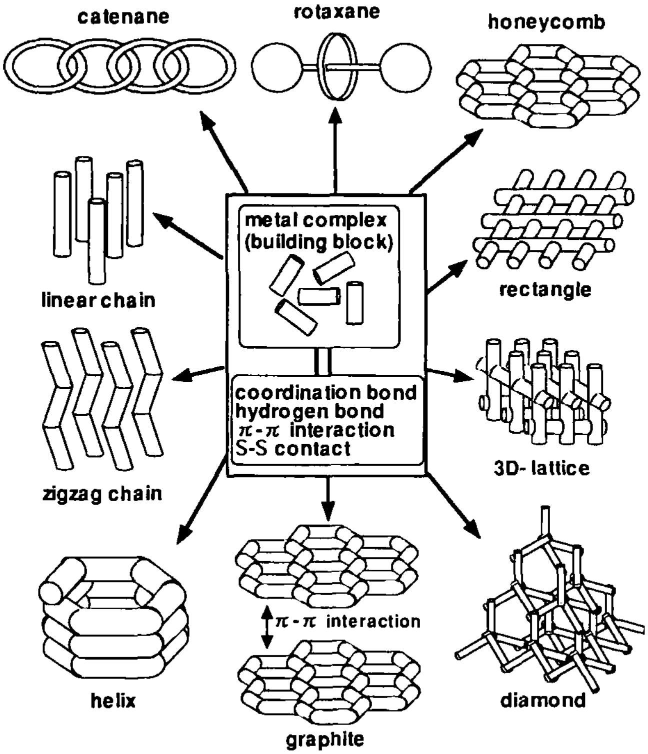
I. Introduction

Recent years have witnessed considerable interest in the development of rational synthetic routes to supramolecular architecture from self-assembly of component metal complexes. These solid materials with well-defined, discrete network topologies are attractive to chemists not only for aesthetic reasons but also for their potential applications in many areas (*1–13*). A major difficulty in controlling such a self-assembling process is the fact that it involves several stages, such as recognition between the components, correct orientation so as to allow growth, and termination of the process leading to the predesigned species (*14*). In addition, the intermolecular forces that control these stages are directional and weak enough to enable closely related molecules to give widely different aggregates under slightly modified conditions. Usually, the synthetic strategy involves selecting the coordination geometry of metal ions, the chemical structure of organic ligands, and the favorable reaction conditions such as solvents and counterions. In this context, a fundamental principle of the designed chemistry of the intermolecular bond is the utilization of the intermolecular forces, which may consist of hydrogen bonding, S---S contacts, aromatic stackings, host–guest interactions, van der Waals forces, and other electrostatic attractions. Unfortunately, these forces are much less well understood than classical chemical bonds in terms of their energetic and geometric properties. Therefore, the control of molecular assembly using supramolecular interactions is probably a new challenge to chemists.

The copper(I) and silver(I) ions are regarded as extremely soft acids favoring coordination to soft bases, such as ligands containing S and unsaturated N (*15*, *16*). 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 six all occurring. 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, attributable to the spherical d^{10} configuration. Under suitable conditions, these simple coordination compounds with the presence of two rodlike or four sticky sites can be used as tectons to form the self-assembly of predictable supramolecular aggregates. On the other hand, account should be taken of careful selection of the multifunctional organic ligands and controlling the assembly and orientation of the individual building blocks—in other words, a combination of coordination bonds and noncovalent intermolecular interactions in a mutually compatible manner. Much study has centered on the use of multifunctional ligands. One of the simplest and most widely employed methods is to use a bifunctional rodlike diatomic CN^- anion and bidentate N,N′-donor linking groups such as pyridine-, pyrazine-, and imidazol-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 polyhedral arrangement of ligands. The recent efforts in this field have even been extended to the novel oligopyridines, calixarenes, crown ethers, cryptands, and tetrathiafulvalene derivatives. Such an approach opens the possibility of rational synthesis of functional solid-state supramolecular metal complexes containing copper(I) and silver(I) with multidimensional helical, honeycomb channel, interwoven diamondoid, and graphite frameworks among other novel structures, Scheme 1.



SCHEME 1. The self-assembly pathway for formation of copper(I) and silver(I) coordination supramolecules.

Polynuclear Cu(I) and Ag(I) compounds belong to very diverse stoichiometries. In general, they can be prepared either directly by a reaction between reactants or by electrochemistry. It is the aim of the present review to give a cursory examination of recent developments in construction of the supramolecular frameworks, which combine the covalent bond-forming capability of the metal ion with the ligand surface capable of forming noncovalent interactions. Because of the great volume of literature on compounds, it has been necessary to be highly selective in the choice of material for inclusion. Emphasis throughout is on compounds isolated in the solid state. In a review some 130 pages long one cannot expect to do justice to the depth and extent of investigation into these systems. Some of the topics were reviewed previously (*17*, *18*), but the articles soon become outdated because of the rapid growth of the fields.

II. Helical Frameworks

In this section helical complexes of copper(I) and silver(I) are reviewed as examples of self-assembly in metallosupramolecular systems. One of the most intriguing dissymmetric shapes in the natural system is the helix. Organic and inorganic polymers existing in helical structures are of special interest because of their structural similarities to nucleic acids. They are also intrinsically interesting for their potential applications in the fields of supramolecular chemistry, asymmetric catalysis, and nonlinear optical materials. Since the early pioneering work of Lehn on double-helical copper(I) complexes with oligopyridines (*1*, *19*), there has been an enormous worldwide interest in helical complexes over the past decade. Most of the work has concentrated on the use of oligopyridines and oligophenanthrolines to control the assembly of helical supramolecular systems. An enormous number of infinite single-helical complexes and double- and triple-stranded helicates have appeared in the literature (see Table I). Many comprehensive reviews have appeared in recent years, usually covering helical structures in general without special reference to copper(I) or silver(I) complexes (*8*, *20–22*). In this section, the complexes with single-, double-, and triple-stranded structures are dealt with separately. The ligands involved in this section are listed in Fig. 1.

TABLE I

COPPER(I) AND SILVER(I) COMPLEXES WITH HELICAL FRAMEWORKS

Complex	Stereochemistry of M	Structure	Ref.
$[Cu(\mathbf{L_1})]BF_4 \cdot CHCl_3$	tetrahedral	infinite single strand	*23*
$[Ag(\mathbf{L_2})] \cdot 2H_2O$	tetrahedral	infinite single strand	*24*
$[Ag(R,R\text{-}\mathbf{L_3})]O_3SCF_3$	linear	infinite single strang	*25*
$[Ag(S,S\text{-}\mathbf{L_3})]O_3SCF_3$	linear	infinite single strand	*25*
$[Ag(\mathbf{L_4})](NO_3)\}$	3-coordinate	infinite single strand	*26*
$[(C_6H_5)_4P]_x^1[Cu_3I_4]$	tetrahedral	tetrahelix chain	*27*
$[Ag\{Ag_2(\mathbf{L_5})\}]$	linear, 3-coordinate	infinite single helical chain	*28*
$[Cu(\mathbf{L_6})(Me_2CO)_{0.5}]BF_4$	trigonal pyramidal	3-D single helix	*29*
$[M_2(\mathbf{L_7})_2]X_2$, M = Cu or Ag, X = PF_6^- or BF_4^-	tetrahedral	dinuclear double helicate	*30, 31*
$[Cu_2\{(MeS)_2\mathbf{L_7}\}_2](PF_6)_2$	tetrahedral	dinuclear double helicate	*32*
$[Cu_2(\mathbf{L_8})_2](PF_6)_2$	tetrahedral	dinuclear double helicate	*33*
$[Cu_2(\mathbf{L_9})_2](PF_6)_2$	tetrahedral	dinuclear double helicate	*34*
$[Cu_2(\mathbf{L_{10}})_2](ClO_4)_2 \cdot H_2O$	tetrahedral	dinuclear double helicate	*35*
$[Cu_2(\mathbf{L_{11}})_2](ClO_4)_2$	tetrahedral	dinuclear double helicate	*36*
$[Ag_2(\mathbf{L_{12}})_2](PF_6)_2$	tetrahedral	dinuclear double helicate	*37*
$[Cu_2(\mathbf{L_{13}})_2](BF_4)_2$	tetrahedral	trefoil knot	*38, 39*
$[Cu_2(\mathbf{L_{14}})_2](ClO_4)_2$	tetrahedral	dinuclear double helicate	*40*
$[Cu_2(\mathbf{L_{15}})_2](PF_6)_3$	octahedral, tetrahedral	dinuclear double helicate	*41*
$[CoAg(\mathbf{L_{15}})_2](ClO_4)_3$	octahedral, tetrahedral	heterodinuclear double helicate	*42*
$[Ag_2(Me_2\mathbf{L_{15}})_2](ClO_4)_2$	trigonal bipyramidal	dinuclear double helicate	*43*
$[Ag_2\{(MePh)_2\mathbf{L_{15}}\}_2](ClO_4)_2$	tetrahedral	dinuclear double helicate	*43*
$[Ag_2(\mathbf{L_{16}})_2](PF_6)_2$	5-coordinate	dinuclear double helicate	*44*
$[Cu_2(\mathbf{L_{17}})_2](PF_6)_2$	linear, tetrahedral	dinuclear double helicate	*45*
$[Cu_2(\mathbf{L_{18}})_2](PF_6)_2$	linear, tetrahedral	dinuclear double helicate	*46*
$[Cu_3(\mathbf{L_{19}})_2](PF_6)_3$	tetrahedral	trinuclear double helicate	*47*
$[Ag_3(\mathbf{L_{20}})_2](CF_3SO_3)_3$	tetrahedral	trinuclear double helicate	*48*
$[Ag(\mathbf{L_{21}})]CF_3SO_3$	linear	infinite double helicate	*50*
$[Cu_2(\mathbf{L_{22}})_2](ClO_4)_2$	linear	infinite double helicate	*51*
$[Ag_3(\mathbf{L_{23}})_3](BF_4)_3$	2-coordinate	triple helicate	*61*

A. INFINITE SINGLE-HELICAL COMPLEXES

The number of one-dimensional infinite single-helical copper(I) and silver(I) complexes is rather limited. They are characterized by a single strand of ligands twisting around the helical axis defined by metal ions [Fig. 2(a)]. It may be left-handed or right-handed. When ligand $\mathbf{L_1}$ reacted with two equivalents of $[Cu(MeCN)_4]BF_4$ in a mixture of

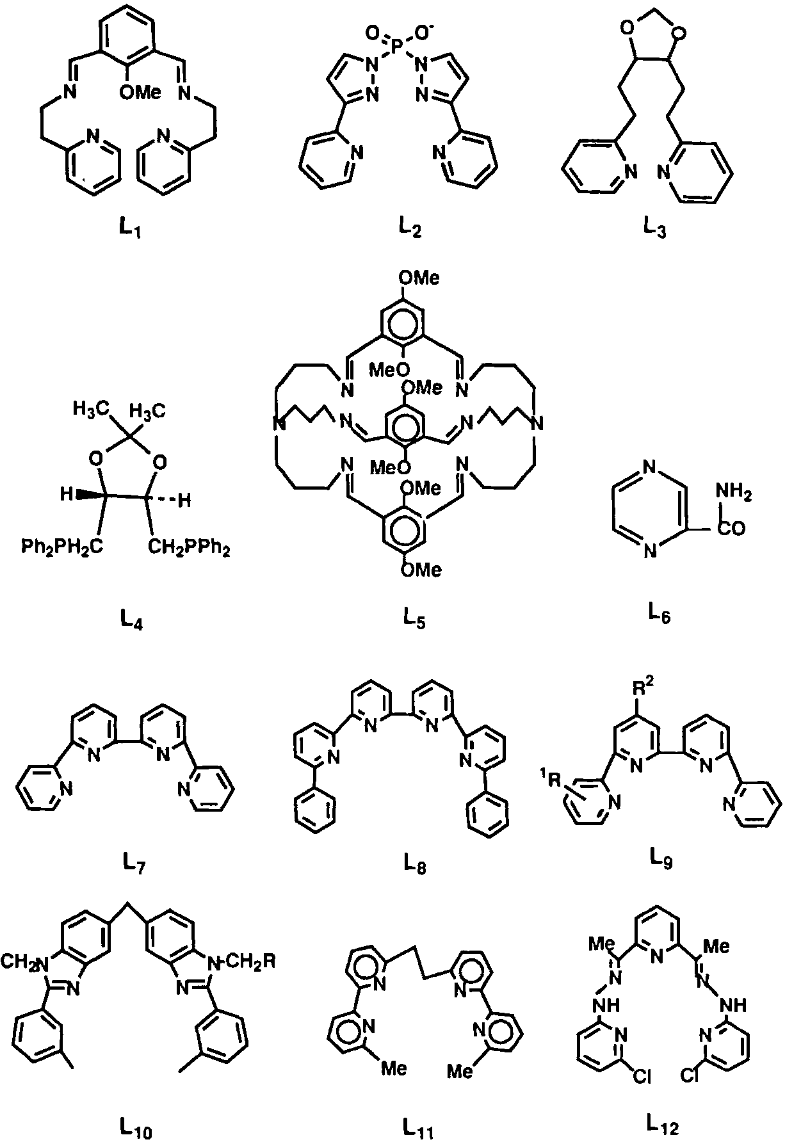
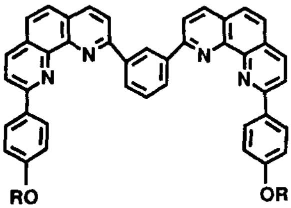
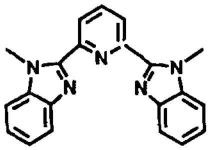


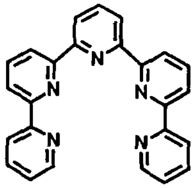
FIG. 1. List of organic ligands in copper(I) and silver(I) helical complexes.



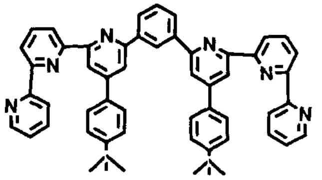
L_{13}



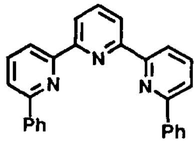
L_{14}



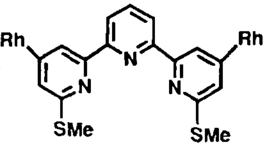
L_{15}



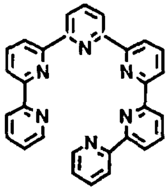
L_{16}



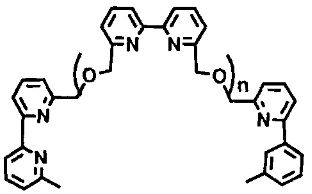
L_{17}



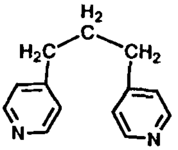
L_{18}



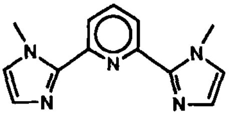
L_{19}



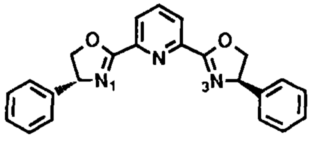
L_{20}



L_{21}



L_{22}



L_{23}

FIG. 1. *(continued)*

$CHCl_3$ and MeCN, bright orange crystals of $[Cu(\mathbf{L}_1)]BF_4 \cdot CHCl_3$ were obtained (*23*). In the cation each Cu atom is four-coordinated, with two pyridylethylimine bidentate units from two different ligand molecules in a distorted tetrahedral geometry, and each $\mathbf{L}_1$ exhibits a bis (bidentate) fashion, bridging two metal centers forming a linear helical strain (Fig. 3). The recently synthesized ligand bis[3-(2-pyridyl) pyrazol-1-yl]phosphinate ($\mathbf{L}_2$) contains two bidentate compartments linked by a flexible phosphinate bridge (*24*). Its flexibility means that it can adapt to the specific preferences of the metal ions. Its complex

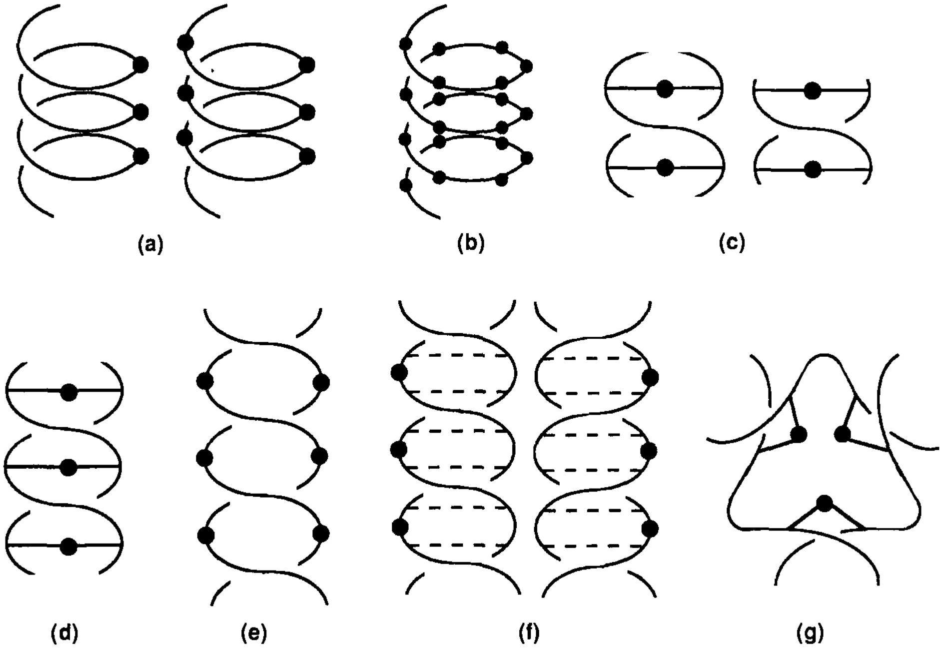


FIG. 2. Schematic views of copper and silver helical arrangements: (a) infinite single strand; (b) 3-D single helical copper(I) complex with mixed ligands; (c) dinuclear double helicate; (d) trinuclear double helicate; (e) infinite double helicate; (f) infinite chiral double helicate of copper(II) with arginine and *m*-phthalate; (g) triple helicate of silver(I).

with Ag^+, $[Ag(\mathbf{L}_2)]\cdot 2H_2O$ contains infinite helical chains of the cation in which each ligand donates one N,N′-bidentate arm to each of two metals and each metal ion is four coordinated by two arms from different ligands. There are interligand aromatic stacking interactions (3.2–3.6 Å) both within each helical strand and between strands. The strands are further held together via a hydrogen-bonding network involving the phosphinate groups and lattice water molecules (Fig. 4).

Tetrahedral coordination of the metal ion is not an essential requirement for formation of this type of helical structure. Two-coordinate silver(I) ion plays an important role in the formation of a helical framework, that is, the stereoconformation of the ligand itself is maintained on coordination to Ag(I) and arranged in a one-dimensional helical chain. Reaction of the bidentate optically active ligands (4*R*,5*R*)- and (4*S*,5*S*)-4,5-bis(2-(2-pyridyl)ethyl)-1,3-dioxolane (*R*,*R*-$\mathbf{L}_3$ or *S*,*S*-$\mathbf{L}_3$) with silver(I) trifluoromethanesulfonate in metha-

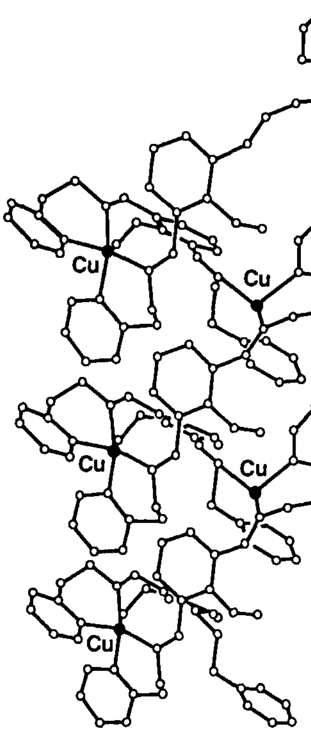


FIG. 3. Structure of $[Cu(L_1)]BF_4 \cdot CHCl_3$. (From Fig. 1 in Gelling, O. J.; van Bolhuis, F.; Feringa, B. L. *J. Chem. Soc., Chem. Commun.* **1991,** 917.)

nol gave two isomeric complexes, $[Ag(R,R\text{-}\mathbf{L}_3)]O_3SCF_3$ and $[Ag(S,S\text{-}\mathbf{L}_3)]O_3SCF_3$ (*25*). Each complex cation has an extended structure consisting of Ag^+ with a slightly distorted linear geometry and the bridging ligands. Projection array along the screw axis for each isomer exhibits the left-handed helicity for the former (Fig. 5), and the right-handed for the latter. Helical complexes with nonpolypyridine ligands can give diverse structures and functions. The three-coordinate silver(I) complex with helical structure was observed in $[Ag(\mathbf{L}_4)(NO_3)]$, where $\mathbf{L}_4$ is the chiral ligand (*R,R*)-(4*R*,5*R*)-*trans*-4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyl-1,3-dioxalane] (*26*). The structure contains an infinite right-handed helical strand consisting of silver atoms, each coordinated by two phosphorus atoms of two adjacent $\mathbf{L}_4$ ligands and an oxygen atom of the nitrate ion. The unusual iodine tetrahelix was observed in $[(C_6H_5)_4P]_{\infty}^{1}[Cu_3I_4]$, in which tetraphenylphosphonium ions are accompanied by a helical chain of face-sharing

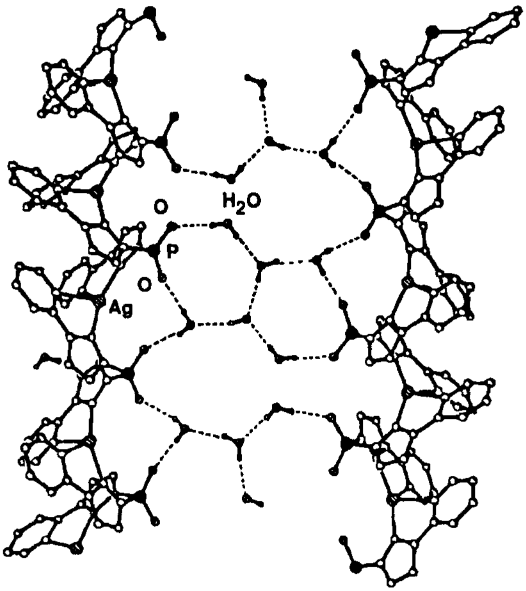


FIG. 4. Structure of $[Ag(L_2)] \cdot 2H_2O$. (From Fig. 3 in Psillakis, E.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1997,** 1645.)

tetrahedra formed by iodocuprate(I) anions (*27*). Another infinite single-helical structure was reported in a polymeric silver(I) cryptate (*28*). The polymeric cation $[Ag\{Ag_2(\mathbf{L}_5)\}]$ consists of dinuclear $[Ag_2(\mathbf{L}_5)]$ units in which each of the two silver atoms located inside the cavity of the ligand is coordinated to two imino nitrogens and one bridgehead nitrogen in a distorted trigonal environment. The third Ag ion links two dinuclear units by coordinating to one of the imino nitrogens of two different $\mathbf{L}_5$ ligands. Therefore, the cation can be regarded as the conjugate bis(iminobenzene) moieties linked together by linear N–Ag–N bridges in an alternate in- and out-conformations relative to the benzene rings, resulting in the formation of an infinite single-helical chain (Fig. 6). The structure determination reveals that $\mathbf{L}_5$ is a unique polydentate ligand with all eight N atoms involved in coordination to the metal. To satisfy the steric requirement of the assembling process, both bond distances and bond angles of the ligand show appreciable differences compared with those in the corresponding cryptate compounds. At the same time, the coordination environment around the silver ion is significantly distorted from ideal linear or trigonal geometry as a stereochemical compromise for formation of the helix.

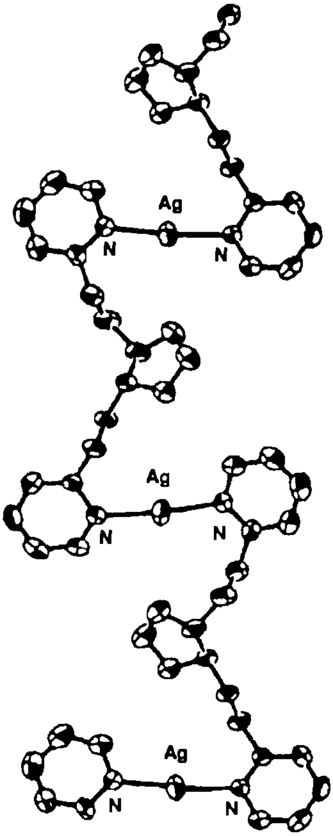


FIG. 5. Structure of [Ag(*R*,*R*-L_3)]O_3SCF_3. (From Fig. 1 in Suzuki, T.; Kotsuki, H.; Isobe, K.; Moriya, N.; Nakagawa, Y.; Ochi, M. *Inorg. Chem.* **1995,** *34,* 530.)

Recently an unusual type of three-dimensional single-helical framework, [Fig. 2(b)], has been reported in the copper(I) complex [Cu($\mathbf{L}_6$)(Me_2CO)$_{0.5}$]BF_4, where $\mathbf{L}_6$ is a derivative of pyrazine, 2-pyrazinecarboxamide (*29*). In the extended structure of the cation each metal atom is linked to two $\mathbf{L}_6$ ligands, forming a distorted trigonal planar structure, and axially bridged to another metal center by one acetone molecule with a Cu–O distance of 2.423(9) Å giving rise to an infinite helical structure (Fig. 7). The most remarkable feature of the complex is that the infinite helices generate a three-dimensionally extended hexagonal array of Cu atoms with a large cavity in which the counteranions are placed. In this structure the primary coordination involves $\mathbf{L}_6$ tridentately bridging two copper atoms, and the helical

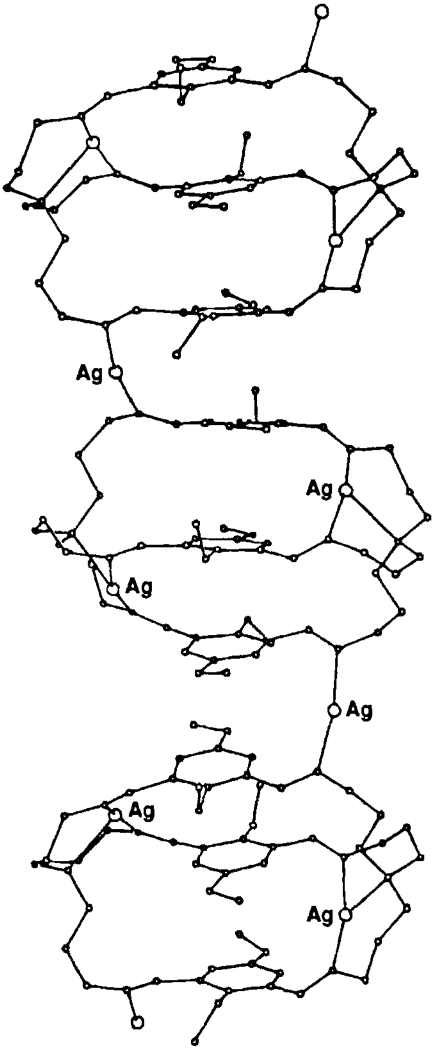


FIG. 6. Structure of the polymeric cation [Ag{Ag$_2$(L$_5$)}]. (From Fig. 2 in Yu, S.-Y.; Luo, Q.-H.; Wu, B.; Huang, X.-Y.; Sheng, T.-L.; Wu, X.-T.; Wu, D.-X. *Polyhedron* **1997,** *16,* 453.)

structure is further stabilized by secondary interactions between Cu atoms and the bridging acetone as the continuous strand. It demonstrates that assembled helical structures of copper(I) complexes with tridentate oligopyrazine ligands can be achieved by introducing a suitable spacer groups such as acetone between the metal-binding sites to match the metal ion stereochemical preference.

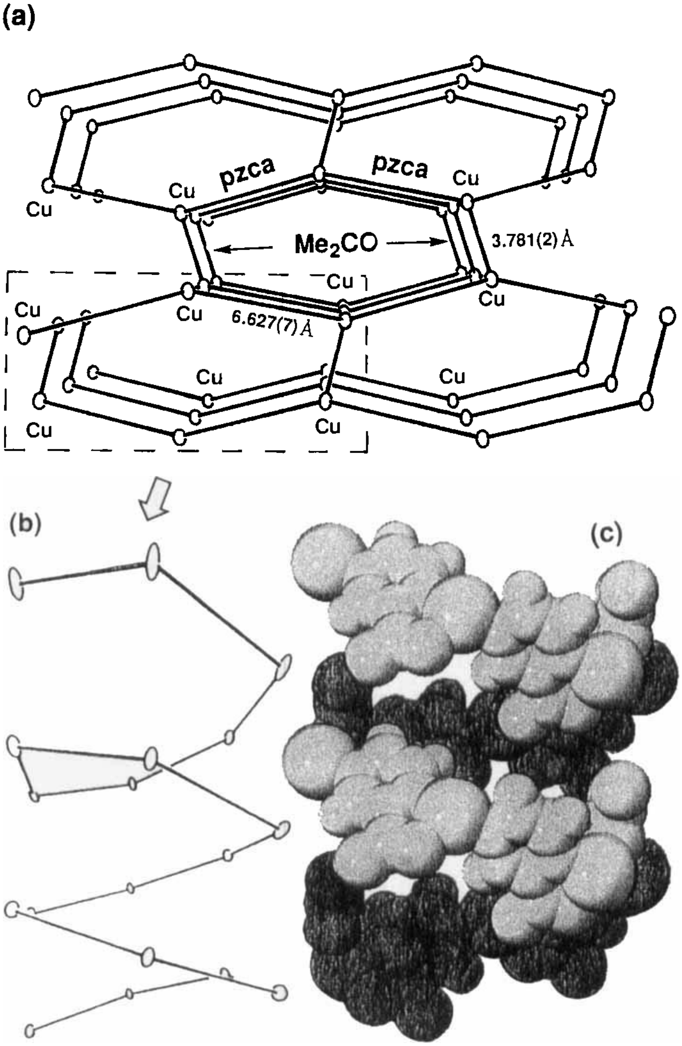


FIG. 7. The hexagonal framework in $[Cu(L_6)(Me_2CO)_{0.5}]BF_4$ (a) is generated by the helical cyclic array (b), where only copper atoms are shown. (c) Space-filling model of the complex, where BF_4^- are omitted. (From Fig. 4 in Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Moriwaki, K.; Kitagawa, S. *Inorg. Chem.* **1997,** *36,* 5416.)

B. DOUBLE-HELICAL COMPLEXES

Double helicates constitute the most abundant species among the copper(I) and silver(I) helical complexes. In the presence of the tetrahedral Cu(I) and Ag(I) ions, two oligopyridines can wrap around each other in a double-helical fashion with the metal ions holding them together [Fig. 2(c)]. Rational design of double-helical structures containing up to five metal ions and those with infinite frameworks has been developed by different groups (*8*, *20–22*).

Among double-helical complexes, dinuclear helicates with two ligand molecular threads twisting around two metal ions predominate. Based on the description of these complexes made by Constable (*8*), they can be defined as [4 + 4], [5 + 5], and [6 + 4] dinuclear helicates, the two numbers in the square bracket indicating the number of nitrogens to which the two metal ions are bounded. The most common are the dinuclear [4 + 4] helicates with the tetradentate quaterpyridine derivatives. They include complexes of quaterpyridine in $[Cu_2(\mathbf{L}_7)_2](PF_6)_2$, $[Ag_2(\mathbf{L}_7)_2](PF_6)_2$, and $[Ag_2(\mathbf{L}_7)_2](BF_4)_2$ (*30*, *31*), the symmetrically methylthio- and phenyl-substituted quaterpyridine derivatives in $[Cu_2\{4',4''\text{-}(MeS)_2\mathbf{L}_7\}_2](PF_6)_2$ (*32*) and $[Cu_2(\mathbf{L}_8)_2](PF_6)_2$ (*33*). To probe the steric control in the self-assembly of directional helicates, Constable has carried out systematic studies on asymmetrically alkyl-substituted quaterpyridine derivatives such as $[Cu_2(\mathbf{L}_9)_2](PF_6)_2$ (*34*). It is found that substituents do not control the self-assembly of quaterpyridines but are responsible for the detailed structure. All these dinuclear helicates with quaterpyridines, $\mathbf{L}_7$–$\mathbf{L}_9$, have general structure features as exemplified by $[Cu_2(\mathbf{L}_7)_2]^+$ (Fig. 8), though there are some slight differences in structural parameters as result of the introduction of the substituents and changes of the metal cations and counteranions. The cation is dinuclear, with each metal ion in a distorted four-coordinate environment, and the two quaterpyridine strands are

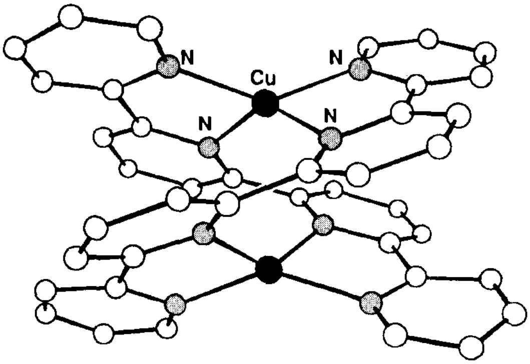


FIG. 8. Structure of dinuclear double helicate with quaterpyridine $[Cu_2(\mathbf{L}_7)_2]^+$. (From Fig. 6 in Constable, E. C.; Elder, S. M.; Hannon, M. J.; Martin, A.; Raithby, P. R.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1996,** 2423.)

wrapped around the binuclear core in a double-helical array. It is also observed that π-stacking interactions between aromatic rings play an important role in stabilizing the double-helical geometry. The fact that the oligopyridine disfavors binding to only a single strand in the system suggests that it contains sufficient molecular information for the recognition of the metal-binding domain in self-assembling processes. Conductivity measurements and UV-visible spectra show that the dinucleating bisbidentate ligand $\mathbf{L}_{10}$ also forms similar double helices with copper(I) in $[Cu_2(\mathbf{L}_{10})_2](ClO_4)_2 \cdot H_2O$ (*35*).

The copper(I) complex with CH_2CH_2-bridged bipyridine ligand $\mathbf{L}_{11}$ is formulated as $[Cu_2(\mathbf{L}_{11})_2](ClO_4)_2$, and again the two equivalent ligands are arranged in a helical manner by complexation with two copper ions (*36*). Reaction of $\mathbf{L}_{12}$ with Ag(I) resulted in the formation of another [4 + 4] dinuclear double-helical complex $[Ag_2(\mathbf{L}_{12})_2](PF_6)_2$ (*37*). In this complex, the distorted four-coordinate environment of each silver is maintained, but with weak interactions with a fifth ligand. The helical structure is stabilized by π-stacking interactions between parallel pyridyl rings. Another example worthy of comment is $[Cu_2(\mathbf{L}_{13})_2](BF_4)_2$, utilized as a precursor of the trefoil knot system in which the two coordinating molecular threads, $\mathbf{L}_{13}$, are well interlaced on two copper(I) centers, forming a dinuclear double-stranded helical complex (*38*). The synthesis of the first trefoil knot was reported by the same group five years earlier, with the chelate unit, $\mathbf{L}_{13}$, bridged by $(CH_2)_4$ rather than a phenylene group (*39*). Modification of the linker between the two 1,10-phenanthroline chelates certainly increased the yield, but in both cases, the organic precursors are found nicely wound and well adapted to the formation of a knot by connecting the appropriate ends of the strands (Fig. 9).

The metal-ion stereochemical preference and the compatible ligands are the first elements of helical structural control. Interestingly, $\mathbf{L}_{14}$ with pyridine bridging two imidazole apartments formed a dinuclear double-helical complex, $[Cu_2(\mathbf{L}_{14})_2](ClO_4)_2$, similar to those described earlier (*40*). By contrast, the ligand obtained through the replacement of the pyridine in $\mathbf{L}_{14}$ by a benzene group gave a dinuclear nonhelical complex with Cu(I), suggesting the fundamental role played by the spacer for the helical twist. Fully understanding the elements that guide the preferential combination of ligands and metal ions can surely allow the controlled assembly of multicomponent systems.

Copper(I) and silver(I) complexes derived from odd-numbered oligopyridines present a different situation. Quinquepyridine ($\mathbf{L}_{15}$) in dinuclear helicates usually involves a rotation about an interannual

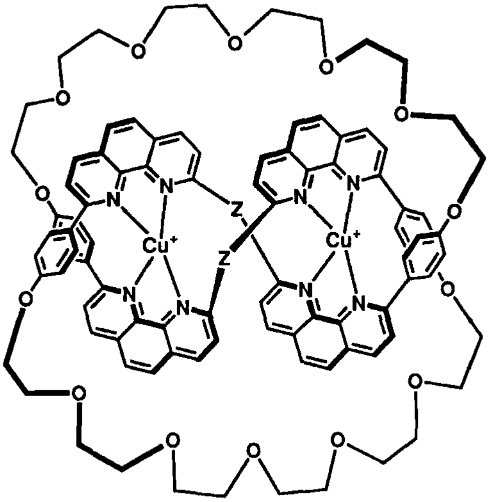


FIG. 9. The dinuclear double-stranded helical complex $[Cu_2(L_{13})_2](BF_4)_2$ is utilized as the precursor of the trefoil knot system. (From Scheme 1 in Dietrich-Buchecher, C. D.; Sauvage, J.-P.; Cian, A. D.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1994,** 2231.)

C–C bond to separate the ligand into a tridentate 2,2′:6′,2″-terpyridine and a 2,2′-bidentate pyridine part. A double-helical array of two L_{15} ligands presents a total of ten nitrogen donor atoms, which can be arranged to create one six-coordinate [tpy + tpy] and one four-coordinate [bpy + bpy], or two five-coordinate (tpy + bpy) dinuclear units (*8, 21*). So far copper(I) dinuclear [5 + 5] helicates are not known because pentacoordination is not the favorable stereochemistry for Cu(I); instead, it forms a [6 + 4] dinuclear helicate with Cu(II). Reaction of quinquepyridine and $[Cu(MeCN)_4]PF_6$ in air gave a brown mixed-valence complex, $[Cu_2(L_{15})_2](PF_6)_3$, in which the divalent copper is in an octahedral [tpy + tpy] and the monovalent copper is in a tetrahedral [bpy + bpy] environment (*41*). The heterodinuclear double-helical complex containing Ag(I) and Co(II) has been reported. The reaction of the two mononuclear cations, $[Co(L_{15})(MeOH)_2]^{2+}$ and $[Ag(L_{15})]^+$, in a 1:1 ratio gave $[CoAg(L_{15})_2](ClO_4)_3$ (*42*). The helical structure is reminiscent of that observed for the mixed-valence copper complex $[Cu_2(L_{15})_2](PF_6)_3$, in which the Cu(II) is replaced by Co(II).

In contrast to these observations, a dinuclear [5 + 5] helical structure has been observed in the silver(I) complex $[Ag_2(Me_2L_{15})_2](ClO_4)_2$ in which the ligand, 6,6″″-dimethyl-quinquepyridine, twists around the dinuclear core, with two nitrogens coordinated to one Ag and the other three nitrogens to the second Ag, adopting the usual [2 + 3] mode (*43*). As expected, both silver(I) ions are five-coordinated with a flattened and distorted trigonal bipyramidal geometry. Interestingly, another quinquepyridine derivative with two further phenyl groups at the 4′ and 4‴ positions forms a [4 + 4] helicate in $[\mathrm{Ag}\{(\mathrm{MePh})_2\mathbf{L}_{15}\}_2](\mathrm{ClO}_4)_2$, in which $(\mathrm{MePh})_2\mathbf{L}_{15}$ actually acts as a tetradentate ligand and the central pyridyl ring plays the role of a rigid spacer rather than a donor (*43*). Because spacers linking the oligopyridine units have a notable impact on the versatility of the compounds in accommodating metal ions with different sizes and different geometries, one of the approaches for rational design of helical structures is to use aliphatic ethylene or aromatic 1,3-phenylene groups as spacers (*36*). For example, $\mathbf{L}_{16}$ with 1,3-phenylene as a spacer linking two terpyridine units exhibits essentially a pentadentate coordination mode in $[\mathrm{Ag}_2(\mathbf{L}_{16})_2](\mathrm{PF}_6)_2$ (*44*). The crystal structure reveals a [5 + 5] double-helical bimetallic silver complex in which each Ag(I) adopts an irregular five coordination.

Terpyridine is the simplest oligopyridine capable of forming a double-stranded helicate. Copper(I) complexes with terpyridine derivatives have been reported. In $[\mathrm{Cu}_2(\mathbf{L}_{17})_2](\mathrm{PF}_6)_2$ (*45*) and $[\mathrm{Cu}_2(\mathbf{L}_{18})_2](\mathrm{PF}_6)_2$ (*46*), the ligands have essentially distributed themselves to present bidentate domains to one metal center and a single pyridine donor to the other, to give a [4 + 2] double helicate. The two copper atoms involve different coordination environments, one with a distorted tetrahedral geometry and the second in a approximately linear two-coordinate environment (Fig. 10).

Dinuclear double helicates are too numerous to be fully discussed here. In contrast, tri, tetra, penta-, and polynuclear double-helical complexes of copper(I) and silver(I) appeared only in a limited num-

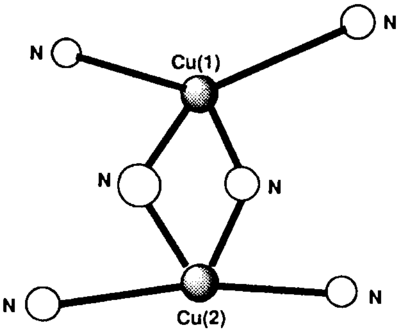


FIG. 10. Schematic representation of the two copper atoms involving different coordination environments in a [4 + 2] double helicate.

ber. A ligand with three bipyridiyl binding sites such as $\mathbf{L}_{19}$ can bind up to three cations, giving a trinuclear helical complex. Trinuclear double helicates $[Cu_3(\mathbf{L}_{19})_2](PF_6)_3$ (*47*) and $[Ag_3(\mathbf{L}_{20})_2](CF_3SO_3)_3$ (*48*) were prepared by treatment of sexipyridine and the relevant metal salts. Structure analysis and molecular modeling studies indicate that the two ligand groups fit three metal ions inside the double-helical array by twisting around the helical axis [Fig. 2(d)]. Each metal center is coordinated to a pair of adjacent pyridine residues from each ligand in a distorted tetrahedral environment. The functionalized oligopyridines of $\mathbf{L}_{20}$ with $n = 4$ and 5 formed tetra- and pentanuclear double helicates, respectively, with Ag(I) (*48*) and Cu(I) (*49*). Their overall structural features are analogous to those of the trinuclear double helicates, but their total length is estimated to be as long as around 22 Å and 27 Å, respectively. These self-organized nanostructures promise potential applications in the field of functional nanoscale species and molecular devices.

Discrete infinite double helices are quite rare in inorganic and coordination chemistry [Fig. 2(e)]. Ciani has reported that reaction of $\mathbf{L}_{21}$ with Ag^+ salts in the ratio 2 : 1 gave completely different and noteworthy products, one of which is the infinite double-helical coordination polymer $[Ag(\mathbf{L}_{21})]CF_3SO_3$ (*50*). The structure shows the balanced packing of left-handed and right-handed double helices of cationic —Ag—L—Ag—L— chains (Fig. 11). The period of the helices is 21.1 Å, and the two strands are bridged by weak Ag–Ag aurophlic (d^{10}–d^{10}) interactions. The copper(I) complex $[Cu_2(\mathbf{L}_{22})_2](ClO_4)_2$ has been prepared and structurally characterized (*51*). The basic dinuclear unit has a structure similar to that observed in $[Cu_2(\mathbf{L}_{14})_2]^{2+}$ (*40*). The ligands bind in a bis-monodentate coordination mode and form the strands of the helix that twist around the helical axis on

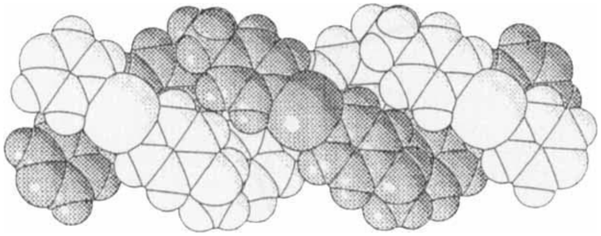


FIG. 11. Space-filling model of the infinite double helix of $[Ag(\mathbf{L}_{21})]CF_3SO_3$. (From Fig. 2 in Carlucci, L.; Ciani, G.; W. v. Gudenberg, D.; Proserpio, D. M. *Inorg. Chem.* **1997,** *36,* 3812.)

which the copper ions lie. Each Cu(I) center is nominally linear coordinated by two imidazole units, and the interactions with the two bridging pyridines are weak. The double-helical subunits stack together in parallel columns of constant but different helicity, leading to infinite double-helical columns.

Chiral helical complexes are of interest in connection with the manifestation of functions such as optical activity, molecular recognition, and enantioselective catalysis (*52–56*). With spirobisindanol and dimethylbiphenic acid as chiral templates, Siegel has successfully obtained bipyridine based double helicates containing up to three copper(I) ions by enanthoselective synthesis (*57*). The spectroscopic results confirmed the complex as a single enantiomer of the head-to-head isomer whose stereochemistry is controlled by the single stereoelement of the template throughout a span of 20 Å, demonstrating the ability to transmit stereochemical information over nanometer distances in the compounds. Chiral double-helical structures of copper(II)-L- and -D-arginine complexes with aromatic dicarboxylates have been reported, although the corresponding copper(I) species are not known (*58*). These crystals reveal that the complex with L-Arg forms a right-handed helix, whereas the complex involving D-Arg gives a left-handed helix [Fig. 2(f)]. This indicates that the handedness of the double helices in the solid state is governed by ligand chirality. These and other synthetic routes open new ways for development of enantioselective reagents and may contribute to the understanding of spontaneous aggregation of conjugated helical molecules in biological systems (*59*, *60*).

C. TRIPLE-HELICAL COMPLEXES

There is only one example of a triple helix containing Ag(I), reported recently by Williams and his co-workers (*61*). The colorless crystals $[Ag_3(\mathbf{L}_{23})_3](BF_4)_3$ were obtained by diffusion of benzene into a solution of the compound in acetonitrile. The structure consists of an equilateral triangle of silver ions with the ligands bridging the sides of the triangle [Fig. 2(g)]. The silver ion is not in a strictly linear environment, with an N–Ag–N angle of 153.3(6)°. Each ligand binds to one metal from below the plane of the silver atoms and to a second metal from above the plane. The structure may be considered as a triple helix in which the ligands wrap around the threefold axis and are held in place by coordination to the Ag_3 triangle.

III. S---S Contact-Assembled Frameworks

Some sulfur-rich dithiolates and the tetrathiafulvalene (TTF)-based species involved in the following discussion are listed in Fig. 12. Following the observation that TTF (**L$_{24}$**) forms a stable radical when treated with chlorine (*62*) and the discovery that a partial charge transfer between separately stacked donor and acceptor molecules leads to the first organic metal, TTF · TCNQ (tetracyanoquinodimethane) (*63*), the use of sulfur-containing molecules as precursors for synthesis of conductive or superconductive materials has been of unabated interest for over two decades. Because the large sulfur atomic orbitals are capable of promoting effective intermolecular overlap in the organic metals, partial oxidation of TTF and its substituted derivatives, when coupled with suitable electron acceptors, can give rise to low-dimensional arrays of these donors through sulfur–sulfur molecular interactions, providing an effective pathway for electronic conduction. A tremendous number of studies have been carried out on the

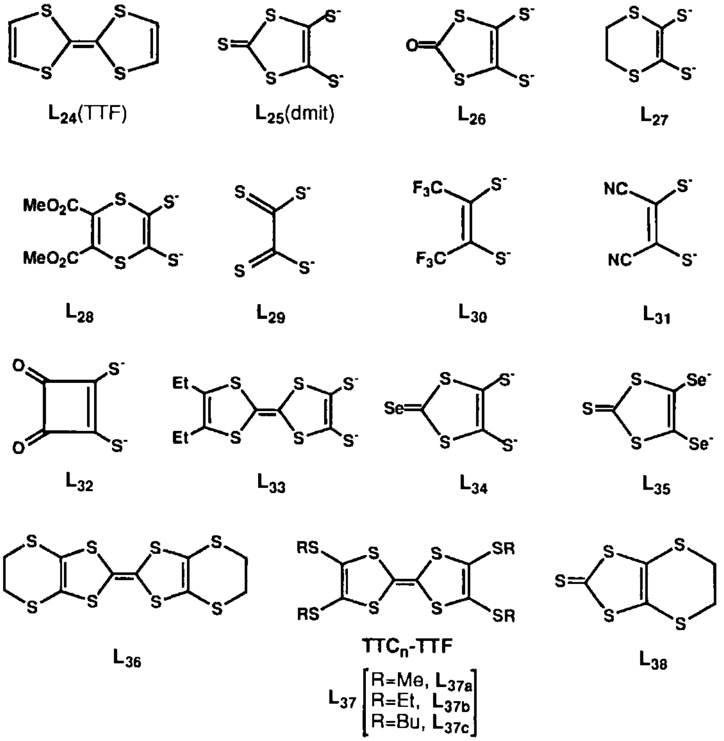


FIG. 12. Sulfur-rich dithiolates and TTF derivatives.

solid-state conductive properties of the TTF · TCNQ–like organic and inorganic metals by modifications of TTF (*64–66*).

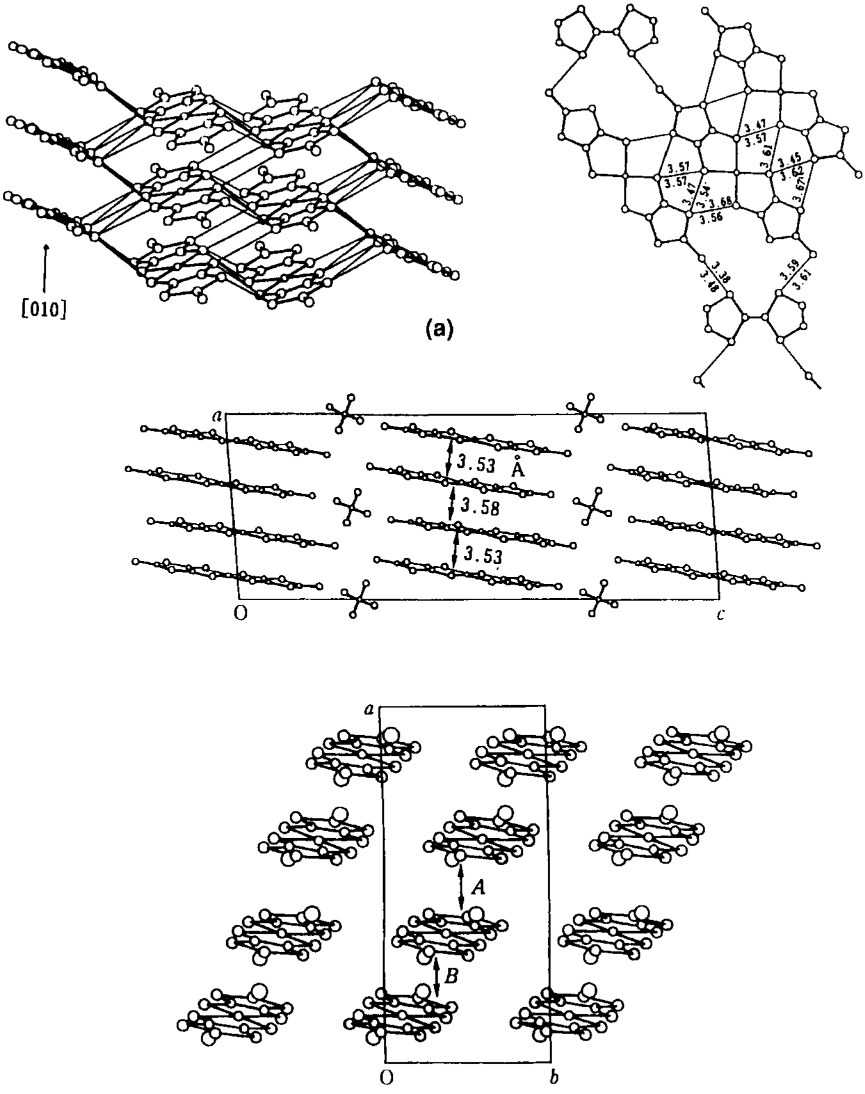
By contrast, the study of TTF-based species as building blocks in supramolecular chemistry has attracted attention only recently (*67*). With a preference for a soft donor such as the sulfur atom, both silver(I) and copper(I) readily form metal complexes with the sulfur-rich TTF-based organic molecule, with a high possibility of generating one- two- and three-dimensional supramolecular and macromolecular system by the covalent bonds as well as by S---S contacts. 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). This section focuses on construction of the supramolecular frameworks through S---S contacts based on dmit, BEDT-TTF, TTC$_n$-TTF, $C_5H_4S_5$ and the related species.

A. dmit AND THE RELATED LIGANDS

The sulfur-rich 1,3-dithiole-2-thione-4,5-dithiolate (dmit) ($\mathbf{L_{25}}$) has received considerable attention. Using square planar coordinating metal ions such as Ni, Pd, and Pt, many electrically conducting materials derived from planar metal complexes $[M(dmit)_2]^{n-}$ have been synthesized, and some of them have been found to undergo a superconducting transition at low temperature by applying high pressure. The nonplanar bulky metal complexes $[M(dmit)_3]^{n-}$ (M = Fe, Re, Mo, or W) have received equal attention. Numerous papers and reviews have focused on the study of the role of the intermolecular and intramolecular interactions in determining the electrical properties in the system (*68–83*). As an example, Fig. 13 shows a uniform segregated stacking arrangement of the constituent $Ni(dmit)_2$ units with the open-shell π-acceptor TTF and the closed-shell cation $(CH_3)_4N$ in the superconductors $(TTF)[Ni(dmit)_2]_2$ (*84*) and $[(CH_3)_4N][Ni(dmit)_2]_2$ (*85*), respectively, where close intermolecular S---S contacts occur between units in adjacent stacks leading to an infinite network.

Furthermore, extensive studies have also been carried out by using other ligands resembling dmit, such as $\mathbf{L_{26}}$–$\mathbf{L_{33}}$ (*86–92*). Along the same line, the selenium analogs ($\mathbf{L_{34}}$ and $\mathbf{L_{35}}$) are also of much interest, because even more effective molecular interactions are expected to occur owing to Se having more extended orbitals than sulfur (*93, 94*).

Although a number of Cu(II) complexes with the dmit-like ligands have been reported in which the metal ion involves a significant dis-



(a)

(b)

FIG. 13. Molecular packing of superconductors (TTF)[Ni(L_{25})$_2$]$_2$ (a) and [(CH$_3$)$_4$N][Ni(L_{25})$_2$]$_2$ (b). (From Figs. 5 and 6 in Bousseau, M.; Valade, L.; Legros, J.-P.; Cassoux, P.; Garbauskas, M.; Interrante, L. V. *J. Am. Chem. Soc.* **1986,** *108,* 1908, and Figs. 1 and 4 in Kim, H.; Kobayashi, A.; Sasaki, Y.; Kato, R.; Kobayashi, H. *Chem. Lett.* **1987,** 1799.)

tortion from planar to tetrahedral (*73, 83, 89, 93*), few nonplanar Cu(I) or Ag(I) metal complexes of dmit are known. The most interesting of these is $[mpy]_2[Cu_4(dmit)_3]$, prepared, like its Cu(II) analog, by a route of direct reaction of copper(I) salt and Na_2dmit in the presence of excess of [mpy]I (*95*). The structure contains dimerized anion units, each consisting of a tetranuclear Cu_4S_6 cluster. Each Cu(I) ion involves a distorted tetrahedral coordination comprised of four dmit-sulfur atoms. The dimeic units further interact with each other through close sulfur–sulfur contacts to form a two-dimensional molecular interaction sheet. The cations are located between the anion sheets.

B. BEDT-TTF

BEDT-TTF ($\mathbf{L_{36}}$) is another electron donor molecule and in combination with inorganic anions has provided several air-stable superconductors at low temperature (*96–99*). In fact, both dmit and $\mathbf{L_{36}}$ superconductors have the characters of (i) good orbital overlap between extended π-electron systems (S---S contacts) and (ii) partial filling of the conduction band through either partial oxidation or partial reduction. Here again the radical cation salts of square planar transition metal complexes dominate, and they feature S---S interactions between planar $\mathbf{L_{36}}^{\rho+}$ molecules leading to segregated columns of donors. On the other hand, the reported copper(I) and silver(I) coordination complexes of $\mathbf{L_{36}}$ are scarce. They include $(\mathbf{L_{36}}^+)Cu_2Br_3$, prepared by a redox reaction between $\mathbf{L_{36}}$ and $[CuBr_4]^{2-}$ (*100*). The most unique feature of the complex is that the $\mathbf{L_{36}}$ molecules are not stacked in a column but are coordinated to the tetrahedral copper(I) centers in a —Cu—Br—Cu—(μ-Br)$_2$—Cu— chain (Fig. 14). Due to lack of close S---S contacts between radical cations, the complex shows low conductivity.

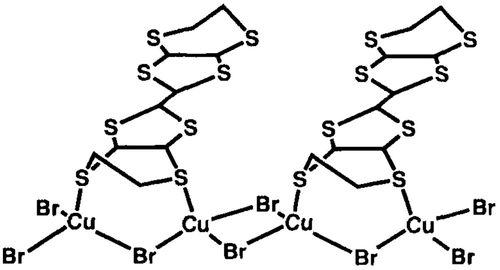


FIG. 14. Structure of $(\mathbf{L_{36}}^+)[Cu_2Br_3]$.

C. TTC$_n$-TTF SYSTEMS

Several copper(I) and silver(I) complexes with tetrakis(alkylthio) tetrathiafulvalene (TTC$_n$-TTF) (**L**$_{37}$) have appeared in the literature, and various S---S contact-assembled frameworks have been observed. **L**$_{37}$ contains a central TTF (**L**$_{24}$) π-system, which keeps the electron-donor property. As single-component organic semiconductors with low electrical conductivity, their physical properties have been widely investigated. They can be easily oxidized to the stable radical cation; accordingly, their chemistry is dominated by electrotransfer processes. They react with organic electron acceptors such as TCNQ and HCBD (hexacyanobutadiene), and inorganic oxidants to form partially or completely oxidized materials containing $\mathbf{L}_{37}{}^{\rho+}$, where ρ ranges from about 0.6 to 2.0 (*101–104*). In most of these charge-transfer compounds the donors and acceptors are stacked in segregated columns.

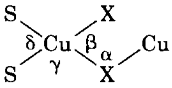
Construction of two- and three-dimensional coordination polymers using the diversity of copper halide frameworks is an area of considerable importance. Besides its electron-donor character, **L**$_{37}$ possesses alkylthio groups, which have coordination ability to metal ions through the sulfur atoms. This gives **L**$_{37}$ species a unique ability in linking metal ions to form coordination polymer structures. Six **L**$_{37}$ complexes with copper(I) halides, $[(\mathrm{CuX})_2(\mathbf{L}_{37})]$ (where n = 1 or 2 and X = Cl$^-$, Br$^-$, or I$^-$), have been structurally characterized (*105–107*). The syntheses of these compounds are straightforward, usually carried out by direct reaction of copper(I) halide and **L**$_{37}$ in a nonaqueous solution. The structural determination of these complexes reveals three different copper halide frames, namely rhomb, helix, and zigzag chain (Table II). Although the metal ions in all cases involve a tetrahedral coordination comprising two halogen atoms and two sulfur atoms of the **L**$_{37}$ moiety, with a certain degree of distortion, which in turn acts as a bis(bidentate) linker between the two metal centers through alkyl thioether groups, the resulting compounds often exhibit novel structures dramatically changed by the halogen. In **L**$_{37a}$, for example (*105*), the chloride complex consists of novel two-dimensional sheets of **L**$_{37a}$ molecules arranged between zigzag frames of $\{\mathrm{CuCl}\}_\infty$. Within the two-dimensional sheet no significant S---S contacts are observed because the long Cu---Cu separation of 5.78 Å on the same side of the CuCl zigzag frame gives a long interplanar spacing (4.90 Å) of **L**$_{37a}$. However, between the parallel sheets there are close intermolecular S---S contacts of 3.53 Å, giving a three-dimensional network (Fig. 15). By contrast, a novel framework of $\{\mathrm{CuBr}\}_\infty$, helixes

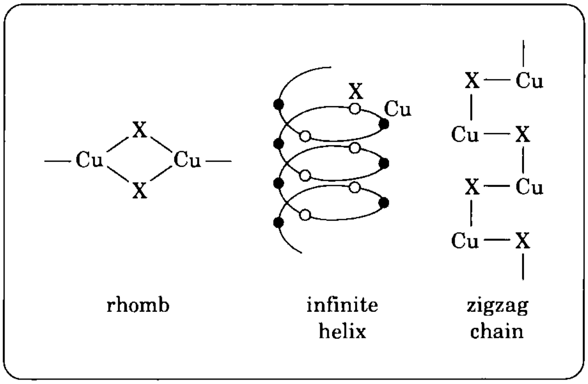
TABLE II

BOND ANGLES AND CuX FRAMEWORKS IN TTC$_n$-TTF (L_{37}) COMPLEXES OF COPPER(I) HALIDE

	α	β	γ	δ	CuX framework	Ref.
$[(CuI)_2(L_{37a})]$	66.6	113.4	113.1^a	88.8	rhomb	*105*
$[(CuI)_2(L_{37b})]$	66.9	116.0^a	111.8	89.9	rhomb	*107*
$[(CuBr)_2(L_{37b})]$	70.9	109.1^a	113.6	91.1^a	rhomb	*106*
$[(CuBr_2(L_{37a})]_2$	74.4	112.6^a	106.5		rhomb	*108*
$[(CuBr)_2(L_{37a})]$	94.5	116.1	116.8	87.1	helix	*105*
$[(CuCl)_2(L_{37b})]$	99.4	116.1	112.5	86.9	helix	*106*
$[(CuCl)_2(L_{37a})]$	111.3	111.8	113.2	90.9	zigzag chain	*105*

[a] Average value.





which are further linked to each other by coordination of L_{37a} to the metal was observed in the bromide complex. The L_{37a} molecules are stacked together, with the dihedral angle between the neighboring molecules being essentially zero on the stacking axis. The unique feature of the structure is that the $\{CuBr\}_\infty$ helixes orientate alternately in the reverse direction and the L_{37a} molecular stacks are mutually perpendicular to each other along the *c*-axis. The S---S contacts of 3.68 Å between the stacked L_{37a} molecules lead to a two-dimensional framework. The iodide complex contains an infinite chain of the bent L_{37a} molecules perpendicularly bridged on the methyl thioether groups by rhomboid Cu_2I_2 moieties. The S---S distances of 3.75 Å between the chains indicate weak interaction present, associating the adjacent chains of —L—CuX—L— together, giving a two-dimensional network. Similar results have been observed in the corresponding L_{37b} complexes (*106*, *107*), in which the chloride complex involves helical

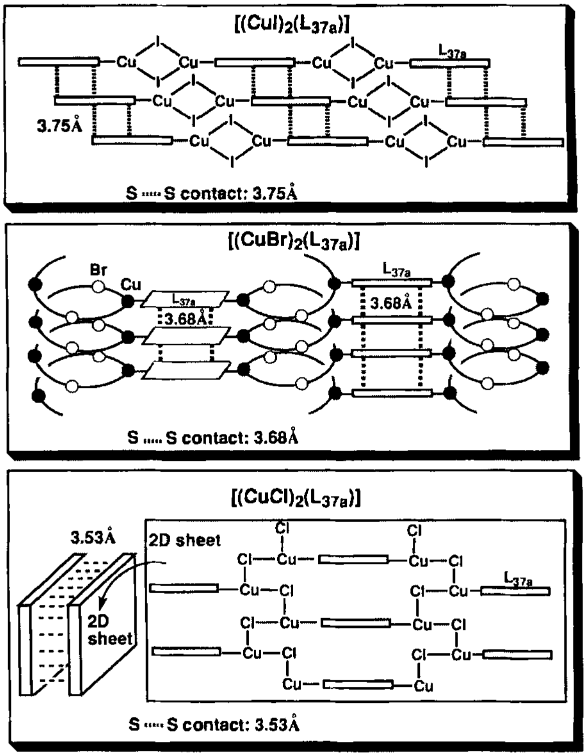


FIG. 15. Schematic views of different frames of CuX in $[(CuX)_2(L_{37a})]$ complexes.

$\{CuCl\}_\infty$ frames whereas the bromide and the iodide both contain Cu_2X_2 rhombs. Bond angles of copper(I) halide complexes with L_{37b} are summarized in Table II. It can be seen that the main factor determining the framework of the CuX unit seems to be connected with the Cu—X—Cu angle (α). As α increases smoothly from 66.6 to 111.3°, the framework changes from rhomb to zigzag chain through infinite helix, whereas other angles do not show such correlation. The $L_{37a}{}^+$ cation coordination complex $(L_{37a})[CuBr_2]_2$ also falls nicely into this category (*108*).

As a comparison, it is instructive to briefly mention the corresponding $L_{37b}{}^+$ complexes of copper(II) halide $(L_{37b})_2[Cu_2X_6]$ (where X = Cl^- or Br^-) prepared by oxidation of L_{37b} with $CuCl_2$ or $CuBr_2$ (*109*). Unlike the copper(I) halide complexes with L_{37} bridging between two metal atoms, both structures consist of two segregated stacks of $L_{37b}{}^+$ donors and $Cu_2X_6{}^{2-}$ acceptors associated via short S---S contacts (Fig.

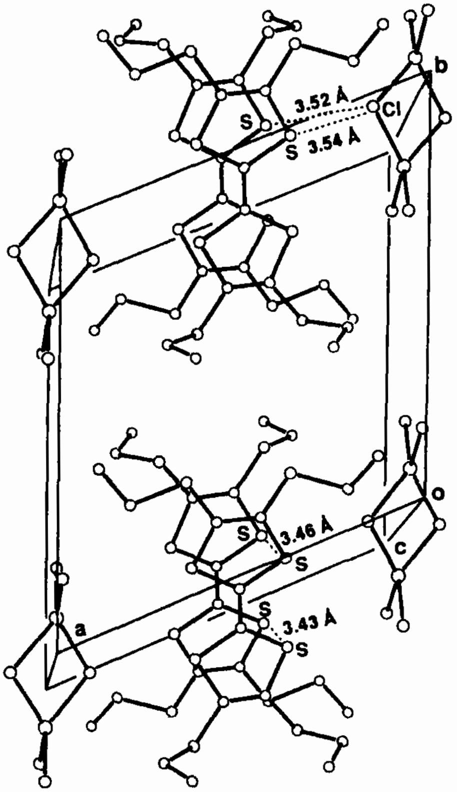


FIG. 16. Packing diagram of $(L_{37b})[Cu_2Cl_6]$ showing S---S and S---Cl. (From Fig. 1 and Fig. 2 in Wu, L. P.; Gan, X.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y. *Mol. Cryst. Liq. Cryst.* **1996,** *285,* 75.)

16). The donors face to each other to assume a dimeric structure, with close intradimeric S---S conducts of 3.43–3.52 Å. Consistent with the absence of significant interdimeric S---S interactions, the two compounds exhibit low electric conductivity. The diversity of copper halide frameworks, affected by several elements such as the metal ions, coordination of the halogen atoms, and the stereofactors of the ligand, makes it possible to design two- and three-dimensional coordination polymers.

Copper(I) perchlorate and tetrafluoroborate salts have also been found to form coordination compounds with the neutral ligands L_{37} ($n = 2$ or 3), but the structures vary little due to nonparticipation of the counteranions ClO_4^- and BF_4^- for their weak coordinating ability (*110, 111*). In fact, they are 1 : 1 metal–ligand compounds in which each Cu(I) ion is tetrahedrally coordinated by four sulfur atoms from the bridging $\mathbf{L}_{37}$ molecules to form infinite polymeric chains separated from each other by the anions. The shortest S---S distances between the adjacent chains in all cases are over 3.8 Å, suggesting negligible S---S interactions in the system. Same conclusion can be drawn from the $\mathbf{L}_{37a}$ complex $[Ag(\mathbf{L}_{37a})(O_3SCF_3)]$ (*112*), in which each Ag(I) ion is six-coordinated by four sulfur atoms from the bridging $\mathbf{L}_{37a}$ and two oxygen atoms from the bidentate O_3SCF_3 anion, resulting in a structure of two interwoven polymeric chains. The closest S---S distance between the two chains is 4.00 Å, precluding any significant S---S contacts present.

Apart from the varieties of interesting structures observed in the $\mathbf{L}_{37}$ system, it is worth noting the preparation of these complexes and the conductivity of the I_2-doped species. As mentioned previously, these complexes are easily prepared without elaborate synthetic procedures or particular precautions. However, successful preparation of the single crystals of these complexes largely depends on the reaction temperature. Again take $\mathbf{L}_{37a}$, for example. The preparation was carried out by allowing the mixture solution of CuX salt and $\mathbf{L}_{37a}$ to stand in a water bath at a constant temperature of 70, 55, and 23°C for the chloride, bromide, and iodide, respectively (*105*). The same reactions performed at other nondesignated temperatures may lead to a mixture of precipitate and tiny single crystals unsuitable for X-ray analysis. This is also true for the preparation of the corresponding $\mathbf{L}_{37b}$ complexes (*106*, *107*). Iodine oxidation is a viable synthetic route to highly conducting mixed-valence materials. Although copper(I) and silver(I) complexes with neutral $\mathbf{L}_{37}$ ligands are insulators ($\sigma_{25°C} < 10^{-12}\ S \cdot cm^{-1}$) at room temperature, their iodine-doped products behave as semiconductors, with conductivities increasing in the order $[(CuCl)_2(\mathbf{L}_{37})] < [(CuBr)_2(\mathbf{L}_{37})] < [(CuI)_2(\mathbf{L}_{37})]$ (Fig. 17). A partial oxidation can be assumed to occur in the I_2-doped species and the mixed-valence ligand–ligand interactions might cause electrical conduction pathways.

D. $C_5H_4S_5$

4,5-Ethylenedithio-1,3-dithiole-2-thione ($C_5H_4S_5$) ($\mathbf{L}_{38}$) is well known as an electron donor (*113*, *114*). It is also a derivative of dmit and has a structure similar to half of $\mathbf{L}_{36}$. The structure determination of its metal complexes has demonstrated the unique coordination versatility of $\mathbf{L}_{38}$ (Table III). It can act as a monodentate, bidentate, or even

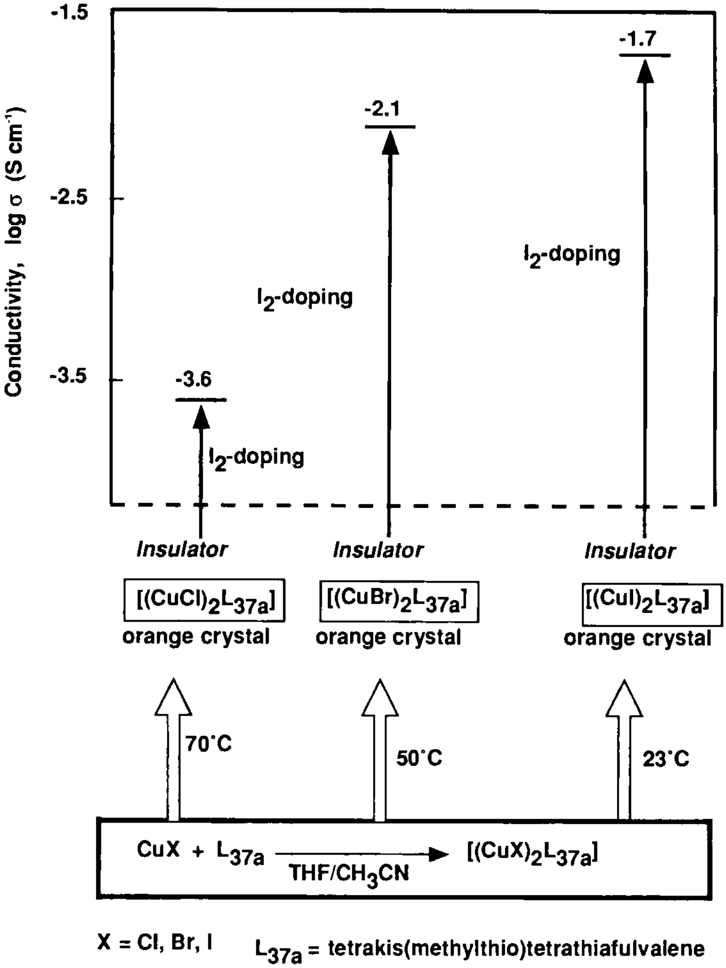


FIG. 17. Preparation scheme and conductivity of $[(CuX)_2(L_{37a})]$.

tridentate ligand, binding one and bridging two or three metal ions through the thiocarbonyl group alone or by both thiocarbonyl and thioether groups.

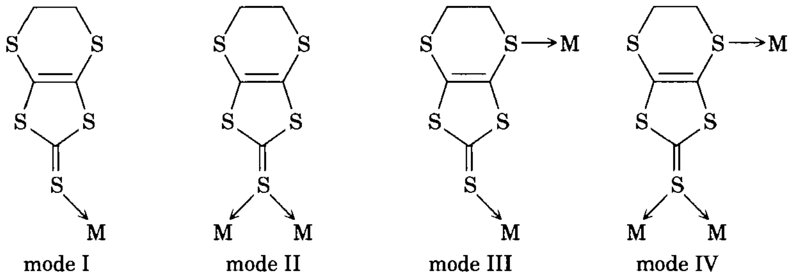
Up to now, three silver(I) and one copper(I) complexes of L_{38} have been synthesized and crystallographically characterized. They display a variety of one- to three-dimensional frameworks based on coordination bonds as well as intermolecular S---S contacts. Reaction of $AgClO_4 \cdot H_2O$ and L_{38} in acetonitrile gave red brick crystals of $\{[Ag(L_{38})_3]ClO_4 \cdot CH_3CN\}_2$ (*115*). The compound has a dimeric structure

TABLE III

COORDINATION MODES OF $C_5H_4S_5$ (L_{38}), THE METAL COMPLEX STRUCTURE AND THE CONDUCTIVITY OF THE I_2-DOPED PRODUCTS

Complex	Mode[a]	Structure of the complex	Conductivity $S \cdot cm^{-1}$	Ref.
$[Ag_2(L_{38})_6](ClO_4)_2$	I, (II)	dimer	6.9×10^{-5}	*115*
$[Ag(L_{38})_2NO_3]$	III	infinite dinuclear chain	3.0×10^{-5}	*116*
$[Ag(L_{38})CF_3SO_3]$	IV	2-D sheet	1.5×10^{-4}	*115*
$[Cu_4I_4(L_{38})_4]$	I, III	infinite tetranuclear chain	2.2×10^{-4}	*117*

[a] Coordination modes of $C_5H_4S_5$.



with two nonequivalent intercoordinated quasi-trigonal $[Ag(L_{38})_3]^+$ units, which are further assembled by very close S------S contacts of 3.284(4)–3.569(2) Å to form a one-dimensional chain structure (Fig. 18). Replacement of the anion by triflate in preparation gave a poly-

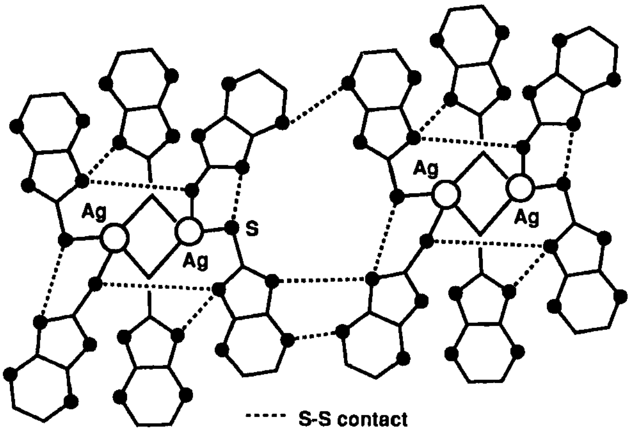


FIG. 18. Schematic representation of S---S contacts in $\{[Ag(L_{38})_3]ClO_4 \cdot CH_3CN\}_2$.

nuclear complex with a different stoichiometry, $[Ag(\mathbf{L_{38}})CF_3SO_3]$ (*115*). The structure contains two crystallographically independent five-coordinate silver(I) ions, very rare stereochemistry for Ag(I). Both the $\mathbf{L_{38}}$ group and the CF_3SO_3 ion bridge between two Ag atoms, forming a one-dimensional chain along the *c*-axis. All the ligand groups are approximately perpendicular to the chain, and between the chains there are several close S---S contacts (the shortest one being 3.262 Å), resulting in a two-dimensional polymer structure (Fig. 19). The third silver(I) complex belonging to this family is $[Ag(\mathbf{L_{38}})_2NO_3]$ (*116*). Each $\mathbf{L_{38}}$ displays a bidentate fashion through both thiocarbonyl sulfur and thioether sulfur atoms bridging two octahedral silver atoms, giving an infinite chain. The strong S---S interactions with a distance of 3.41 Å between two nearby chains along the *b*-axis generate a two-dimensional network.

The corresponding copper(I) complex $[Cu_4I_4(\mathbf{L_{38}})_4]$ was prepared by reaction of $\mathbf{L_{38}}$ and CuI in acetonitrile (*117*). The structure consists of stepped Cu_4I_4 clusters bridged by $\mathbf{L_{38}}$ groups, and the resultant polymeric chains are further assembled by short interchain S---S contacts (3.257 Å) to form a three-dimensional network (Fig. 20).

Unusually short S---S contacts have been noticed among the $\mathbf{L_{38}}$ complexes; for example, 3.23 Å in $(TTF)[Pt(\mathbf{L_{38}})_2]_3$ and 3.26 Å in $(TTF)[Pd(\mathbf{L_{38}})_2]_2$, $[Ag(\mathbf{L_{38}})CF_3SO_3]$, and $[Cu_4I_4(\mathbf{L_{38}})_4]$ (*115*). The extremely short S---S contacts are attributable to metal–metal bonding in the first two cases, and to the coordination bond linkage as well as the effect of molecular packing in the rest. The copper(I) and silver(I) complexes of $\mathbf{L_{38}}$ were partially oxidized by iodine doping, and the electrical resistivity of the compressed pellet of the compounds as measured by the conventional two-probe technique. Like those of $\mathbf{L_{37}}$, they are nonconducting at room temperature but display semiconduc-

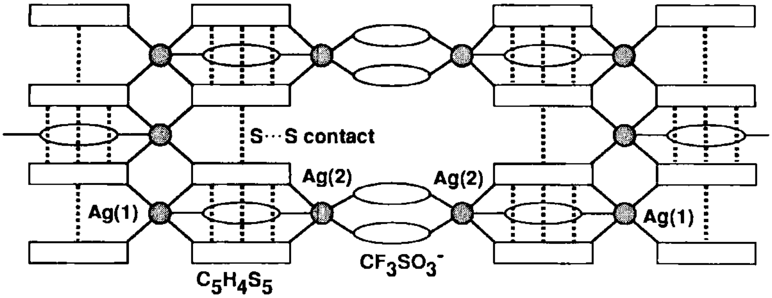


FIG. 19. Schematic representation of S---S contact assembled network in $[Ag(\mathbf{L_{38}})(CF_3SO_3)]$.

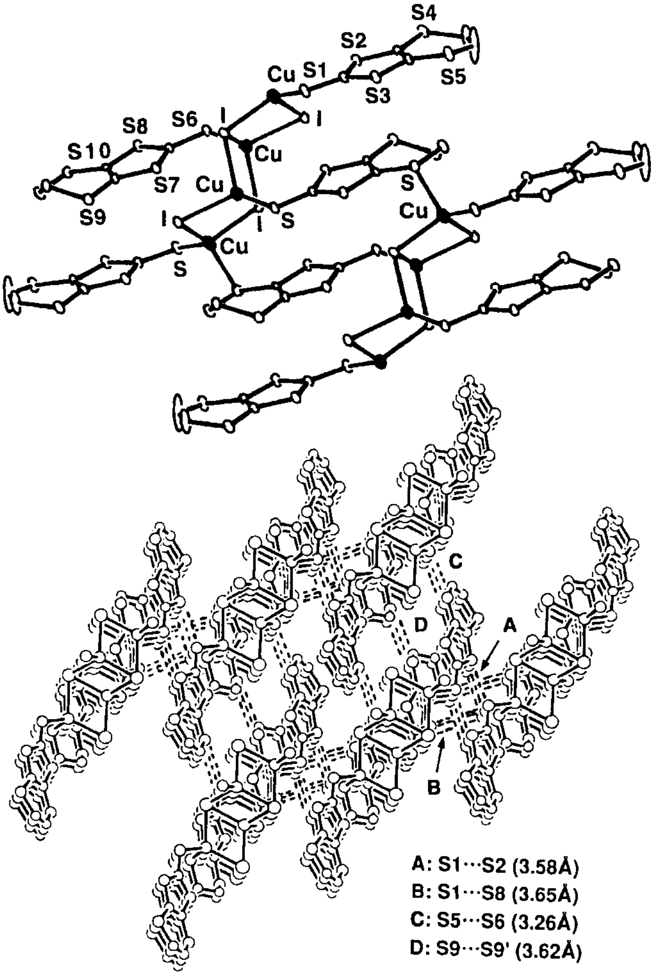


FIG. 20. Structure of $[Cu_4I_4(\mathbf{L}_{38})_4]$.

tivity after I_2 doping, with conductivities of 10^{-4}–10^{-5} S·cm^{-1} (Table III).

IV. Hexagonal Frameworks and Graphite-like Structures

The scaffolding and related microporous materials are receiving widespread interdisciplinary attention, and the borders between chemistry, physics, and materials science are therefore vague and subjective. Several general reviews and textbooks have provided a comprehensive overview of the chemistry and structural properties of these materials (*118–120*). The literature relating to assembly of copper(I) and silver(I) complexes into network structures with a graphite-related lattice has reflected a general interest and advancement in our understanding of the fundamental chemistry and processing characteristics of the system and its potential applications as molecular sieves, catalysts, and optical materials. This section is concerned with construction of hexagonal and graphite-like lattices regulated by the metal-ion stereochemistry, the ligand, and the counteranions, placing emphasis on the nitrogen-containing systems such as pyrazine, phenazine, 2,1,3-benzothiadiazoles, and quinoxaline (quin) (Fig. 21). Metal cyanide will be treated in a cursory manner, leaving the readers to consult recent literature and reviews.

A. Metal Cyanide—Regulated by the Metal Ion

Metal cyanide, which has received little attention for years in many texts concerned with inorganic structures, is now found to possess the most outstanding feature as a building block for infinite polymeric frameworks. Some rather elegant metal cyanide structures with extended frameworks have recently been discovered (*121–128*). The synthetic strategy is based on the combination of a diatomic bifunctional rodlike CN^- ion with a considerable preference for binding metals at each end in a linear fashion together with modification of

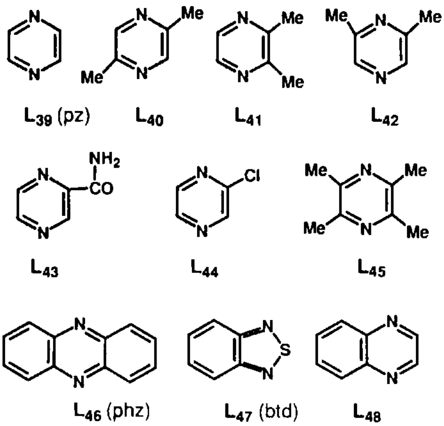


FIG. 21. Some nitrogen-containing ligands in copper(I) and silver(I) complexes having hexagonal frameworks.

the frameworks by metal ions favoring different stereochemistries. The crystal structures of $[N(CH_3)_4][Cu^IZn^{II}(CN)_4]$ and two isomorphous compounds, $Zn(CN)_2$ and $Cd(CN)_2$, have shown that the tetrahedral metal ions favor formation of interpenetrated diamondlike frameworks (*127*). A three-dimensional honeycomb structure containing hexagonal channels has been observed in complexes consisting of simple cyano-cadmium frameworks in which the metal centers are of two types: octahedral and distorted five-coordinate or octahedral and tetrahedral (*122*, *128*). By replacing CN bridges in multidimensional CN-linked octahedral cadmium complexes with linear NC–Ag–CN or NC–Ag(CN)–Ag–CN units, Iwamoto has successfully obtained two cadmium–silver complexes with double and triple interpenetrating frameworks (*123*). An infinite three-dimensional framework related to PtS has been observed in $[NMe_4][CuPt(CN)_4]$, in which tetrahedral Cu(I) and the square planar Pt(II) centers are linked together by CN rods, generating two mutually perpendicular and equivalent sets of hexagonal channels of large cross section together with large empty square channels perpendicular to the hexagonal channels as shown in Fig. 22 (*121*).

B. Pyrazine Systems—Regulated by Substituents

Pyrazine (**L**$_{39}$) and substituted pyrazines have long been known to act as *exo*-didentate ligands to linearly bridge metal ions, generating oligomeric and polymeric metal complexes with infinite chain and

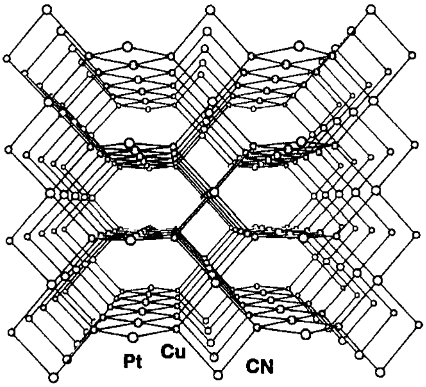


Fig. 22. Extended framework containing hexagonal and square channels observed in $[CuPt(CN)_4]_n^{n-}$. (From Fig. 2 in Gable, R. W.; Hoskins, B. F.; Robson, R. *J. Chem. Soc. Chem. Commun.* **1990**, 762.)

pleated sheet structures, double and triple interpenetrating frameworks, and interwoven honeycomb architecture (*123*, *129–132*). The essential features of some structurally characterized copper(I) and silver(I) complexes with pyrazine and its derivatives including quinoxaline and phenazine are summarized in Table IV. Among them those containing two-dimensional six-membered rings of metal ions linked by $\mathbf{L}_{39}$ bridges are rather common and thus have received considerable attention recently. From the point of view of rational synthesis, it would be possible to obtain polymeric graphite-related cationic lattices in which the three-coordinate metal ions are bonded only to bridging $\mathbf{L}_{39}$ ligands by utilizing noncoordinating anions as the counterions in the synthesis of $\mathbf{L}_{39}$ complexes. However, owing to the effects of substituents, the six-membered rings obtained differ in detail from complex to complex in terms of distortion of planarity, which can be grouped under four heads as shown in Fig. 23. It has been suggested that more than two substituents on a pyrazine ring would hinder four coordination of the metal ion, giving infinite zigzag chains or sheets of the cross-linked chains as observed in disubstituted pyrazine systems (*135*). Therefore, controlling spatial factors plays a key role in building infinite polymeric structures, and the modification of linking ligands by substituents on pyrazine is a practical method for the synthesis of designed copper(I) polymers.

Slightly distorted hexagonal frameworks defined by six $\mathbf{L}_{39}$-bridged copper(I) ions are observed in $[Cu_2(\mathbf{L}_{40})_3(PF_6)_2]$ ($\mathbf{L}_{40}$ = 2,5-dimethylpyr-

TABLE IV

Cu(I) AND Ag(I) COMPLEXES WITH PYRAZINE AND ITS DERIVATIVES

Compound	CN[a]	Frameworks	Ref.
$[Cu_2(\mathbf{L}_{40})_3(PF_6)_2]$	four	2-D hexagonal	*133*
$[Cu_2(\mathbf{L}_{41})_3](ClO_4)_2$	three	2-D hexagonal	*134*
$[Cu_2(\mathbf{L}_{42})_3](ClO_4)_2$	three	2-D hexagonal	*135*
$[Cu_2(\mathbf{L}_{39})_3]SiF_6$	three	2-D hexagonal	*136*
$[Cu_2(\mathbf{L}_{43})_3](ClO_4)_2(Me_2CO)_2$	four, five	2-D hexagonal	*29*
$[Cu_2(\mathbf{L}_{39})_3(CH_3CN)_2](PF_6)_2$	four	2-D hexagonal	*137*
$[Cu_2(\mathbf{L}_{44})_{4.5}](ClO_4)_2$	four	2-D hexagonal, square	*135*
$[Cu(\mathbf{L}_{40})_2]PF_6$	four	*3-D adamantane*	*133*
$[Cu_2(\mathbf{L}_{45})_3](ClO_4)_2$	three, two	linear	*137*
$[Cu_2(\mathbf{L}_{48})_3](ClO_4)]ClO_4$	four	3-D adamantane	*132*
$[Ag_2(\mathbf{L}_{46})(NO_3)_2]$	three	2-D hexagonal	*138*
$[Ag_2(\mathbf{L}_{39})_3](BF_4)_2$	three	2-D hexagonal, 3-D interpenetrating nets	*130*

[a] CN, coordination numbers of the metal ions.

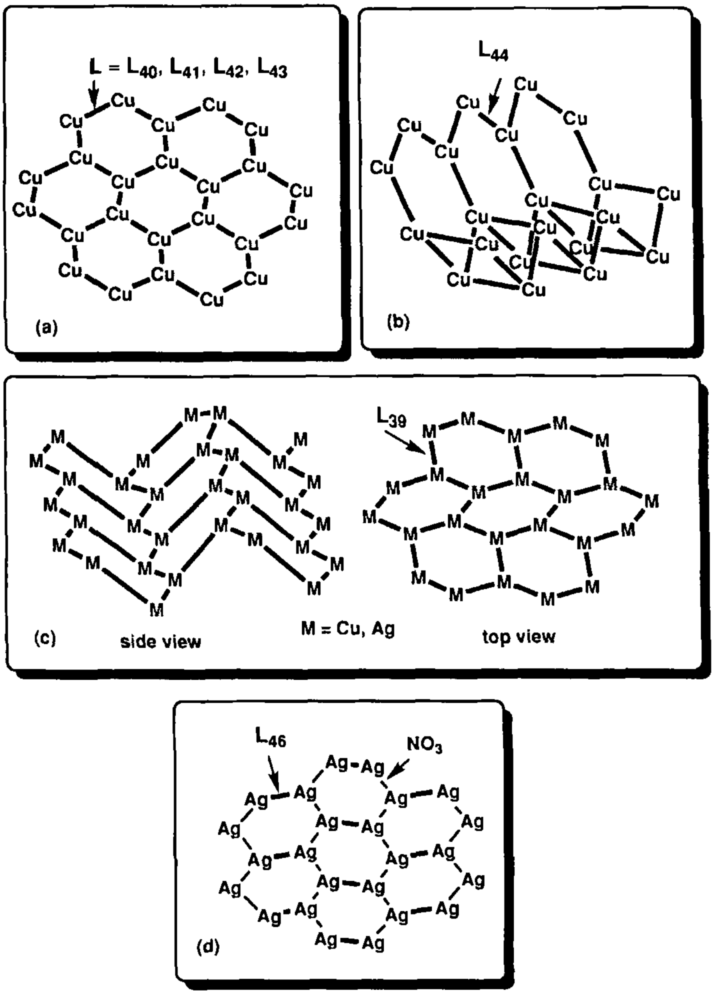


FIG. 23. Cu(I) and Ag(I) complexes of pyrazine and the derivatives having hexagonal frameworks: (a) slightly distorted hexagon; (b) distorted hexagon and square; (c) zigzag 2-D sheet; (d) ternary complex. The molecule in the box represents the ligand involved.

azine) (*133*), $[Cu_2(L_{41})_3])(ClO_4)_2$ (L_{41} = 2,3-dimethylpyrazine) (*134*), $[Cu_2(L_{42})_3](ClO_4)_2$ (L_{42} = 2,6-dimethylpyrazine) (*135*), $[Cu_2(L_{39})_3]SiF_6$ (*136*), and $[Cu_2(L_{43})_3](Me_2CO)_2$ (L_{43} = pyrazineamide) (*29*). Structural studies have established trigonal environments for the metal. These complexes show an infinite sheet structure of macrocations with uninteracting or weakly interacting counterions. If the interaction between the metal and the anion is ignored, the Cu(I) ion in these complexes is essentially in a three-coordinate trigonal planar geometry and the pyrazine ligands bridge adjacent trigonal metal centers to form a graphite-like lattice, Fig. 23(a). Thompson has successfully isolated two Cu(I) complexes from the same reaction mixture of an ethanolic solution of $Cu(PF_6)_2$ and $\mathbf{L_{40}}$, $[Cu_2(\mathbf{L_{40}})_3](PF_6)_2$ and $[Cu(\mathbf{L_{40}})_3]PF_6$ (*133*). The structure of the former is made up of parallel puckered layers of the cation, and within each layer the copper(I) ions are linked by $\mathbf{L_{40}}$, defining hexagons. PF_6^- anions are located between the layers and interact very weakly with the copper(I) ions through one F atom, leaving the Cu(I) ions essentially three coordinate. Except for the puckering of the layers, the structure is reminiscent of that of the intercalated graphite. By contrast, each metal ion in the latter case is bonded to four rather than three $\mathbf{L_{40}}$ molecules, with an angularly distorted CuN_4 chromophore. As a result, the structure exhibits a diamondoid framework of copper(I) ions linked by the rodlike $\mathbf{L_{40}}$ ligands, and the PF_6^- anions are located in cavities within the lattice.

Likewise, the reaction of $Cu(ClO_4)_2$ with $\mathbf{L_{41}}$ in an aqueous solution yields an air-stable complex, $[Cu_2(\mathbf{L_{41}})_3(ClO_4)_2]$, whose structure is also found to contain a similar two-dimensional graphite lattice of tricoordinate copper(I) atoms bridged by $\mathbf{L_{41}}$ ligands (*134*). Although the exact course for reduction of copper(II) complexes with nonchelating ligands is not clear, the most plausible explanation lies in tetrahedral distortion of the square planar copper(II) species by crowding effects of the methyl groups, and consequently, such reduction process is dependent on the substituents, temperature, and solvents (*133*, *134*). On the other hand, copper(I) complexes of $\mathbf{L_{39}}$ can also be prepared by direct reaction of copper(I) salts, $[Cu(CH_3CN)_4]X$, and $\mathbf{L_{39}}$ ligands in nonaqueous solutions, such as $[Cu_2(\mathbf{L_{39}})_3]SiF_6$ (*136*). Here again the $\mathbf{L_{39}}$ ligands bridge adjacent trigonal Cu^I centers to form hexagonal frameworks with bridged copper cations 6.936 and 6.685 Å apart. The SiF_6^{2-} anions are located in channels and are hydrogen bonded to $\mathbf{L_{39}}$ hydrogen atoms. The most significant feature of the complex is that the hexagonal frameworks are interwoven as shown in Fig. 24.

The three-coordinate copper(I) ions can also be linked by the disubstituted $\mathbf{L_{39}}$ on the 2- and 6-positions as observed in $[Cu_2(\mathbf{L_{42}})_3](ClO_4)_2$ (*135*). The graphite-like lattice is constructed by the alternating arrangement of the two crystallographically independent three-coordinate copper atoms. The hexagons generated by the Cu_6 units are slightly distorted due to compression, and the mutually confronted $\mathbf{L_{42}}$ molecules on the sides of the hexagon are sitting out of the plane and parallel to each other, providing a large cavity. It is surprising that neither the anion nor the solvent molecule is included in the cavity,

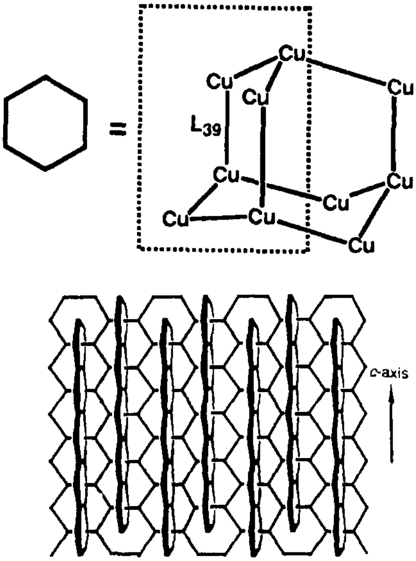


FIG. 24. Schematic view of the interwoven honeycomb grids in $[Cu_2(L_{39})_3]SiF_6$. (From Fig. 4 in MacGillvray, L. R.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc. Chem. Commun.* **1994,** 1325.)

they rather form acetone–perchlorate layers intercalated between the copper sheets.

Formation of trigonal copper(I) polymers with dimethyl-substituted pyrazines is presumably due to the two substituents on the $\mathbf{L}_{39}$ ring, which hinder the formation of tetrahedral coordination of the metal. No examples of hexagonal frameworks are found to be built up by tetrahedral copper(I) ions. This is understandable because formation of graphite-like sheets would require Cu_6 motifs on a plane with each metal center linked to three neighbors. Therefore, trigonal, trigonal pyramidal, and trigonal bipyramidal stereochemistries are necessary. The recently characterized copper(I) complex $[Cu_2(L_{43})_3](ClO_4)_2(Me_2CO)_2$ provides the first example of mixed four- and five-coordinate copper(I) ions composing such a hexagon (*29*). As illustrated in Fig. 25, the cation contains two crystallographically independent copper(I) ions; one involves a distorted trigonal pyramidal CuN_3O core composed of the terminal pyrazine nitrogens of three different $\mathbf{L}_{43}$ molecules and an axial caboxamide oxygen, and the second involves a distorted trigonal bipyramidal structure with two, rather than one, carboxamide oxygen atoms occupying the apical positions. Each $\mathbf{L}_{43}$ molecule exhib-

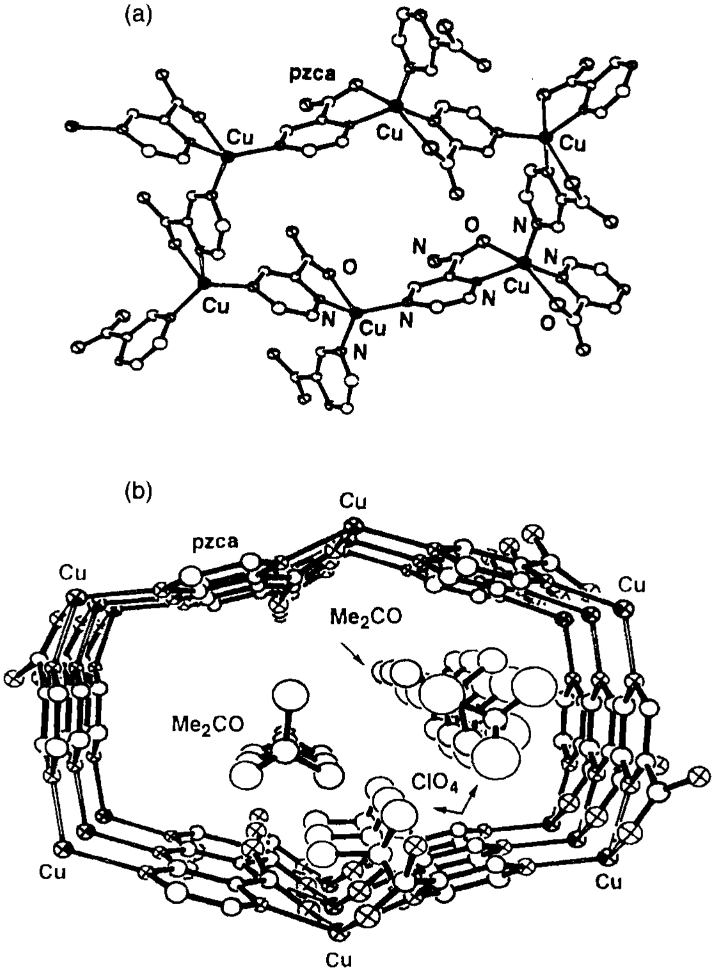


FIG. 25. Molecular structure of $[Cu_2(L_{43})_3](ClO_4)_2(Me_2CO)_2$ in which the four- and five-coordinate Cu(I) ions are bridged by the tridentate L_{43} groups (a) giving a hexagonal channel structure with pores open to accommodate ClO_4^- ions and acetone molecules (b). (From Figs. 1 and 2 in Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Moriwaki, K.; Kitagawa, S. *Inorg. Chem.* **1997,** *36,* 5416.)

its a tridentate coordination mode, bridging two metal centers, giving apparently hexagonal channels with pores open to accommodate the anions and acetone molecules as guests.

The complexes falling into other groups as shown in Fig. 23(b)–(d), are significantly less numerous. The chlorine-substituted pyrazine is reported to form a coordination polymer containing both distorted hexagonal and square frameworks. The reaction of 2-chloropyrazine (L_{44}) with [$Cu(C_2H_4)ClO_4$] in acetone yielded orange brick crystals, [$Cu_2(L_{44})_{4.5}$](ClO_4)$_2$. Structural studies have shown both copper(I) ions involved tetrahedral environments (*135*). As L_{39} and the dimethyl-substituted derivatives do, each L_{44} molecule exhibits a bidentate coordination bridging two metal centers forming a square planar Cu_4 framework. These square planes are linked to each other by sharing the edges to afford one dimensional ribbons. The adjacent ribbons are further bridged by L_{44}, leading to two-dimensional pleated hexagonal Cu_6 sheets (Fig. 26). The results further demonstrate that in metal complexes of L_{39} derivatives, the substituents on pyrazine can greatly

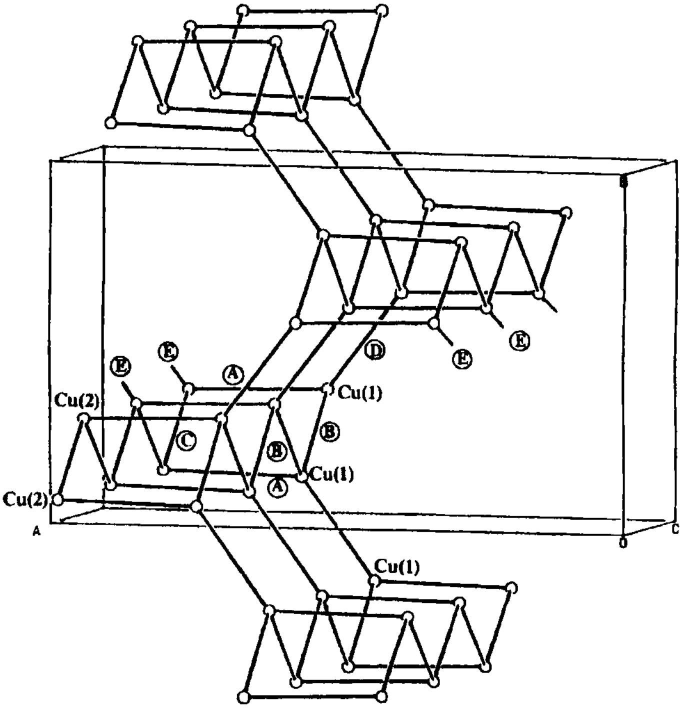


FIG. 26. Schematic drawing of infinite sheets in [$Cu_2(L_{44})_{4.5}$](ClO_4)$_2$. Copper atoms and bridging L_{44} molecules are denoted by open circles and solid lines, respectively. Each pyrazine ring is distinguished by alphabetical label. (From Fig. 2 in Kitagawa, S.; Kawata, S.; Kondo, M.; Nozaka, Y.; Munakata, M. *Bull. Chem. Soc. Jpn.* **1993,** *66,* 3387.)

affect the stereochemistry of the metal, which in turn plays a key role in determining the framework of the structure.

The copper(I) complexes with pyrazine and tetramethylpyrazine (**L**$_{45}$) may be the best examples to elucidate the steric effects imposed on the substituted pyrazine toward rational synthesis of copper pyrazine polymeric complexes in the single-crystal phase (*137*). The single crystals of both $[Cu_2(\mathbf{L}_{39})_3(CH_3CN)_2](PF_6)_2$ and $[Cu_2(\mathbf{L}_{45})_3](ClO_4)_2$ were prepared by reaction of the corresponding ligand and the copper(I) salt in acetone. In contrast to the disubstituted pyrazine complexes, in which the metal ions in most cases are found to be in a trigonal environments, the geometry around the copper atom in $[Cu_2(\mathbf{L}_{39})_3(CH_3CN)_2](PF_6)_2$ is a distorted tetrahedron comprising three **L**$_{39}$ nitrogens and one bent bonding of CH_3CN. Consequently, the hexanuclear unit Cu_6 present in the infinite cationic sheet is in a chair-type cyclohexane-like framework [Fig. 23(c)]. On the other hand, the **L**$_{45}$-bridged copper(I) complex $[Cu_2(\mathbf{L}_{45})_3](ClO_4)_2$ contains a linear chain polymeric framework. The two copper atoms in the unit cell have different coordination environments, one with trigonal planar and the other with perfect linear geometry. The two-coordinate Cu(I) ions form a linear chain framework, and the trigonal ions are attached to the chain just like a pendant (Fig. 27). The fact that a hexagonal or cyclohexane-like framework of copper atoms is not present in the cation is due to the bulky **L**$_{45}$ ligands. The four methyl groups on all the substitutable positions of pyrazine give rise to steric constraints and, as a result, prevent formation of a hexagonal ring unit and give a linear link as a less steric form.

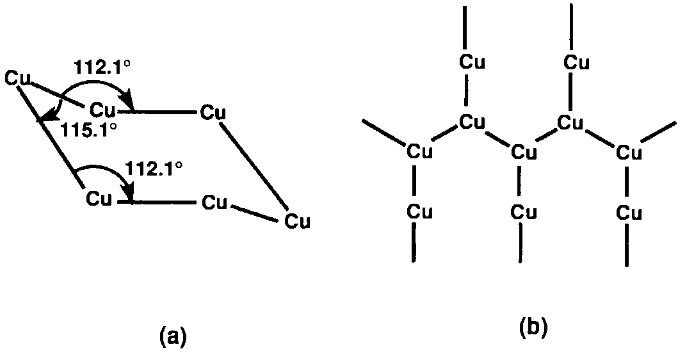


FIG. 27. Schematic views of the chairlike hexagonal framework in $[Cu_2(\mathbf{L}_{39})_3(CH_3CN)_2](PF_6)_2$ (a) and an infinite chain structure in $[Cu_2(\mathbf{L}_{45})_3](ClO_4)_2$ (b). (From Fig. 1b in Kitagawa, S.; Munakata, M.; Tanimura, T. *Inorg. Chem.* **1992,** *31,* 1714.)

C. Phenazine and Benzothiadiazole Systems—Regulated by Counteranions

Like pyrazine, phenazine ($\mathbf{L}_{46}$), 2,1,3-benzothiadiazoles ($\mathbf{L}_{47}$), and quinoxaline ($\mathbf{L}_{48}$) are of interest in the construction of the molecular assembly of the metal complexes because they can also act as bridging ligands linking two metal centers (*138*, *139*). Phenazine formed 1:1 donor–acceptor complexes with PMDA (pyromellitic dianhydride) and TCNQ, whose structures show alternate stackings of donor and acceptor molecules (*140*, *141*). Several copper(I) and silver(I) complexes of $\mathbf{L}_{46}$ have been prepared and their structures determined, and among these silver(I) nitrate, $[Ag_2(\mathbf{L}_{46})(NO_3)_2]$, is of particular interest (*138*). The compound was prepared by reaction of $AgNO_3$ and $\mathbf{L}_{46}$ in methanol at ambient temperature. In this complex each silver atom is coordinated to two nitrate anions and one $\mathbf{L}_{46}$ molecule in a distorted trigonal geometry, and each $\mathbf{L}_{46}$ molecule in turn links two trigonal silver ions as expected, Fig. 23(d). The most remarkable feature of the ternary complex is that the counteranion NO_3^- acts as a spacer linking two $\mathbf{L}_{46}$-bridged Ag atoms, leading to a framework of six-membered rings of silver atoms extending in the direction of the *b*- and *c*-axes (Fig. 28). The Ag–O bond distances of 2.432(6) and 2.569(7) Å are in the range of 2.367 to 2.689 Å for Ag(I) complexes with nitrate, suggesting fairly strong interaction between the metal and the nitrate ion. The six Ag atoms on a two-dimensional sheet lie

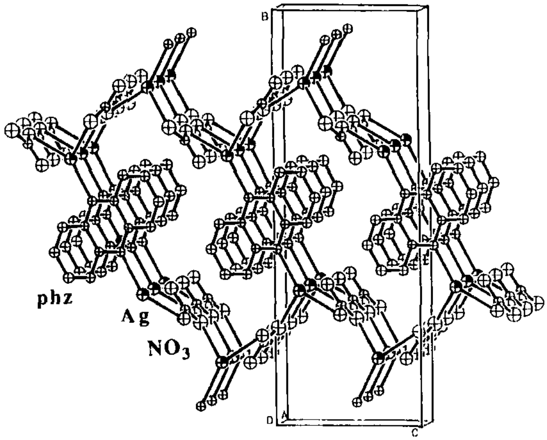


FIG. 28. Hexagonal framework in $[Ag_2(\mathbf{L}_{46})(NO_3)_2]$ is constructed by six metal ions interconnected by $\mathbf{L}_{46}$ and NO_3^-. (From Fig. 10 in Munakata, M.; Kitagawa, S.; Ujimaru, N.; Nakamura, M.; Maekawa, M.; Matsuda, H. *Inorg. Chem.* **1993**, *32*, 826.)

approximately on the same plane, and each sheet is weakly linked to its neighbors by the interaction of Ag and the third oxygen atom of the nitrate anion with an Ag–O distance of 2.669(7) Å, giving a three-dimensional structure composed of the two-dimensional sheets. By contrast, in the corresponding silver perchlorate complex of $\mathbf{L}_{46}$, $[Ag(\mathbf{L}_{46})ClO_4]$, the perchlorate ions are not coordinated, and subsequently the complex is composed of infinite $-Ag-\mathbf{L}_{46}-Ag-\mathbf{L}_{46}-$ linear chains along the a-axis and a π–π interaction of the $\mathbf{L}_{46}$ aromatic rings between the chains. It is informative enough that in the mononuclear copper(I) nitrate complex of $\mathbf{L}_{46}$, $[Cu(\mathbf{L}_{46})_2(NO_3)]$, the Cu(I) ion is coordinated to two terminal $\mathbf{L}_{46}$ molecules and chelated by two oxygen atoms of the nitrate in a distorted tetrahedral environment. The structural differences between the copper(I) nitrate and silver(I) nitrate complexes of $\mathbf{L}_{46}$ are obviously due to the pronounced tendency of copper(I) ion for a tetrahedral coordination. Therefore, in the metal–phenazine system the counteranion as well as metal ion stereochemistry play an important role in regulation of the molecular assembly into different frameworks and stoichiometries.

Three copper(I) complexes of $\mathbf{L}_{47}$ have been reported and it reveals that the frameworks in the compounds are regulated by the counteranions as shown in Fig. 29 (*139*). Because perchlorate ion has weak

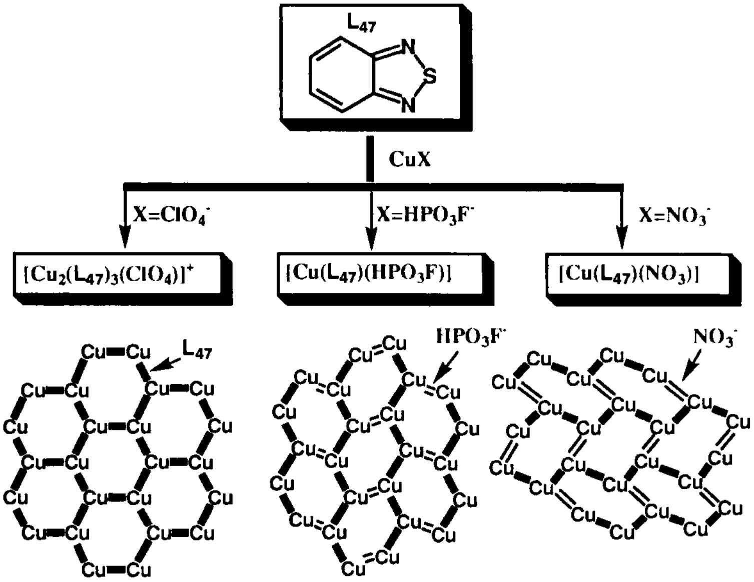


FIG. 29. Regulation of the six-membered ring structures by anions in an $\mathbf{L}_{47}$ system.

coordination ability, in $[Cu_2(\mathbf{L}_{47})_3(ClO_4)]ClO_4$ one ClO_4^- is noncoordinating and the other binds weakly with only one copper ion rather than as a interconnecting ligand. This leaves the two copper atoms in different coordination environments, tetrahedral and trigonal geometry, respectively. As a result, the complex is composed of a $[Cu_6(\mathbf{L}_{47})_6]^{6+}$ framework containing a six-membered ring of copper atoms interconnected only by $\mathbf{L}_{47}$ molecules (Fig. 30). Copper atoms in the two-dimensional sheet are arranged in a staggered conformation with a maximum deviation of 0.50 Å from the mean plane. Replacement of copper(I) perchlorate by copper(I) hexafluorophosphate in reaction with $\mathbf{L}_{47}$ isolated another polymeric complex with the for-

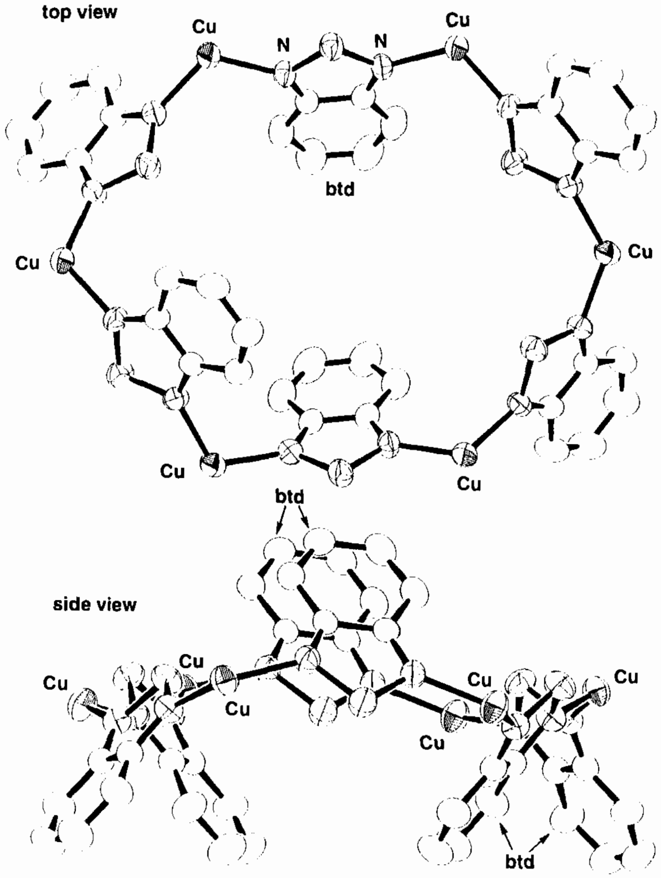


FIG. 30. The six-membered ring of copper atoms in $[Cu_2(\mathbf{L}_{47})_3(ClO_4)]ClO_4$ is composed of $[Cu_6(\mathbf{L}_{47})_6]^{6+}$ unit. The coordination of perchlorate is not shown.

mula [Cu(L_{47})(HPO_3F)]. In this complex each Cu(I) ion is coordinated to two nitrogen atoms of different L_{47} ligands and two oxygen atoms of different HPO_3F^- ions in a distorted geometry. An important feature of the structure is that the HPO_3F^- anion acts as an interconnecting ligand between two Cu atoms and takes part along with L_{47} in formation of the significantly distorted hexagonal framework composed of $[Cu_6(L_{47})_4(HPO_3F)_4]^{2+}$ units (Fig. 31). The copper atoms in the two-dimensional sheet are arranged in a ladder pattern in the *ac*-plane and a shallow roof pattern in the *ab*-plane. As discussed earlier, nitrate ion is expected to change the framework of the six-membered rings of copper atoms because it often functions as a bridging ligand. The copper(I) nitrate complex of L_{47} [Cu(L_{47})(NO_3)] was prepared by reduction of copper(II) nitrate trihydrate under an ethylene atmosphere followed by reaction with L_{47} in THF. In the complex the tetrahedral coordination of each copper ion is achieved by two L_{47} ligands

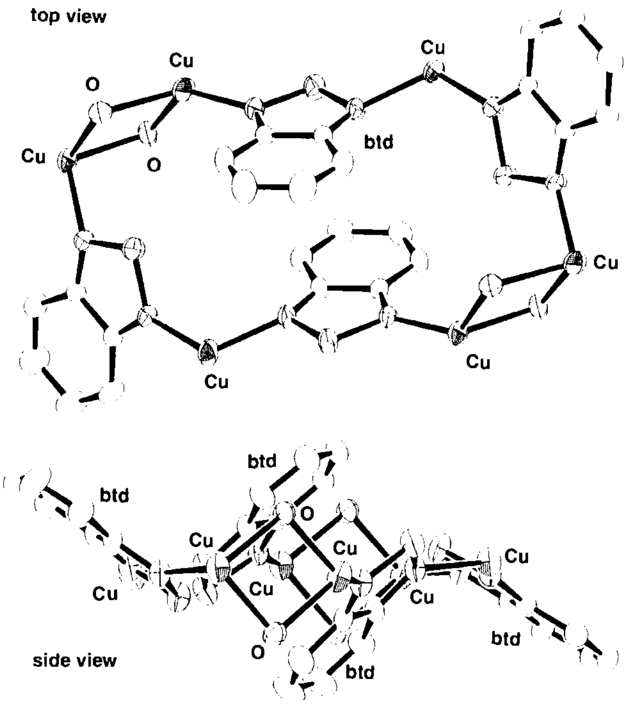


FIG. 31. The anion HPO_3F^- acts as an interconnecting ligand between two Cu atoms (only the coordinating oxygen atom is shown) and takes part in formation of the hexagonal framework in [Cu(L_{47})(HPO_3F)].

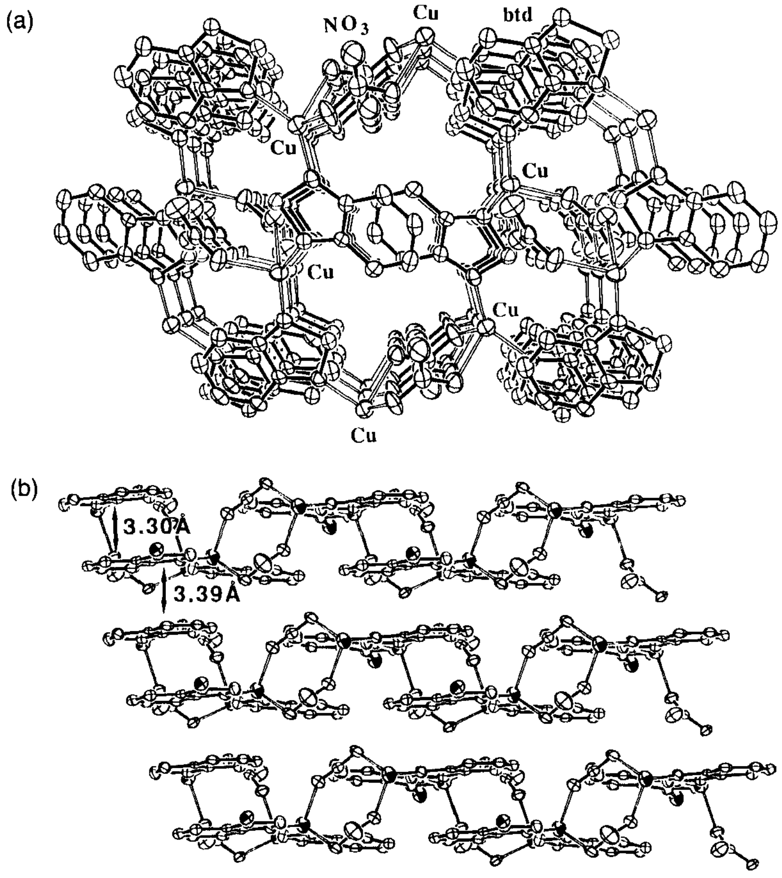


FIG. 32. Top (a) and side (b) views of the stacks of L_{47} molecules within and between 2-D sheets in $[Cu(L_{47})(NO_3)]$. (From Fig. 6 in Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Nakamura, M.; Akiyama, S.; Kitagawa, S. *Inorg. Chem.* **1994,** *33*, 1284.)

and two nitrate anions (Fig. 32). The six-membered rings of metal ions interconnected by L_{47} and NO_3^- are extremely distorted, and are in fact in a chair form, with the maximum deviation of the Cu atom from the mean plane being 2.1–2.4 Å. Examined along the *c*- and *b*-axis, the copper atoms in the sheet are arranged in a ladder and a roof pattern, respectively. In addition, the shortest interplanar spacing distances of L_{47} moeties within and between the sheets are 3.30 and 3.39 Å, respectively. Consistent with the observed π–π interactions in the system, the complex in powder form shows semiconductivity, with electric conductivity σ being $10^{-6.3}$ $S \cdot cm^{-1}$.

It is proposed that a combination of three- and four-coordinate metal ions and bridging pyrazine and pyrazole molecules is highly preferred for construction of a two-dimensional sheet structure composed of six-membered rings of metal ions interconnected by aromatic ligands. The participation of suitable counteranions in coordination environments of the metal ions can regulate the frame of the ring, which governs the orientation of the aromatic ligands and the stack of the aromatic ligand within and between the sheets (*139*).

V. Hydrogen-Bond-Assembled Frameworks

Self-associated intermolecular and intramolecular hydrogen-bonding assemblies have captured the attention of many research groups involved in supramolecular chemistry, molecular recognition, and crystal engineering because suitable matching of hydrogen bond donors and acceptors in number and orientation frequently leads to formation of new molecular aggregates (*142–167*). Hydrogen bonds are of paramount importance in biochemistry for determining the secondary structure of proteins and binding substrates to enzymes, receptors, and carriers. They are weaker than conventional covalent bonds but stronger than van der Waals interactions. Although there is no universal agreement on the best description of the nature of the forces in the hydrogen bond, it is generally accepted that hydrogen bonding, $X{-}H\cdots Y$, occurs only between a hydrogen atom bound to an electronegative atom X and another atom Y that is also highly electronegative and has one or more lone pairs, enabling it to act as a base (*142*). The concept of hydrogen bonding was originally used to explain physical properties of simple organic and inorganic compounds such as abnormally high boiling points and heats of vaporization, but in recent years it has been noted that the introduction of a hydrogen-bonding interaction between ligands in transition-metal complexes is an indispensable tool for creating a variety of molecular architectures in a predictable fashion via self-assembly and molecular recognition. Several important reviews related to this field now are available (*142–147*).

With the combination of the covalent bond forming capability of the metal ion and the inherent capability of the ligand for formation of complementary hydrogen bonds, a diversity of H-bonded structures has been obtained, including intramolecular hydrogen-bonded monomers (*148*), intermolecular hydrogen-bonded dimers, tetramers (*149–151*) and polymers having one-dimensional chain (*152*), two-dimensional sheet (*153–158*) and three-dimensional networks (*159–163*). The most commonly encountered hydrogen-bonding interactions in H-bonded supramolecular frameworks are O—H---O and N—H---O. Additionally, some weak hydrogen bond interactions such as C—H---O, C—H---Cl and even X—H---arene are also reported (*146*). The interaction may involve only one hydrogen bond donor and one acceptor, may be bifurcated or trifurcated, and may occur between atoms, molecules, or ions (*142*). In this respect, the bifunctional ligands should contain the simple functional groups such as carboxyl, amide, amino, cyano, and pyridone. Recent reports have shown that hydrogen bonds can occur in the system between ligand functional groups and some inorganic anions such as BF_4^-, ClO_4^-, SO_4^{2-}, and halides, and even water and ammonia molecules (*146*, *148*, *158*). The ligands involved in the following discussion of the hydrogen-bonded complexes of Cu and Ag are listed in Fig. 33.

Mingos has shown in his recent review how the application of molecular recognition principles based on triple hydrogen bonding resulted in the crystal engineering of aggregates based on ligands that can simultaneously form stable and inert metal–ligand bonds and have recognition sites for complementary arrangements of hydrogen-bond donors and acceptors (*144*), which has been excellently demonstrated by self-assembly of the copper(II) complex [Cu(L_{49})$_2$ · 2 melamine] (**HL_{49}** = 5-(2-pyridylmethylene)-hydantoin) in which **L_{49}** involves simultaneous coordination with Cu and an ADA≡DAD (A = hydrogen-bond acceptor, D = hydrogen-bond donor) triple hydrogen-bonding arrangement with melamine molecules (Fig. 34) (*156*).

Among extended polymeric structures, two-dimensional hydrogen-bonded frameworks are enormously popular, and the resulting assemblies resemble practically crinkled tapes (*153*, *154*) and infinite sheets (*155–158*). Smith and co-workers have structurally characterized a

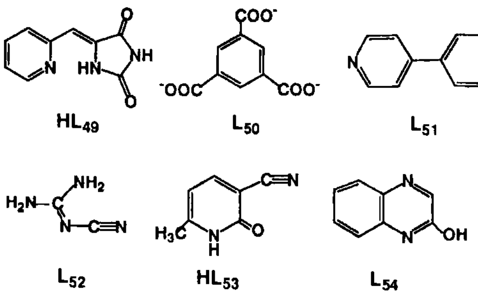


FIG. 33. List of ligands in copper(I) and silver(I) complexes having hydrogen-bonding networks.

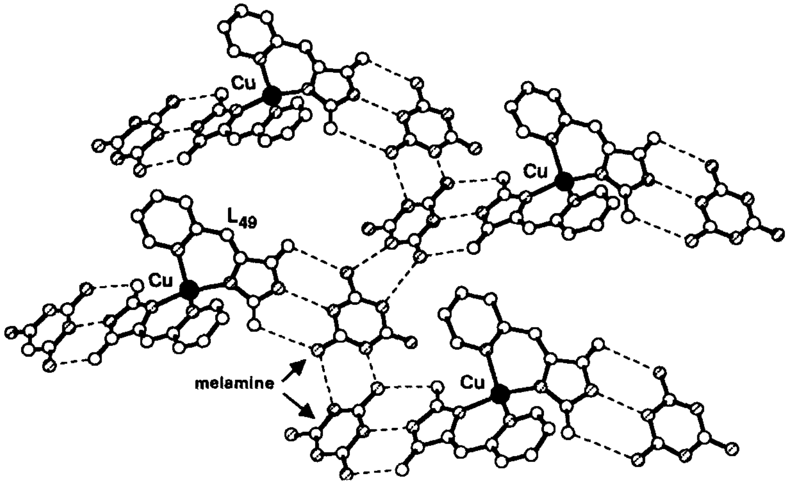


FIG. 34. Hydrogen-bonding networks in [Cu(L_{49})$_2$ · 2 melamine]. (From Fig. 2 in Chowdhry, M. M.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1996,** 899.)

number of silver(I) carboxylates, and among these phthalate and trimesate ($\mathbf{L_{50}}$) have been found to form hydrogen-bonded polymers involving the ammonia molecule (*155*). The silver(I) complex [Ag_2(phthalate)(NH_3)$_2$] contains a phthalate-bridged dimeric unit in which each Ag atom is coordinated to one ammonia molecule and a single phthalate carboxylate oxygen in an essentially linear fashion. All three amine hydrogens are involved in intermolecular hydrogen-bonding interactions, giving a two-dimensional hydrogen-bonded sheet structure extending across the *bc*-direction of the cell (Fig. 35). The adjacent sheets are further linked by hydrogen bonds via the uncoordinated carboxyl oxygens. In the corresponding trimesate complex, [NH_4][Ag_5($\mathbf{L_{50}}$)$_2$(NH_3)$_2$(H_2O)$_2$] · H_2O, a two-dimensional sheet framework is based on a pseudo-centrosymmetric *S*-type trimer unit linked by the carboxylate groups of two independent trimesate residues, and the hydrogen bonds between the uncoordinated carboxylate oxygens and amine and water molecules stabilize the structure. Likewise, in the copper(II) complex of 4,4′-bipyridine ($\mathbf{L_{51}}$), the coordinating water molecule bridges between the metal center and uncoordinated $\mathbf{L_{51}}$, affording two-dimensional rectangular grid sheets (*158*). The structural determination of the Cu(I) complex of 2-cyanoguanidine ($\mathbf{L_{52}}$), [{Cu($\mathbf{L_{51}}$)$_2$}$_2$($\mathbf{L_{51}}$)][BF_4]$_2$ · MeCN, reveals that the structure contains a dinuclear cation in which two T-shaped copper(I) centers are bridged by $\mathbf{L_{51}}$ and terminally coordinated by two $\mathbf{L_{52}}$ molecules

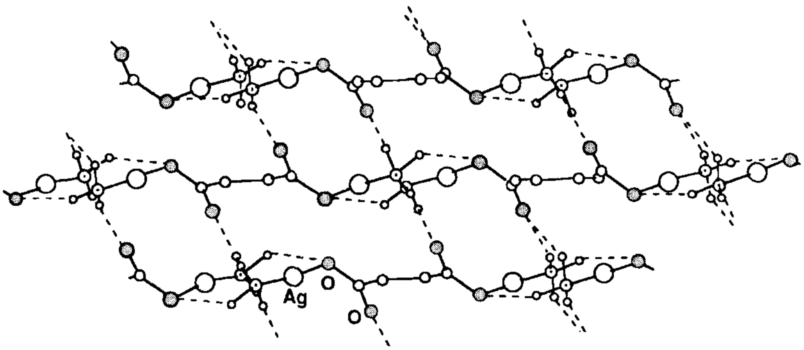


FIG. 35. Hydrogen-bonding networks in $[Ag_2(phthalate)(NH_3)_2]$. (From Fig. 2 in Smith, G.; Reddy, A. N.; Byriel, K. A.; Kennard, C. H. L. *J. Chem. Soc., Dalton Trans.* **1995,** 3565.)

(*157*). An extensive hydrogen-bonding network between BF_4^- ions and L_{52} molecules gave a two-dimensional sheet structure as shown in Fig. 36. It is intresting to note that all four F atoms for each anion are involved in hydrogen bonding, three of which are sitting within the two-dimensional sheets and the fourth bridging the sheets.

The principles of molecular recognition can also be used to assemble three-dimensional structures, but additional requirements on the number and orientation of the complementary hydrogen bonding motifs must be met (*159–163*). Nakasuiji has selected biimidazole, pterine, lumazine, and glycoxime as the target ligands because their chelating ability to a metal element and multi-H-bonding sites, and has constructed a number of three-dimensional hydrogen-bonded networks of metal ions such as Ni(II) and Cu(II) (*160*, *161*). Molecules in which the motifs are related by T_d or even S_4 symmetry are strong potential candidates for the engineering of a three-dimensional network exhibiting microchannels or diamondoid structures (*146*). The system we have worked with are literally double hydrogen bonding of the ligands combined with tetrahedral copper(I) ion in an attempt to design unprecedented two-dimensional and three-dimensional molecular architectures.

A. THREE-DIMENSIONAL SUPRAMOLECULAR Cu(I) COMPLEXES WITH CHANNELS

The bifunctional ligand 3-cyano-6-methyl-2(1*H*)-pyridinone (**HL_{53}**) as shown in Fig. 33, possesses both a coordination group (CN) and a

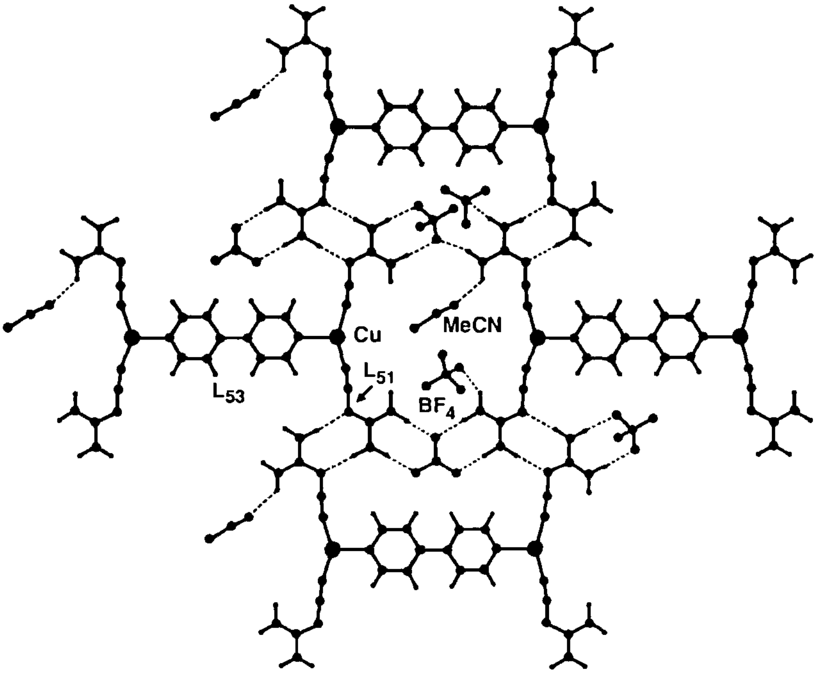


FIG. 36. Two-dimensional sheet structure of $[\{Cu(\mathbf{L}_{52})_2\}_2(\mathbf{L}_{61})][BF_4]_2 \cdot MeCN$ showing hydrogen-bonding associations. (From Fig. 2 in Batsanov, A. S.; Begley, M. J.; Hubberstey, P.; Stroud, J. *J. Chem. Soc., Dalton Trans.* **1996,** 1947.)

hydrogen-bonding site (pyridone), and it would be a suitable candidate for the formation of H-bonded metal complex supramolecules. The second reason for choosing it in the study is its relatively small size, which would reinforce the unidentate coordination of each ligand to the tetrahedral copper(I) ion without steric hindrance. The reactions of copper(I) salts with $\mathbf{HL}_{53}$ in acetone have isolated four coordination polymers, $[Cu(\mathbf{HL}_{53})_4]X$, where X = ClO_4^-, BF_4^-, PF_6^-, and $CF_3SO_3^-$ (*164*). 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 types of different frameworks—namely, square channel and superadamantane networks—depending on the kinds of counteranions. In the complexes with relatively small anions, perchlorate and tetrafluroborate, each $\mathbf{HL}_{53}$ molecule is hydrogen bonded to two adjacent others through pyridone N and O atoms; that is, each $[Cu(\mathbf{HL}_{53})_4]X$ entity is connected to eight neighboring counterparts as shown in Fig. 37. The dihedral

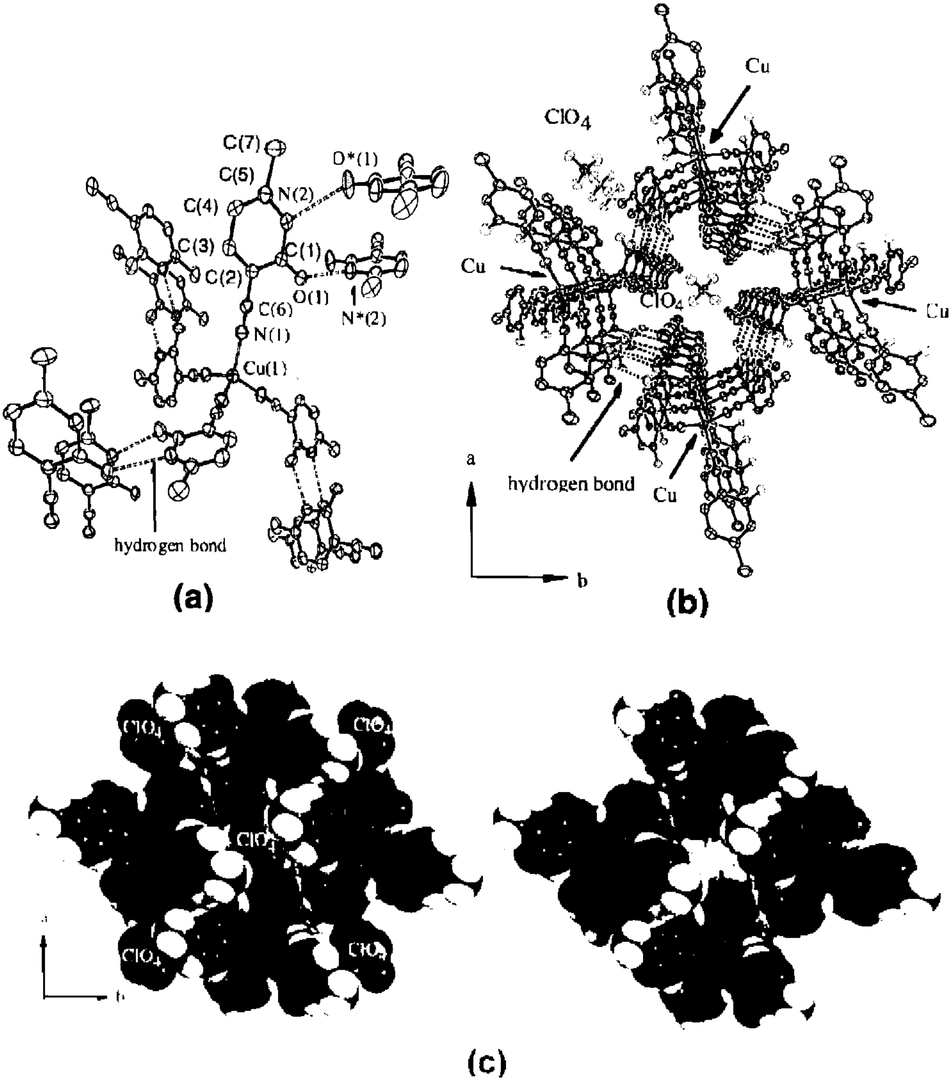


FIG. 37. Part of the hydrogen-bonded structure (a), packing diagram (b), and space-filling model (c) of $[Cu(HL_{53})_4]ClO_4$. (From Figs. 2 and 3 in Munakata, M.; Wu, L. P.; Yamamoto, M.; Kuroda-Sowa, T.; Maekawa, M. *J. Am. Chem. Soc.* **1996,** *118,* 3117.)

angle between the hydrogen-bonded $\mathbf{HL_{53}}$ groups is 83.44° and 84.98° for the perchlorate and the tetrafluroborate, respectively. This results in four $[\mathrm{Cu}(\mathbf{HL_{53}})_4]\mathrm{X}$ monomers interconnected through hydrogen bonds, forming a layer with an open cavity occupied by the counter-anion. The overall structure is made of such layers, each consisting of an infinite square array of copper atoms coordinated with $\mathbf{HL_{53}}$ groups and bridged by hydrogen bonds, leading to the cross-linking of a given layer with those immediately above and below it. A square channel framework is generated with a relatively small size of cavities (*ca.* 12.1 Å in diameter) filled with guest anions. Let us name such hydrogen bonding as **A type**, illustrated schematically in Fig. 38. The hydrogen bonding network in $[\mathrm{Cu}(\mathbf{L_{53}})(\mathbf{HL_{53}})_3]$ is also found to belong to this type (*165*).

When the small anion is changed to the drastically larger one, $\mathrm{PF_6^-}$ or $\mathrm{CF_3SO_3^-}$, 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 destablizing repulsion is to rearrange the hydrogen-bonding mode as **B type**, that is, each $\mathbf{HL_{53}}$ moiety in the monomeric unit of $[\mathrm{Cu}(\mathbf{HL_{53}})_4]\mathrm{X}$ is head-to-tail hydrogen bonded to only one adjacent $\mathbf{HL_{53}}$ molecule, rather than two, with a rather smaller dihedral angle (0°–11.43°). Thus, one $[\mathrm{Cu}(\mathbf{HL_{53}})_4]\mathrm{X}$ entity is connected to four adjacent others, and these repeating units form a three-dimensional adamantane architecture of metal atoms (Fig. 39). The diamondoid frameworks are stacked with each other in such way that all the copper centers are found on lines parallel to the *c*-axis, which defines enormous linear chambers with larger open cavities (*ca.* 13.3 Å in diameter), that just fit the large anions $\mathrm{PF_6^-}$ and $\mathrm{CF_3SO_3^-}$.

To show how the assembling process would respond in the system

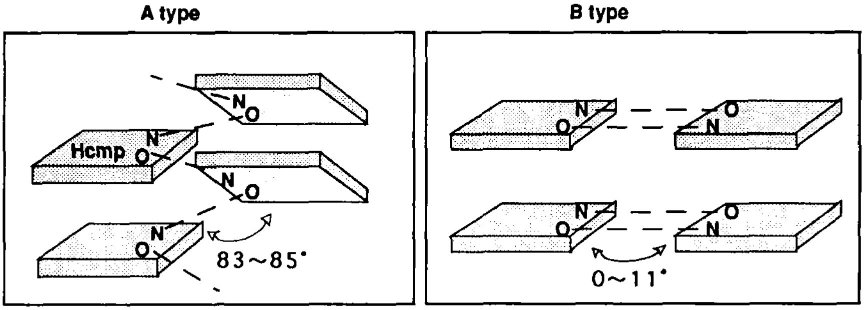


FIG. 38. Schematic presentation of two types of hydrogen bonds in $\mathbf{HL_{53}}$ complexes.

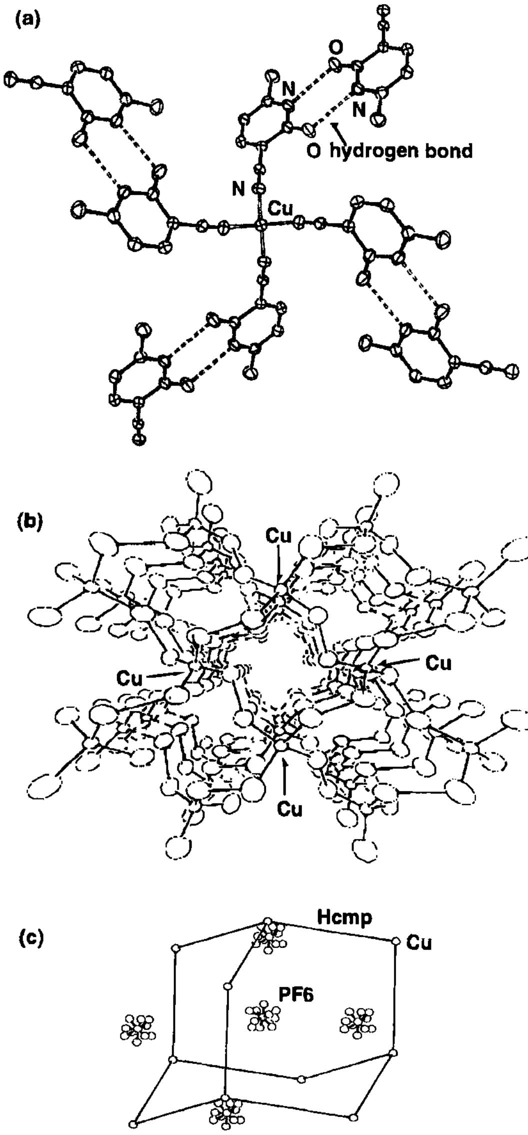


FIG. 39. Part of the hydrogen-bonded structure (a), packing diagram (b), and perspective view of diamondoid framework (c) in $[\mathrm{Cu}(\mathbf{HL}_{53})_4]\mathrm{PF}_6$.

when H-bonding interaction is absent, the structures of two copper(I) complexes of $\mathbf{L}_{53}$ were determined (*165*, *166*). It reveals a completely different stoichiometry and framework in both $[Cu_5(\mathbf{L}_{53})_4]ClO_4$ and $[Cu_{10}(\mathbf{L}_{53})_8](BF_4)_2$, in which each deprotonated $\mathbf{L}_{53}$ monoanion employs all its three functional groups bridging three rather than two copper atoms, forming a supramolecular channel architecture containing a Cu_4 cluster (Fig. 40). These findings suggest that the bifunctional ligand group $\mathbf{HL}_{53}$ possesses unique ability for the molecular recognition, which has 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 at molecular level can effectively facilitate transition of one framework to the other.

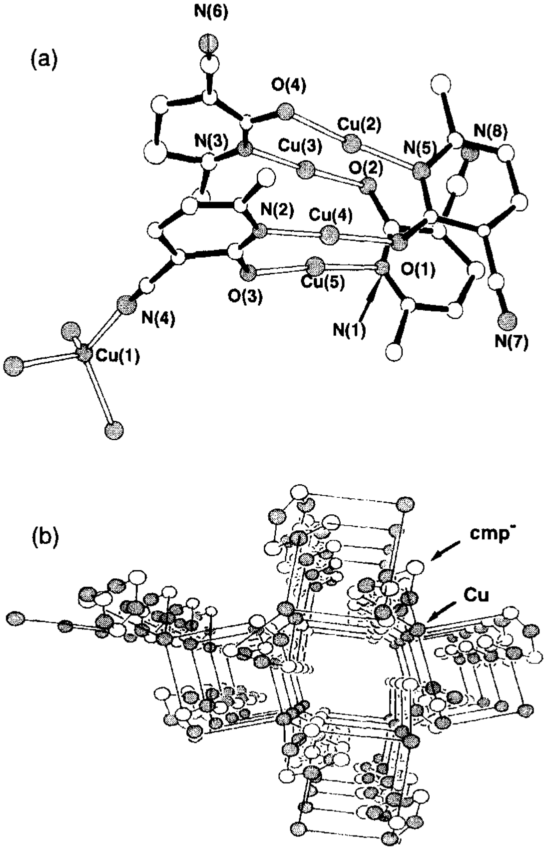


FIG. 40. Part of the molecular structure (a) and extended framework (b) in $[Cu_5(\mathbf{L}_{53})_4]ClO_4$.

B. HYDROGEN-BONDING- AND π–π-STACKING-ASSEMBLED Cu(I) COMPLEXES

The second bifunctional ligand selected to construct the metal architecture is 2-hydroxyquinoxaline ($\mathbf{L}_{54}$), because it also possesses both N-coordination sites and potential double H-bonding sites (CN=COH or CNHC=O if it undergoes tautomerization). The reaction of copper(I) perchlorate and $\mathbf{L}_{54}$ under an atmosphere of ethylene gave the complex $[Cu(\mathbf{L}_{54})_2(C_2H_4)]ClO_4$, whose structure was determined by X-ray analysis (*167*). Its unique feature is the cooperative effect of hydrogen-bonding and aromatic-stacking interactions simultaneously present in the system. The metal center is in a trigonal planar geometry achieved by coordination to one ethylene and two $\mathbf{L}_{54}$ molecules. The cation maintains the fundamental feature of the free ligand in the sense that two $\mathbf{L}_{54}$ molecules are linked to each other by head-to-tail double hydrogen bonds, resulting in formation of an infinite zigzag chain (Fig. 41). The IR spectrum of the complex shows low ν(NH) stretching frequency in the region 2950–3050 cm^{-1}, consistent with the short NH---O hydrogen bonds observed. Between the adjacent chains the H-bond assembled $\mathbf{L}_{54}$ molecule planes are stacked to each other, with the average distance of 3.30 Å. This gives a unique two-dimensional cooperating structure stabilized by hydrogen bonding and π–π interactions as well as covalent bonds, reminiscent of a proton–electron transition (PET) system. It is worth mentioning that ethylene also plays an important role in the construction of the resultant architecture as a spacer because of its relatively small size, which reduces the packing volume, ensuring the effective stacking of the aromatic planes.

VI. π–π-Interaction-Assembled Frameworks

A. INTERMOLECULAR π–π INTERACTION IN DISCRETE COORDINATION COMPOUNDS

Planar coordination compounds with aromatic ligands (Fig. 42), especially those having extended π systems, show π–π interaction in solid states. In alkene or alkyne π-bonded Cu(I) complexes, in-plane coordination of a C=C or C≡C bond to trigonal planar Cu(I) centers often leads to planar molecular conformations (*167–171*). The infinite π–π stacking columns are confirmed in the 2,2′-bipyridine ($\mathbf{L}_{55}$) com-

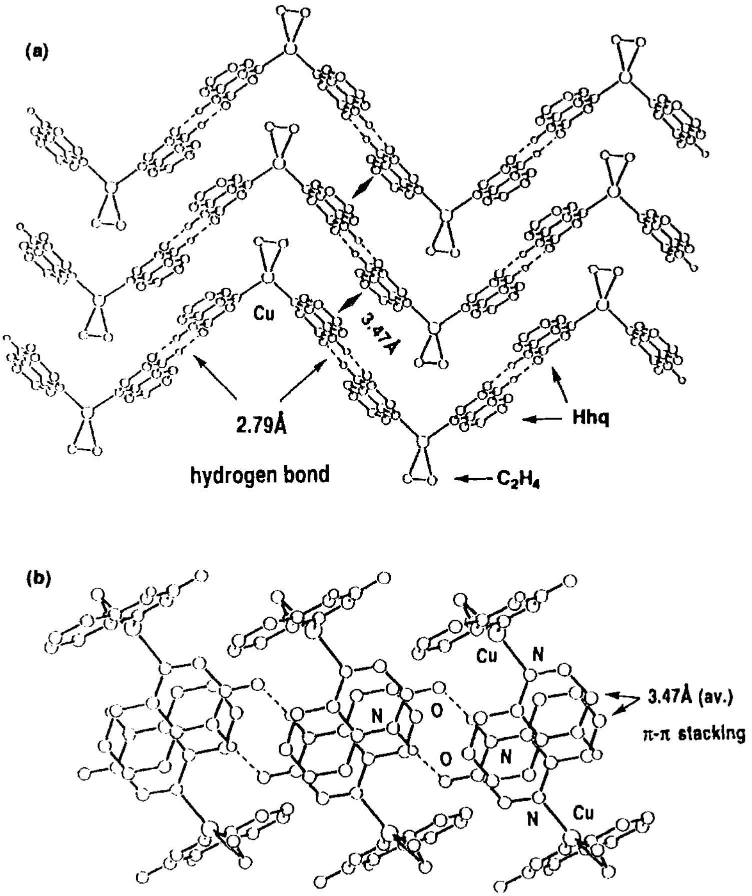


FIG. 41. Packing diagram of $[Cu(L_{64})_2(C_2H_4)]ClO_4$; side view showing H-bonded networks (a) and top view showing aromatic stacking interactions. (From Fig. 2 in Dai, J.; Yamamoto, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Munakata, M. *Inorg. Chem.* **1997,** *36,* 2688.)

plex $[Cu(L_{55})(C_2H_2)]ClO_4$ (*169*) and the 1,10-phenanthroline (L_{56}) complex $[Cu(L_{56})(C_2HCO_2Et)]ClO_4$ (*171*) with nearest carbon-to-carbon distances of 3.31 and 3.37 Å (*172*, *173*), respectively, and dimer formation through π–π interaction can be seen in $[Cu(L_{56})(C_2H_2)]ClO_4$ (*171*) [the nearest carbon-to-carbon distances are 3.42 Å (*172*)].

Flat conformations are also observed in cationic parts of dimeric Cu(I) and Ag(I) compounds bridged by two 1,8-naphthyridine ligands, L_{57}, $[Cu(L_{57})]_2(ClO_4)_2$ and $[Ag(L_{57})]_2(ClO_4)_2$ (*174*). The former compound forms a dimer through π–π interaction of the neighboring L_{57}

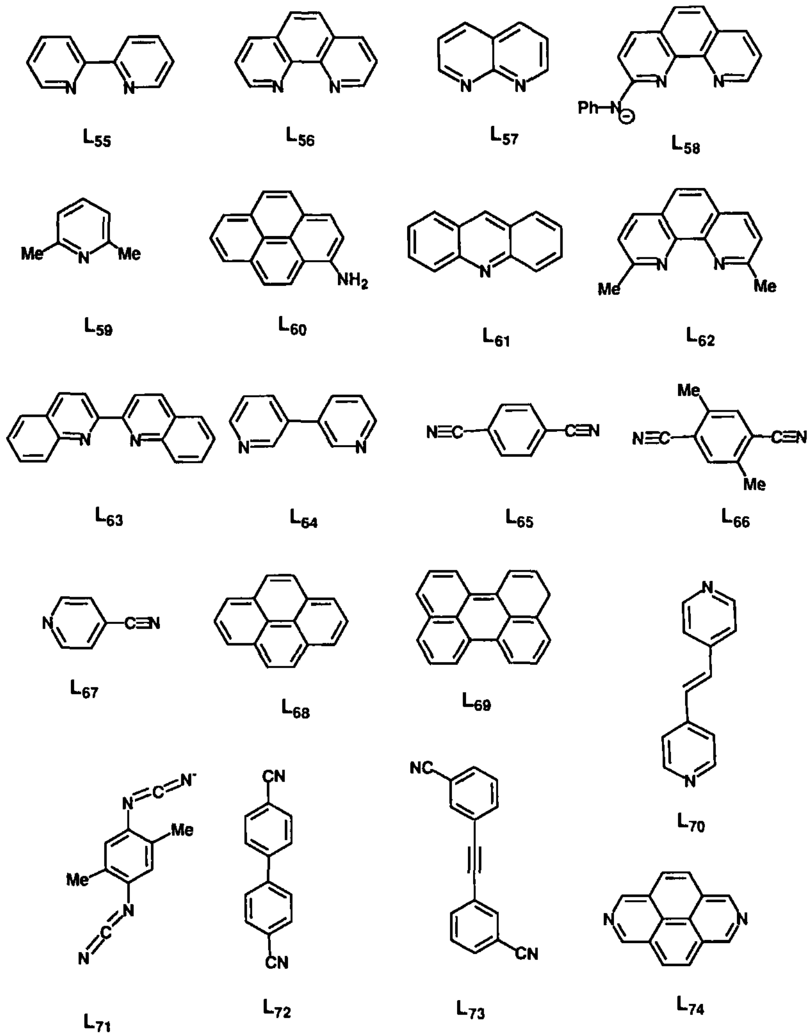


FIG. 42. Ligands that appear in Sections VI and VII.

molecules; the latter shows one-dimensional infinite stacking column of the cationic part with interplane distance of 3.40 Å (*172*) as shown in Fig. 43. Another flat dimer, $[Cu(\mathbf{L}_{68})]_2$ (*175*), also shows a one-dimensional π–π stacking column, with interplanar separation of 3.41 Å (*172*).

Not only planar compounds but also nonplanar ones show π–π stacking interaction. In the crystal structure of $CuI(\mathbf{L}_{59})_2$ (*176*), two

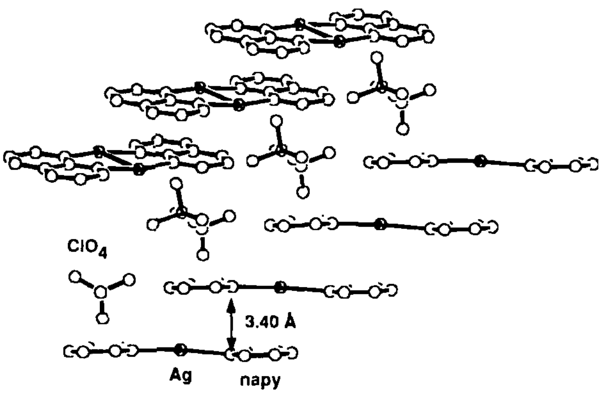


FIG. 43. A crystal-packing view of $[Ag(L_{57})]_2(ClO_4)_2$ showing π–π interaction between planar cationic parts.

2,6-dimethylpyridines L_{59} and an iodine coordinate to a Cu(I) ion in T-shaped trigonal geometry, and the dihedral angles between two ligand planes and the $CuIN_2$ plane are 87.6 and 71.2°, indicating nonplanar conformation. However, one-dimensional π–π stacking can be easily recognized in Fig. 44, with a nearest carbon-to-carbon distance of 3.447 Å. Changing the counteranion from an iodide to a perchlorate ion gives two-coordinated copper(I) or silver(I) compounds. Whereas planar cationic parts of $[M(L_{59})_2]X$ (M = Cu, Ag; X = ClO_4, NO_3) (*177*) with two-coordinated M(I) centers show only weak π–π interaction, with the nearest carbon-to-carbon distances being 3.59 to 3.66 Å, one of the polymorphs of $[Cu(L_{59})_2]ClO_4$ (*178*), with a dihedral angle between two L_{59} ligands of 56.2°, shows a close π–π contact of 3.33 Å (*172*) between two L_{59} ligands residing in adjacent molecules. We can see not a one-dimensional π–π stacking column but a π–π-interaction-assembled one-dimensional structure like $\cdots L_{59}-Cu-L_{59}\cdots L_{59}-Cu-L_{59}\cdots$.

Although a trigonal planar geometry is maintained around a Cu(I) center in the ethylene-coordinated complex $[Cu(L_{54})_2(C_2H_4)]ClO_4$ (*167*), the two L_{54} molecules coordinated to the Cu(I) ion have a dihedral angle of 102.5°, giving a butterfly structure. Repetitions of double hydrogen bonds between two L_{54} ligands in neighboring complexes form an infinite zigzag chain (Fig. 41). Additionally, a π–π interaction between two L_{54} ligands residing in neighboring chains (the interplanar separation of 3.30 Å) forms a two-dimensional structure as shown in Fig. 41. This gives a unique two-dimensional cooperating structure, which is a fundamental characteristic of proton–electron transfer (PET) systems (*179*, *180*).

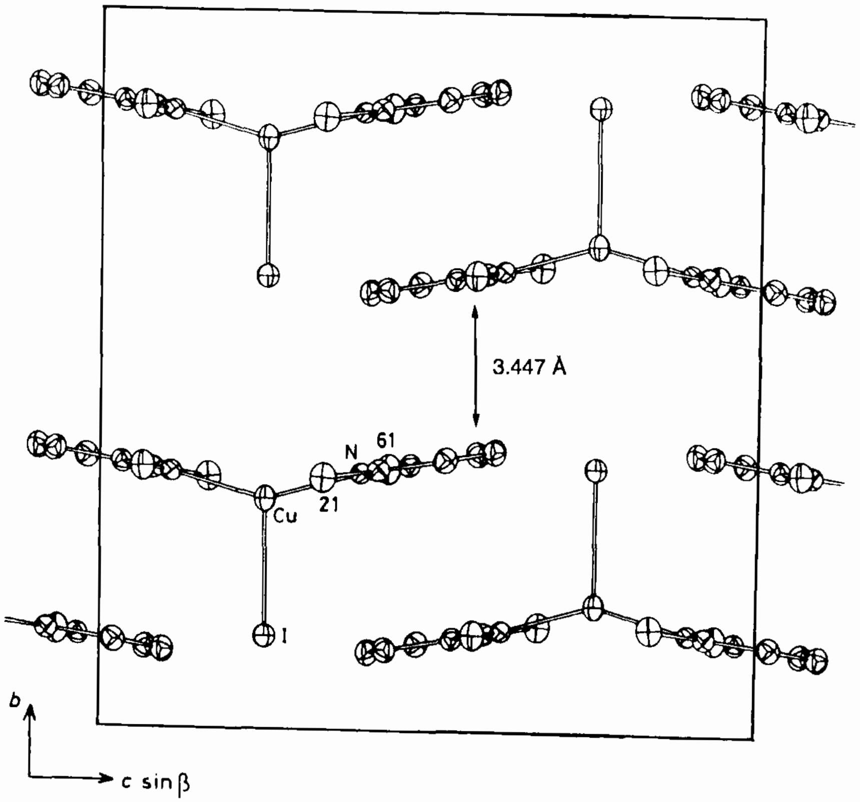


FIG. 44. A crystal-packing view of $CuI(\mathbf{L}_{59})_2$ showing π–π interaction between $\mathbf{L}_{59}$ ligands. (From Fig. 5 in Healy, P. C.; Pakawatchai, C.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983,** 1917.)

The copper(I) ion in $[Cu(\mathbf{L}_{60})_3]ClO_4 \cdot MeOH$ (*181*) has a distorted trigonal geometry with three nitrogen atoms of three 1-aminopyrenes ($\mathbf{L}_{60}$). Two of them are parallel to each other, whereas the rest lie approximately perpendicular to the other two as shown in the molecular-packing view (Fig. 45). Intra- and intermolecular π–π interactions of the former two form a one-dimensional stacking column with interplane separations of 3.40–3.43 Å. Moreover, intercolumn π–π interactions between $\mathbf{L}_{60}$ ligands with an interplane separation of 3.52 Å result in the formation of a two-dimensional structure.

The copper(I) ion in $[Cu(\mathbf{L}_{46})_2(H_2O)]ClO_4$ (*138*) has a distorted trigonal geometry with coordination of two nitrogen atoms of two terminal

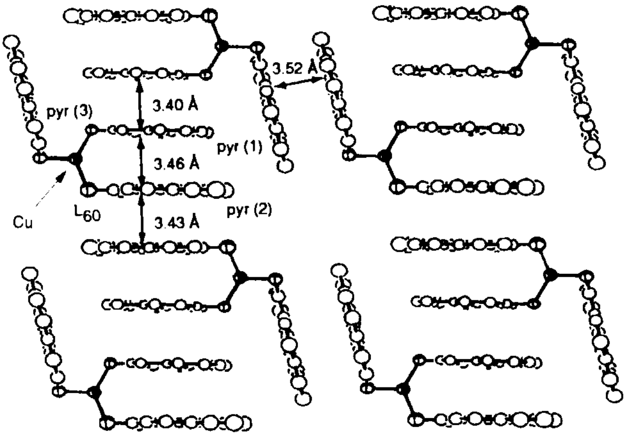


FIG. 45. Molecular packing view of $[Cu(L_{60})_3]ClO_4 \cdot MeOH$. (From Fig. 2 in Munakata, M.; Dia, J.; Maekawa, M.; Kuroda-Sowa, T.; Fukui, J. *J. Chem. Soc., Chem. Commun.* **1994,** 2331.)

$\mathbf{L_{46}}$ molecules and a water oxygen. The coordinated $\mathbf{L_{46}}$ molecules form an alternating π–π stacking column, with the nearest intermolecular separation being 3.46 Å.

Because basicity of acridine ($\mathbf{L_{61}}$) is stronger than that of $\mathbf{L_{46}}$ (*182*), adding a solution of $\mathbf{L_{61}}$ in methanol to a solution containing copper(I) and $\mathbf{L_{46}}$ gives a discrete complex, $[Cu(\mathbf{L_{61}})_2NO_3](\mathbf{L_{46}} \cdot H_2O)_{0.5}$ (*183*). The copper(I) ion is trigonally coordinated by the two nitrogen atoms of $\mathbf{L_{61}}$ and one of the oxygen atoms of the NO_3^- anion. Two coordinated $\mathbf{L_{61}}$ molecules are not parallel to each other at a dihedral angle of 63.6°, and each has a π–π interaction with an adjacent $\mathbf{L_{61}}$ molecule coordinated to another copper atom (Fig. 46). The interplane separations of these intermolecular π–π interactions are 3.41 and 3.49 Å. A metal-free $\mathbf{L_{46}}$ is sandwiched between $\mathbf{L_{61}}$ ligands, forming an infinite columnar stacking along the a-axis with a $\mathbf{L_{46}}-\mathbf{L_{61}}-\mathbf{L_{61}}$ repeating unit. The closest C---C distance of 3.39(1) Å indicates a significant π–π interaction between $\mathbf{L_{46}}$ and $\mathbf{L_{61}}$.

An $\mathbf{L_{46}}$-bridged Cu(I) dimer complex, $[Cu_2(\mathbf{L_{46}})_3(MeOH)_2](\mathbf{L_{46}})(PF_6)_2$ (*138*) shows an alternate π–π stacking of coordinated and uncoordinated $\mathbf{L_{46}}$. Two copper(I) ions are crystallographically the same: a T-shaped three-coordination of a methanol and terminal and bridging $\mathbf{L_{46}}$ with a remarkably large N(terminal $\mathbf{L_{46}}$)–Cu–N(bridging $\mathbf{L_{46}}$) angle of 156.1°. A metal-free $\mathbf{L_{46}}$ molecule is located near the bridging $\mathbf{L_{46}}$, with a dihedral angle of 7.6° and with a nearest carbon-to-carbon sepa-

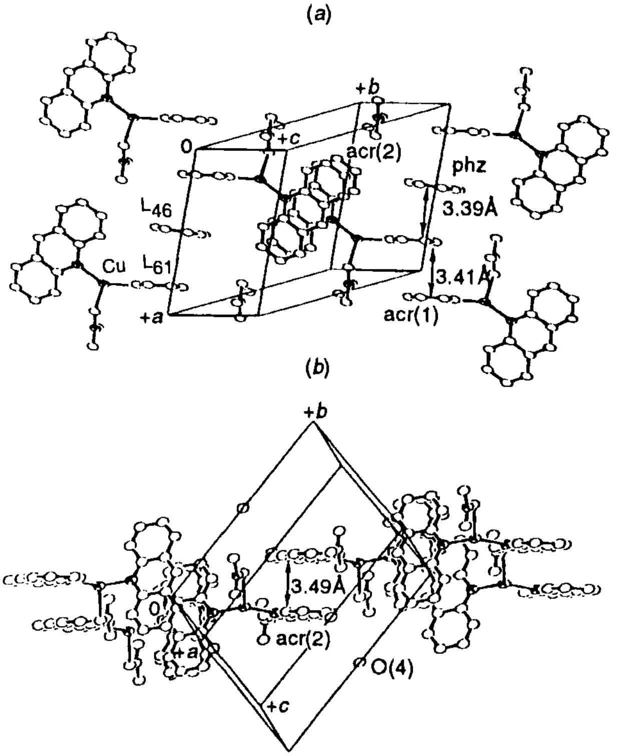


FIG. 46. Molecular views of $[Cu(L_{61})_2NO_3](L_{46} \cdot H_2O)_{0.5}$ indicating π–π interaction between L_{46} and L_{61} (a) and between two L_{61} ligands (b). (From Fig. 4 in Kuroda-Sowa, T.; Munakata, M.; Matsuda, H.; Akiyama, S.; Maekawa, M. *J. Chem. Soc., Dalton Trans.* **1995,** 2201.)

ration of 3.42 Å, indicating a significant π–π interaction between them. Molecular packing along the *c*-axis reveals one-dimensional π–π stacking of bridging and metal-free L_{46} alternately.

B. INTER- AND INTRAPOLYMER π–π INTERACTION

One-dimensional polymeric structures are observed in copper(I) complexes with 2,9-dimethyl-1,10-phenanthroline, $[Cu(L_{62})(CN)]$ and $[Cu(L_{62})(NCS)]$ (*184*). Cn$^-$ or NCS$^-$ acts as a bridging ligand, and L_{62} chelates to a copper(I) ion to block two of four coordination sites of the tetrahedral center, resulting in the infinite zigzag chain. In both compounds, zigzag chains are connected through π–π interaction between L_{62} molecules residing in neighboring chains, which form two-dimensional polymeric structures. Similar two-dimensional network formations are also observed in the trinuclear copper(I) complex with 2,2′-biquinoline (**L**$_{63}$) [Cu$_3$(**L**$_{63}$)$_2$(CN)$_3$] (*185*), in which tetrahedral copper(I) ions coordinated by chelating **L**$_{63}$ ligands are bridged alternately by $Cu(CN)_2^-$ and CN^-.

When **L**$_{46}$ is used as a bridging ligand to construct coordination polymer compounds, interpolymer π–π interactions are often observed. A one-dimensional zigzag chain composed of bridging **L**$_{46}$ and a tetrahedral copper(I) ion can be seen in [Cu(**L**$_{46}$)(NO$_3$)] (*183*) (Fig. 47). The copper(I) ion is coordinated by the two nitrogen atoms of the two **L**$_{46}$ molecules and by the two oxygen atoms of the NO_3^- anion.

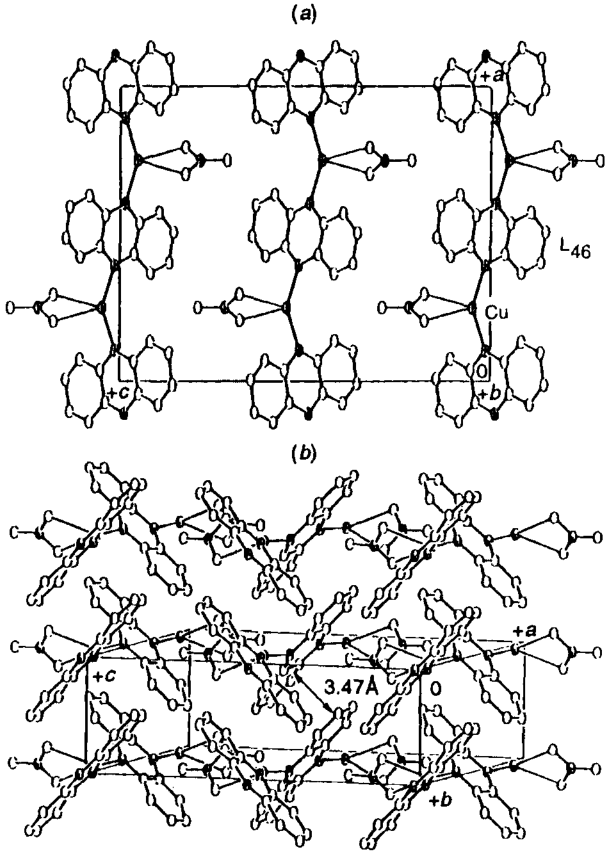


FIG. 47. Top (a) and side views (b) of the crystal packing of [Cu(**L**$_{46}$)(NO$_3$)] showing the **L**$_{46}$ columnar stacks. (From Fig. 2 in Kuroda-Sowa, T.; Munakata, M.; Matsuda, H.; Akiyama, S.; Maekawa, M. *J. Chem. Soc., Dalton Trans.* **1995,** 2201.)

Two $\mathbf{L}_{46}$ molecules coordinated to the same copper atom are inclined to each other at a dihedral angle of 82.2°. As can be seen in Fig. 47, the $\mathbf{L}_{46}$ molecules are stacked in the *b*-axis direction, with an interplane separation of 3.47 Å. Thus, the compound consists of one-dimensional zigzag chains of copper atoms and $\mathbf{L}_{46}$ molecules, interconnected through $\mathbf{L}_{46}$ π–π interactions, resulting in a two-dimensional interaction. A similar zigzag chain composed of bridging $\mathbf{L}_{46}$ and a trigonal planar copper(I) ion is observed in $[\mathrm{Cu}(\mathbf{L}_{46})(\mathrm{MeCN})]_2(\mathbf{L}_{68})(\mathrm{PF}_6)_2$ ($\mathbf{L}_{68}$: pyrene) (*183*). The $\mathbf{L}_{46}$ molecules are stacked in the *c*-axis direction with an interplane separation of 3.47 Å. Thus, the compound consists of one-dimensional zigzag chains of copper atoms and $\mathbf{L}_{46}$ molecules interconnected through $\mathbf{L}_{46}$ π–π interactions, resulting in a two-dimensional interaction.

A series of halogen-bridged copper(I)–$\mathbf{L}_{46}$ compounds, $[\mathrm{Cu}_2(\mu\text{-X})_2(\mathbf{L}_{46})]$ (X = I, Br, or Cl) (*186*), show one-dimensional (X = I) or two-dimensional (X = Br or Cl) polymer frameworks. $\mathrm{Cu}_2\mathrm{I}_2$ rhomboids in the iodide compound are connected by bridging $\mathbf{L}_{46}$ ligands through trigonal planar Cu(I) centers, forming an infinite straight chain. The dihedral angle of the rhomboid and $\mathbf{L}_{46}$ plane is 75.28°. The π–π interaction between $\mathbf{L}_{46}$ molecules of adjacent chains (interplanar distances of 3.46 Å) gives the complex two-dimensional structure. On the other hand, both the bromide and the chloride compounds have almost same structure: CuX infinite stairs bridged by $\mathbf{L}_{46}$ through coordination to distorted tetrahedral (Cu(I) ions, forming a two-dimensional network structure as shown in Fig. 48 for the bromide compound. Intrasheet π–π interactions betwen $\mathbf{L}_{46}$ molecules are also observed in both compounds, with interplanar distances of 3.40 and 3.36 Å for the bromide and the chloride compounds, respectively. In the solid-state ^{13}C NMR spectra of these compounds, the increase of the upfield shifts of the resonances assigned to the quaternary carbon atoms of $\mathbf{L}_{46}$ upon coordination (−2.4, −2.9, and −3.9 ppm for the iodide, the bromide, and the chloride compounds, respectively) are well correlated to the decrease in the interplanar distances of $\mathbf{L}_{46}$ molecules (3.46, 3.40, and 3.36 Å, respectively).

Not zigzag but completely straight one-dimensional chains can be seen in $[\mathrm{Ag}(\mathbf{L}_{46})](\mathrm{ClO}_4)$ (*138*), in which the Ag(I) ion has a linear two coordination of two nitrogen atoms of bridging $\mathbf{L}_{46}$ ligands. All the $\mathbf{L}_{46}$ molecules are parallel, as shown in Fig. 49, which results in the formation of a one-dimensional chain structure like a flat ribbon. The shortest intermolecular distance is 3.36 Å, indicating significant π–π interaction, though the overlap between them is not so large. Because one chain interacts with four neighboring chains through π–π interac-

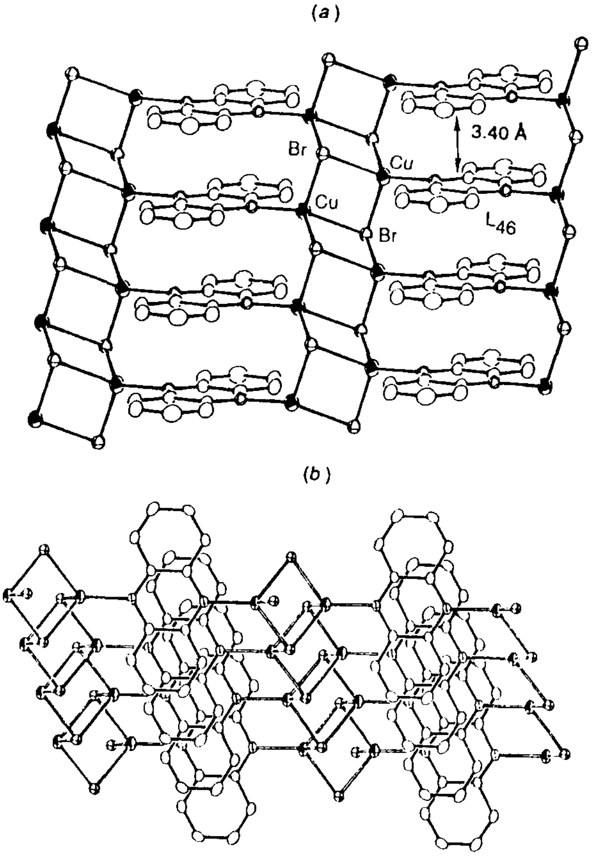


FIG. 48. Top (a) and side views (b) of the packing arrangement of $[Cu_2(\mu\text{-}Br)_2(\mu\text{-}\mathbf{L}_{46})]$. (From Fig. 4 in Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Honda, A.; Kitagawa, S. *J. Chem. Soc., Dalton Trans.* **1994,** 2771.)

tions, this system has a three-dimensional network assembled by π–π interaction.

A two-dimensional sheetlike structure in $[Ag_2(\mathbf{L}_{46})(NO_3)_2]$ (*138*) is composed of bridging $\mathbf{L}_{46}$ and bridging nitrate anions coordinated to trigonal Ag(I) ions, forming six-membered rings of Ag(I) ions. The significant π–π interaction between two $\mathbf{L}_{46}$ molecules in the neighboring sheets (the shortest intermolecular distance of 3.34 Å) indicates the formation of a π–π-interaction-assembled three-dimensional network structure.

Perylene molecules ($\mathbf{L}_{69}$), having an extended π-system, easily form π–π interaction. Four peripheral C=C moieties of $\mathbf{L}_{69}$ coordinate to

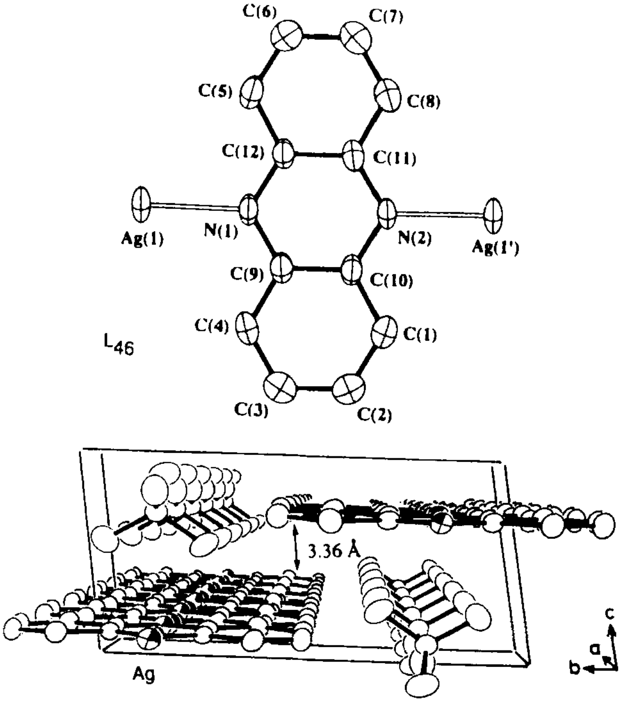


FIG. 49. Molecular structure (a) and a perspective view of the packing arrangement (b) of [Ag(L_{46})](ClO_4). (From Figs. 7 and 8 in Munakata, M.; Kitagawa, S.; Ujimaru, N.; Nakamura, M.; Maekawa, M.; Matsuda, H. *Inorg. Chem.* **1993,** *32,* 826.)

four Ag(I) ions in η^2-fashion in [Ag_2(L_{69})(ClO_4)$_2$] (*187*). The silver(I) ion has a distorted tetrahedral geometry with two C=C groups of two L_{69} molecules and two oxygen atoms of two perchlorate anions. The resulting two-dimensional sheet shows a W-type wavy conformation as shown in Fig. 50, which enables effective π–π interaction (3.31 Å) between L_{69} molecules in adjacent sheets. Thus, the π–π interaction promotes the network dimensionality from two to three dimensions.

Chair-formed six-membered rings of Cu(I) ions in [Cu(L_{47})(NO_3)] (*139*) form a two-dimensional sheet with a certain thickness, in which each Cu(I) ion is bridged by two L_{47} and two nitrate anions. Because L_{47} molecules are almost parallel to the two-dimensional sheet, both intra- and intersheet π–π interaction can be seen, with inter-L_{47} separations of 3.30 and 3.39 Å respectively. The latter interaction enables the three-dimensional network structure assembled through π–π interaction.

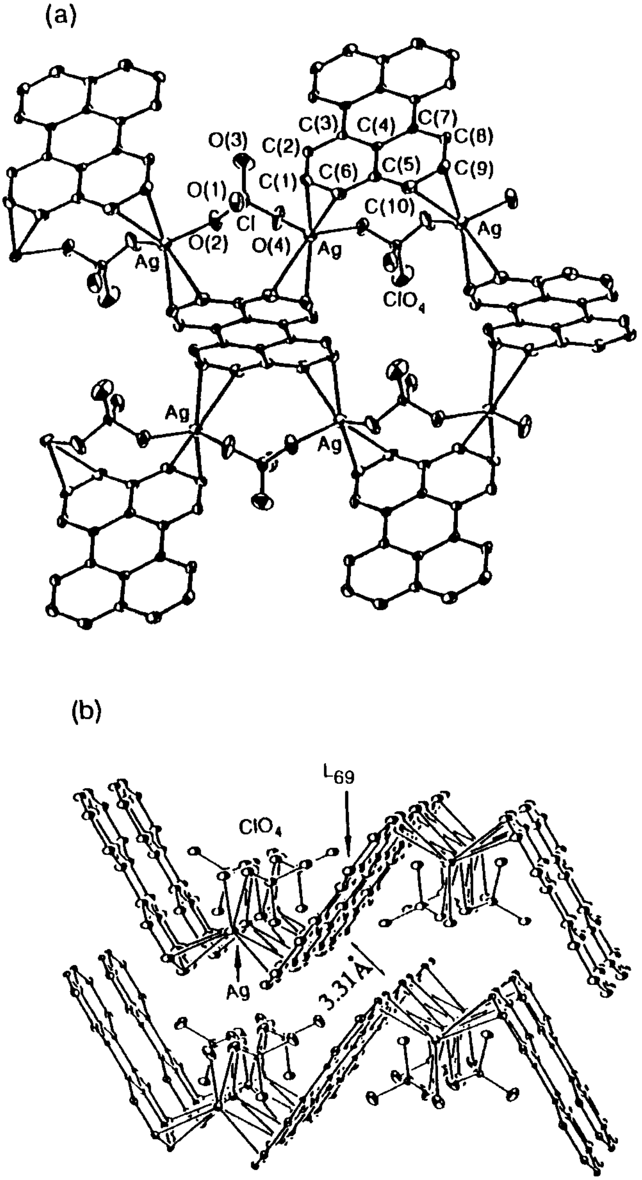


FIG. 50. W-type wavy conformations of two-dimensional sheets in [$Ag_2(L_{69})(ClO_4)_2$]. (From Fig. 2 in Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sugimoto, K. *Inorg. Chem.* **1997,** *36,* 4903.)

VII. Diamondoid Frameworks

We can imagine a formation of a cubic or a hexagonal diamond-related framework (Fig. 51) from a combination of a tetrahedral metal ion and a rodlike bridging ligand. Although both types of frameworks are found in minerals or polymorphs of ice *(188)*, so far as we know, only the former type of framework is known in coordination compounds. Hereafter, we use the terms "diamond" or "diamondoid framework" to mean cubic diamond-related framework. As Hoskins and Robson have proposed *(127)*, a compound having a diamondoid framework, if it can have a large cavities or channels inside, can offer a number of features of potential interest such as molecular sieve properties, heterogeneous catalytic properties, and mechanically strong materials with an unusually low density. Additionally, π–π interaction between aromatic bridging ligands often controls the degree of interpenetration of diamondoid frameworks and sometimes gives electronic conducting material.

In this section, we will focus on coordination compounds with diamondoid frameworks, especially containing copper(I) and silver(I) ions. These ions having d^{10} electronic configuration are suitable for a tetrahedral metal center in a diamondoid framework. Table V lists the coordination polymers having diamondoid frameworks reported so far, together with other coordination polymers having related frameworks.

A. BRIDGED BY PYRIDINE OR PYRAZINE DERIVATIVES

Pyrazine, L_{39}, and its derivatives are the shortest bridging ligands next to cyanide. The copper(I) ion in $[Cu(L_{40})_2]PF_6$ *(133)* has a tetrahedral geometry, with coordination of four N atoms of L_{40}. The other end of the N atoms of each L_{40} coordinate to other copper(I) ions re-

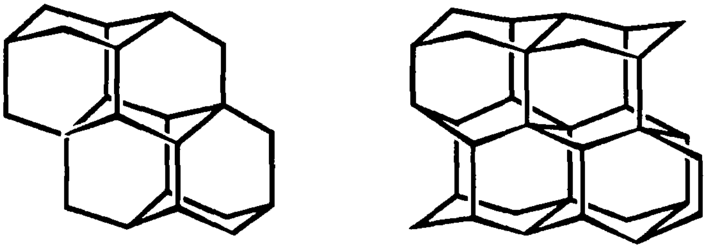


FIG. 51. Cubic (left) and hexagonal (right) diamond-related frameworks.

TABLE V

COORDINATION POLYMERS HAVING DIAMONDOID AND RELATED FRAMEWORKS

Compound	Bridged M---M distance (Å)	Degree of interpenetration	Remarks	Ref.
$NMe_4[CuZn(CN)_4]$[a]	5.03	1		*127*
$[Zn(CN)_2]$	5.11	2		*127, 204, 205*
$[Cd(CN)_2]$	5.46	2		*127, 204, 205*
$[Cu(\mathbf{L}_{40})_2]PF_6$	6.99	1		*133*
$[Cu(C(C_6H_4CN)_4)]BF_{4x}C_6H_5NO_2$ ($x = 7.7$)[a]	8.856[a]	1		*127*
$[Cu(\mathbf{L}_{64})_2]X$ ($X = BF_4, PF_6$)	8.9	2	π–π	*193*
$[CuCN(\mathbf{L}_{67})]$[a]	5.04, 9.54	3		*206*
$[Ag(\mathbf{L}_{67})_2]BF_4$	9.93	4	π–π	*190*
$[Ag_2(O_2C(CH_2)_2CO_2)]$	*ca.* 10	3		*208*
$[Cu(\mathbf{L}_{74})_2]PF_6$	10.90	3	π–π	*207*
$[Cu(\mathbf{L}_{60})_2]PF_6$	11.16	4		*136*
$[Ag(\mathbf{L}_{60})_2]CF_3SO_3$	11.6	4		*190*
$[Cu(\mathbf{L}_{65})_2]BF_4$	11.76	5		*4*
$[Cu(\mathbf{L}_{66})_2](\mathbf{L}_{66})(THF)X$ ($X = ClO_4, BF_4$)	11.9	3	π–π	*195, 196*
$[Cu(NC(CH_2)_4CN)_2]NO_3$	12.09	6		*194*
$[Cu(\mathbf{L}_{71})_2]$	12.76	7	π–π	*197, 198*
$[Cu(\mathbf{L}_{53})_4]X$ ($X = PF_6, CF_3SO_3$)	13.5	4	π–π	*164*
$[Cu(\mathbf{L}_{70})_2]BF_4(0.5CH_2Cl_2)$	13.55	5	π–π	*192*
$[Ag(\mathbf{L}_{72})_2X$ ($X = PF_6, AsF_6, SbF_6$)	16.4	9	π–π	*201, 202*
$[Ag(\mathbf{L}_{73})_2](ClO_4)H_2O$	17.0	8	π–π	*203*

[a] Zinc-blende structure.

[b] Cu---Cu distance.

sulting in the formation of a diamondoid framework (Fig. 52). The shortness of the bridged Cu---Cu separation of 6.99 Å together with the presence of the PF_6^- counteranion and methyl groups in $\mathbf{L}_{40}$ prevent the interpenetration of any other framework. Although coordination chemistry of Ag(I) and $\mathbf{L}_{39}$ (*130, 189*) revealed several compounds having interesting three-dimensional observed such as α-$ThSi_2$ or ReO_3 types, no diamondoid framework has been observed in this system.

When 4,4′-bipyridine, $\mathbf{L}_{60}$, is used instead of $\mathbf{L}_{40}$ fourfold interpenetrated diamondoid frameworks are obtained for both Cu(I) and Ag(I) ions. The Cu(I) compound $[Cu(\mathbf{L}_{60})_2]PF_6$ (*136*) exists as four independent concatenated diamondoid frameworks with Cu---Cu separations of 11.16 Å. The Cu(I) centers occupy crystallographic $\bar{4}$ positions and hence all Cu–N bonds are identical, 2.034 Å. The PF_6^- counteranions

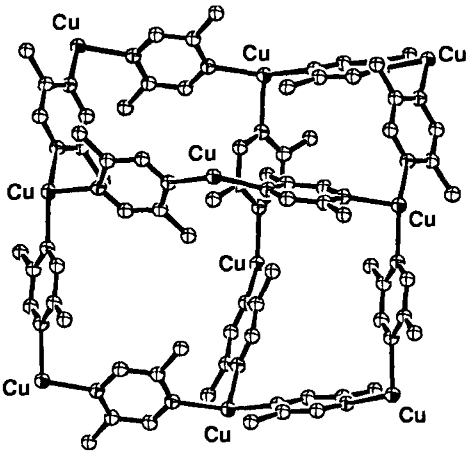


FIG. 52. A single diamondoid framework in $[Cu(L_{40})_2]PF_6$. For clarity, the PF_6 anions are omitted.

occupy channels that are parallel to the *c*-axis and they sit on fourfold crystallographic axes. The Ag(I) analog $[Ag(L_{60})_2CF_3SO_3$ (*190*) also contains four interpenetrating diamondoid frameworks (Ag---Ag intraframe separations of *ca.* 11.6 Å). The Ag(I) cations display a distorted tetrahedral geometry, with Ag–N contacts different for the two independent L_{60} ligands (mean 2.270 vs. 2.380 Å). Interconnection of trigonal Cu(I) centers through L_{60} was achieved by hydrothermal synthesis (*191*). The resultant crystalline compound $[Cu(L_{60})_{1.5}] \cdot NO_3(H_2O)_{1.25}$ shows sixfold interpenetrated α-$ThSi_2$-type frameworks.

By lengthening the linking bipyridyl ligand via insertion of a *trans* C=C double bond between the pyridyl units, the length of the resultant briding ligand, 1,2-*trans*-(4-pyridyl)ethene (L_{70}), is extended by about 2.4 Å and the interpenetration in diamondoid frameworks is also changed. The L_{70} compound with Cu(I), $[Cu(L_{70})_2]BF_4(0.5CH_2Cl_2)$ (*192*), has fivefold interpenetrated diamondoid frameworks. The Cu---Cu distances bridged by L_{70} range from 13.33 to 13.82 Å to create large cavities within the diamondoid framework as shown in Fig. 53. All five independent frameworks are polycatenated with channels throughout the structure: these channels accommodate BF_4^- counteranions and CH_2Cl_2 solvent molecules.

Among the bipyridine derivatives, L_{64} can also act as a linear bridging ligand if the *transoid* conformation is maintained. $[Cu(L_{64})_2]X$ (X = BF_4, PF_6) (*193*), having a twofold interpenetrated diamondoid framework, can be obtained as yellow-green triangular crystals. The

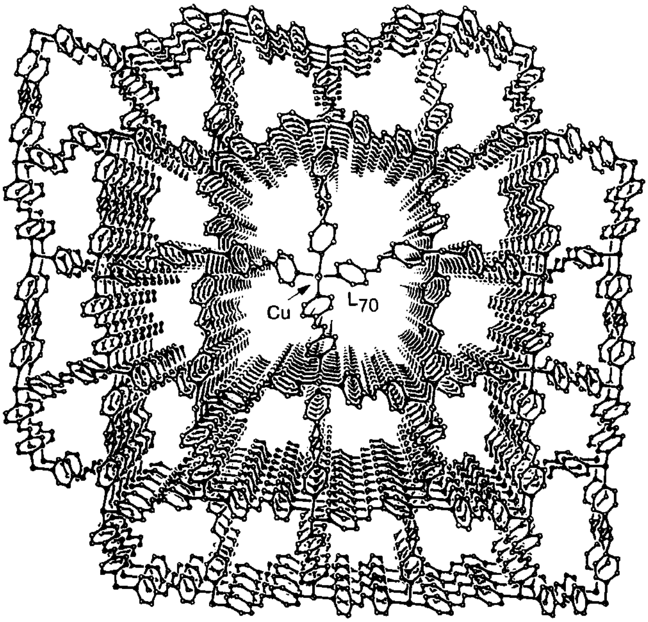


FIG. 53. View of the structure of [Cu(L_{70})$_2$]BF$_4$. (From Fig. 2 in Blake, A. J.; Champness, N. R.; Chung, S. S. M.; Li, W.-S.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1997,** 1005.)

L_{64} has surely a *transoid* conformation, but the rings twist out of plane relative to each other by about 30°. In addition, the Cu–N bond is bent out of the plane of the aromatic ring by 19°, leading to a closing of the Cu–L–Cu angle to 134°. Bridged by this large ligand, the resulting framework contains copper atoms separated by 8.9 Å and significant void volume. The extra space is occupied by an identical network forming a twofold interpenetrated structure (Fig. 54).

B. BRIDGED BY BISNITRILE LIGANDS

Nitrile compounds are generally accepted to be weaker donors than pyridine derivatives; still, they can coordinate to d^{10} metal ions. A bisnitrile compound, if the two CN groups have opposite directions, can act as a rodlike bridging ligand in the construction of diamondoid frameworks.

Although directions of two CN groups in alkyldicarbonitrile, NC(CH$_2$)$_n$CH, are not fixed *a priori* due to free rotation around methylene carbons, a Cu(I)–adiponitrile ($n = 4$) complex, [Cu(NC(CH$_2$)$_4$

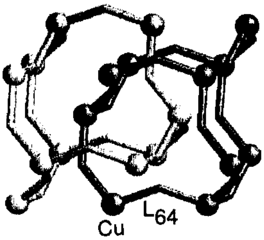


FIG. 54. A schematic illustration of twofold interpenetrated diamondoid frameworks of $[Cu(L_{64})_2]X$ ($X = BF_4$, PF_6). The spheres represent the copper atoms, and the twisted bipyridine ligands are shown as the bet cylinders linking the copper centers together. (From Fig. 2 in Lopez, S.; Kahraman, M.; Harmata, M.; Keller, S. W. *Inorg. Chem.* **1997,** *36,* 6138.)

$CN)_2]NO_3$ (*194*), shows a diamondoid framework. In the crystal, four methylene groups of the adiponitrile form a planar zigzag chain and the terminal CN groups align almost antiparallel, which allows the adiponitrile to behave as a linear bridging ligand. The bridged Cu---Cu distance of 12.09 Å together with the small size of the counteranion (NO_3^{-3}) enable it to show sixfold interpenetration of independent diamondoid frameworks.

Terephthalonitrile, $\mathbf{L_{65}}$, having two CN groups at the 1- and 4-positions in a benzene ring, is a good candidate for a rodlike bridging ligand for d^{10} metal coordination polymers. When the aceonitrile ligands of $[Cu(CH_3CN)_4]BF_4$ are substituted by $\mathbf{L_{65}}$, the crystals formed have the composition $[Cu(\mathbf{L_{65}})_2]BF_4$ (*4*). Diamondoid frameworks are indeed formed (the bridged Cu---Cu distance of 11.76 Å), but the structure contains fivefold interpenetrated independent frameworks. Channels of rhombic cross section are generated in which the BF_4^- ions are located.

Methyl substitution of $\mathbf{L_{65}}$ causes a drastic change in the interpenetration of the diamondoid frameworks. Crystals of $[Cu(\mathbf{L_{66}})_2]X(\mathbf{L_{66}})(THF)$ ($X = BF_4$, ClO_4) (*195, 196*) were obtained by slow diffusion of the $\mathbf{L_{66}}$ solution into the corresponding copper(I) solution. X-ray crystal structure analysis revealed that both compounds contain threefold interpenetrated diamondoid frameworks as shown in Fig. 55. Because the bridged Cu---Cu distance in these compounds (11.9 Å) is almost same as that bridged by $\mathbf{L_{65}}$ in $Cu(\mathbf{L_{65}})_2BF_4$ (*4*), the lesser interpenetration in $\mathbf{L_{66}}$ complexes should be caused by the bulkiness of methyl groups in $\mathbf{L_{66}}$. This is also strongly correlated to the incorporation of guest molecules, a metal-free $\mathbf{L_{66}}$, and THF. The metal-free dmtpn incorporated in the $Cu(\mathbf{L_{66}})_2$ lattice participates in the formation of a π–π stacking column (discussed later).

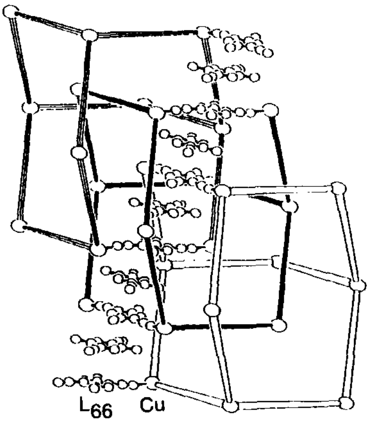


FIG. 55. A threefold interpenetrated diamondoid framework in $[Cu(L_{66})_2]X(L_{66})$ (THF). For clarity, the L_{66} ligands are represented by lines and the PF_6 molecules are omitted.

Among the compounds having diamondoid frameworks listed in Table V, the copper complex with 2,5-dimethyl-*N,N'*-dicyanoquinonediimine (L_{71}), $[Cu(L_{71})_2]$ (*197, 198*), has a quite interesting conducting property. Recent developments on this and related compounds show other interesting features including metal–insulator–metal transition (reentrant behavior) (*199*), three-dimensional Fermi surface character (*200*), and so on. The structure of $[Cu(L_{71})_2]$ shows sevenfold interpenetrated diamondoid frameworks with strong π–π interaction (the interplanar distances between the neighboring L_{71} molecules are 3.1–3.2 Å). It should be noted that not even-number-fold but sevenfold interpretation in this class of complexes probably disturbs the dimer formation between adjacent L_{71} molecules, which contribute to the aforementioned conducting behavior.

A ninefold interpenetration of diamondoid frameworks, the highest degree thus far reported, is observed in a series of Ag(I) complexes with 4,4'-biphenyldicarbonitrile, L_{72} (*201, 202*). Crystallization of L_{72} with AgX (X = PF_6, AsF_6, SbF_6) (1 : 1 molar ratio) by heating and slow cooling from ethanol produces yellow crystals of $[Ag(L_{72})_2]X$ (X = PF_6, AsF_6, SbF_6). All of these structures show ninefold interpenetrated diamondoid frameworks. This highest degree of interpenetration is a result of the rather large ligand used (the bridged M---M distance of 16.4 Å). The large amount of void volume created by a single network is filled by eight identical nets (Fig. 56). These nets consist of parallel ligands offset along the long axis and display π–π stacking at a plane-to-plane distance of 3.4 to 3.6 Å. Columns of counterions are revealed

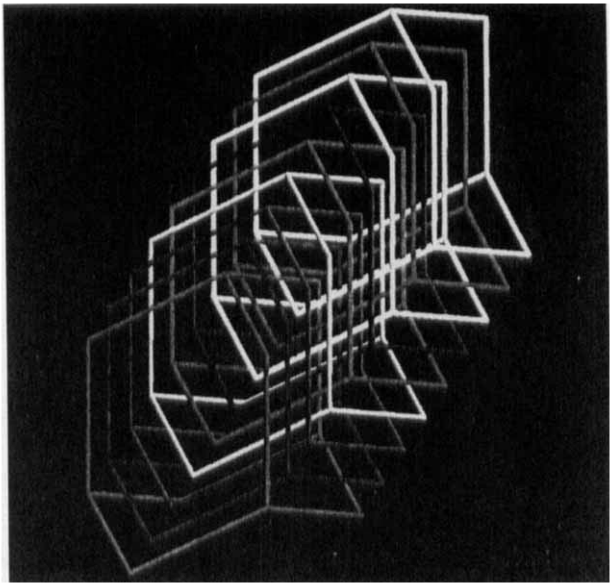


FIG. 56. A ninefold interpenetation of diamondoid frameworks of $[Ag(\mathbf{L}_{72})_2]X$ (X = PF_6, AsF_6, SbF_6). For clarity, the $\mathbf{L}_{72}$ are represented by lines and the PF_6 are omitted. (From Fig. 1 in Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Chem. Eur. J.* **1997,** *3,* 765.)

down the fourfold *c*-axis. A packing model for this system proposed by Moore *et al.* (*202*) explains a relationship between the degree of the interpretation and the bridged M---M distance. Their model also explains the effect of the anion size on the height of adamantoid cages in a series of compounds $[Ag(\mathbf{L}_{72})_2]X$ (X = PF_6, AsF_6, SbF_6).

The longest M---M distance in a diamondoid framework is observed in $[Ag(\mathbf{L}_{73})_2](ClO_4)H_2O$ (*203*). The *transoid* conformation of 3,3′-dicyanodiphenylacetylene, $\mathbf{L}_{73}$, bridges two Ag(I) ions separated by 17.0 Å. The obtained structure shows eightfold interpenetrated diamondoid frameworks (Fig. 57). A majority of the large amount of void space created in a single diamondoid framework is filled through interpenetration, resulting in an eightfold diamondoid network. The remaining space within the lattice is filled by perchlorate ions and water. Interpenetration in this structure is mediated by π–π stacking of $\mathbf{L}_{73}$ (discussed later).

C. OTHER BRIDGING LIGANDS

One of the simplest bridging ligands in constructing diamondoid frameworks is a cyanide, CN^-. It is well known that Zn(II) and Cd(II)

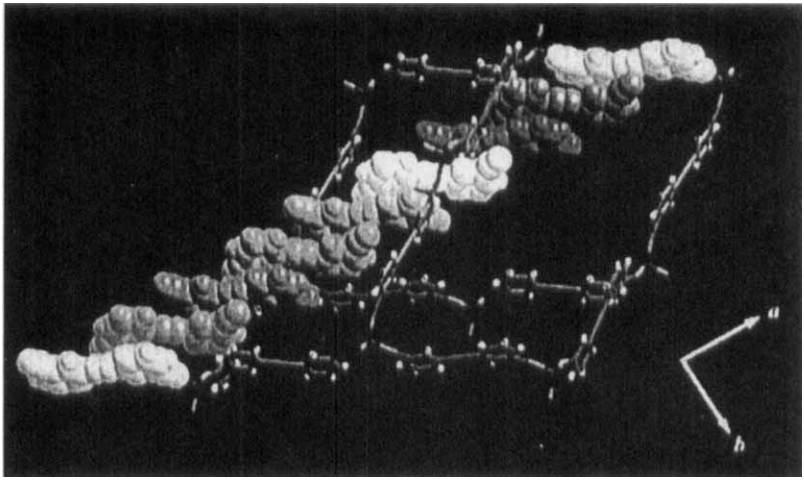


FIG. 57. Diamondoid framework in $[Ag(\mathbf{L}_{73})_2](ClO_4)H_2O$ representing π–π stacking along the *a*-axis. (From Fig. 8 in Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Inorg. Chem.* **1997,** *36,* 2960.)

ions bridged by cyanide form doubly interpenetrated diamondoid frameworks of $M(CN)_2$ (*127*, *204*, *205*). A partial replacement of the metal site by a Cu(I) ion needs incorporation of countercations due to the charge neutrality, as exemplified in the case of $NMe_4[CuZn(CN)_4]$ (*127*). The incorporated NMe_4 cation prevents the interpenetration of another network, resulting in the formation of a single framework, although the framework is no longer a diamondoid but a zinc blende structure. A detailed structural analysis concluded that carbon atoms in cyano groups coordinate to Cu(I) centers to form Cu–CN–Zn rods. A similar zinc blende structure is also seen in $[Cu(C(C_6H_4CN)_4]BF_4 \cdot xC_6H_5NO_2$ (x = 7.7) (*125*, *127*), in which $C_6H_4CN^-$ can be regarded as a bridging ligand between Cu(I) and C^{4+} centers. The large void space created by the bridging ligand is filled by a counteranion and solvent molecules.

A bridging ligand having mixed functional groups also affords a diamond-related framework. 4-Cyanopyridine, $\mathbf{L}_{67}$, having both a cyano group in one end and a pyridine nitrogen in the other, is such a typical asymmetric bridging ligand. Cuboidal crystals of $[Ag(\mathbf{L}_{67})_2]BF_4$ (*190*) were obtained by slow diffusion of an ethanolic solution of $AgBF_4$ placed over $\mathbf{L}_{67}$ dissolved in THF (molar ratio 1:2). The fourfold interpenetrated diamondoid frameworks have a Ag---Ag intraframe separation of 9.93 Å. The Ag(I) ions, lying on *mm* special positions, exhibit markedly flattened tetrahedral geometry, with

N(py)–Ag–N(py), N(cn)–Ag–N(cn), and N(py)–Ag–N(cn) angles of 127.7(5), 126.5(5), and 101.45(12)°, respectively. These local distortions result in a global compression of the diamondoid framework along *c*. The Ag–N bond lengths have values of 2.270(6) Å [Ag–N(py)] and 2.350(10) Å [Ag–N(cn)]. The presence of iso-oriented anisobidentate (with donor ends differing both in steric need and in basic character) ligands gives rise for $[Ag(\mathbf{L}_{67})_2]BF_4$ to a polar axis (*c*). A π–π stacking column of aromatic rings could be observed along the *c*-axis (interplanar distance of 4.0 Å). $\mathbf{L}_{67}$ also forms a diamond-related framework with CuCN. A Cu(I) ion in $[CuCN(\mathbf{L}_{67})]$ (*206*) is coordinated by one carbon atom and three different types of nitrogen atoms. The structure was first interpreted as triply interpenetrated three-dimensional polymers with one-dimensional zigzag chains of CuCN bridged by $\mathbf{L}_{67}$ and has recently been reappraised to have diamond-related networks (*190*).

2,7-Diazapyrene ($\mathbf{L}_{74}$), having an extended π-system, also produces a Cu(I) coordination polymer, $[Cu(\mathbf{L}_{74})_2]PF_6$ (*207*), which shows threefold interpenetrated diamondoid frameworks. The spaces within each diamondoid framework in $[Cu(\mathbf{L}_{74})_2]PF_6$ are filled by two other diamondoid frameworks, and the three interpenetrating arrays are related to each other by a 90° rotation (Fig. 58). This form of interpenetration contrasts with that observed for other diamondoid frameworks appearing in Table V, which are related to each other by simple translation. Adjacent frameworks interact with each other via face-to-face π–π interactions between $\mathbf{L}_{74}$ molecules, which are arranged so that the N---N axes of the ligand are at 90° to one another. Because of the greater lateral steric bulk of $\mathbf{L}_{74}$, the number of interpenetrating frameworks of three is smaller than other bridging ligands, giving similar M---M distances (Table V). This represents the identification of another factor controlling the degree of interpenetration in diamondoid frameworks.

Although $\mathbf{HL}_{53}$ has both a CN group and a pyridone group, a dimerization of two $\mathbf{HL}_{53}$ molecules through head-to-tail hydrogen bonds between the pyridone groups brings a symmetric rodlike bridging ligand. In the crystals of $[Cu(\mathbf{HL}_{53})_4]X$ (X = PF_6, CF_3SO_3) (*164*), each $\mathbf{HL}_{53}$ moiety in the monomeric unit of $[Cu(\mathbf{HL}_{53})_4]X$ is head-to-tail hydrogen-bonded to one adjacent $\mathbf{HL}_{53}$ molecule. Thus, one $[Cu(\mathbf{HL}_{53})_4]X$ entity is connected to four adjacent others, and these repeating units form a three-dimensional diamondoid framework. The structure exists as fourfold interpenetrated diamondoid frameworks with intraframe Cu---Cu separations of 13.5 Å in both cases. The diamondoid frameworks in both complexes are stacked with each other in such way that all the copper centers are found on lines parallel to the

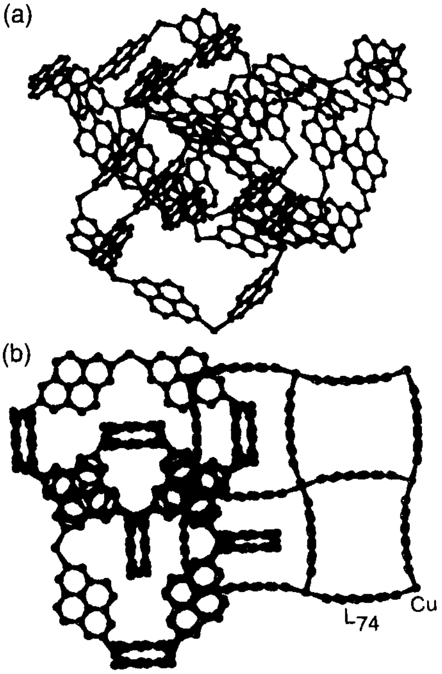


FIG. 58. Threefold interpenetrated diamondoid frameworks observed in [Cu(L_{74})$_2$] PF_6. (From Fig. 1 in Blake, A. J.; Champness, N. R.; Khlobystov, A. N.; Lemenovskii, D. A.; Li, W.-S.; Schroder, M. *J. Chem. Soc., Chem. Commun.* **1997,** 1339.)

c-axis, which defines enormous linear chambers. The counteranions PF_6 and CF_3SO_3 occupy channels that run along the fourfold crystallographic axes.

Not a single metal ion but a tetranuclear silver cluster plays a role of a tetrahedral center in a diamondoid framework in [$Ag_2(O_2C(CH_2)_2CO_2)$] (*208*). The compound consists of planar tetrasilver clusters bridged by succinate anions as shown in Fig. 59. The Ag_4 cluster exhibits pseudo-S_4 symmetry and is linked though its four ligands to four neighboring clusters, resulting in the formation of triply interpenetrated diamondoid frameworks. This is the first example of a three-dimensional coordination polymer containing metal clusters.

D. π–π INTERACTION IN DIAMONDOID FRAMEWORKS

Interpenetration in diamondoid frameworks is often mediated by π–π interaction between aromatic bridging ligands (Table V). A pack-

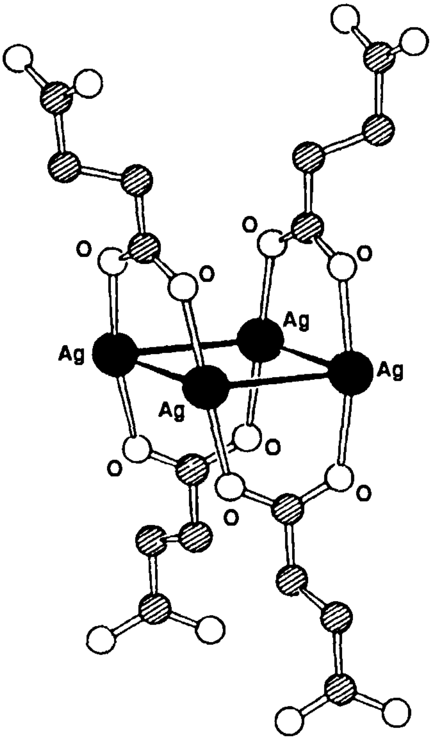


FIG. 59. A view of the Ag_4 cluster and the surrounding ligands in $[Ag_2(O_2C(CH_2)_2CO_2)]$. (From Fig. 1 in Michaelides, A.; Kiritsis, V.; Skoulika, S.; Aubry, A. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 1495.)

ing model for such systems proposed by Moore *et al.* (*202*) explains a relationship between the degree of the interpenetration and the bridged M---M distance, and also explains why two polymorphs can be obtained in $[Ag(\mathbf{L}_{72})_2]AsF_6$ (*202*).

Face-to-face π–π-stacking interactions between sets of $\mathbf{L}_{70}$ ligands in $[Cu(\mathbf{L}_{70})_2]BF_4(0.5CH_2Cl_2)$ (*192*) (3.659 and 3.855 Å) control the separations between adjacent diamondoid frameworks. The π–π-stacking interaction is clearly important in the overall control of this extended structure, and the presence of this interaction is along the direction in which the long-range structure is formed during crystallization.

In case of $[Cu(\mathbf{L}_{66})_2]X(\mathbf{L}_{66})(THF)$ (X = BF_4, ClO_4) (*195, 196*), metal-free and coordinated $\mathbf{L}_{66}$ ligands stack alternately, with a nearest carbon-to-carbon separation of 3.37(2) and 3.51(2) Å, to form a one-dimensional π–π-stacking column as shown in Fig. 55.

π–π-Stacking columns in $[Ag(\mathbf{L}_{73})_2](ClO_4)H_2O$ (*203*) occur along both the *a*- and *b*-directions, with a plane-to-plane distance of 3.51 Å. Along *a*, adjacent ligands in the stack are flipped 180° relative to one another such that nitrile groups are not overlaid (Fig. 57). The stacking along *b* is unusual in that a large offset angle causes a $\mathbf{L}_{73}$ molecule to stack between two fragments each consisting of two halves of $\mathbf{L}_{73}$ coordinated to silver(I). To allow stacking in two directions, mutually perpendicular stacks organize in alternating layers.

A close interplane separation of 3.38 Å between adjacent $\mathbf{HL}_{53}$ molecules in $[Cu(\mathbf{HL}_{53})_4]X$ ($X = PF_6$, CF_3SO_3) (*164*) suggests the presence of strong π–π interactions between pyridone rings. This separation is slightly shorter than the 3.40 Å observed in the copper(I)–$\mathbf{L}_{60}$ complex (*186*).

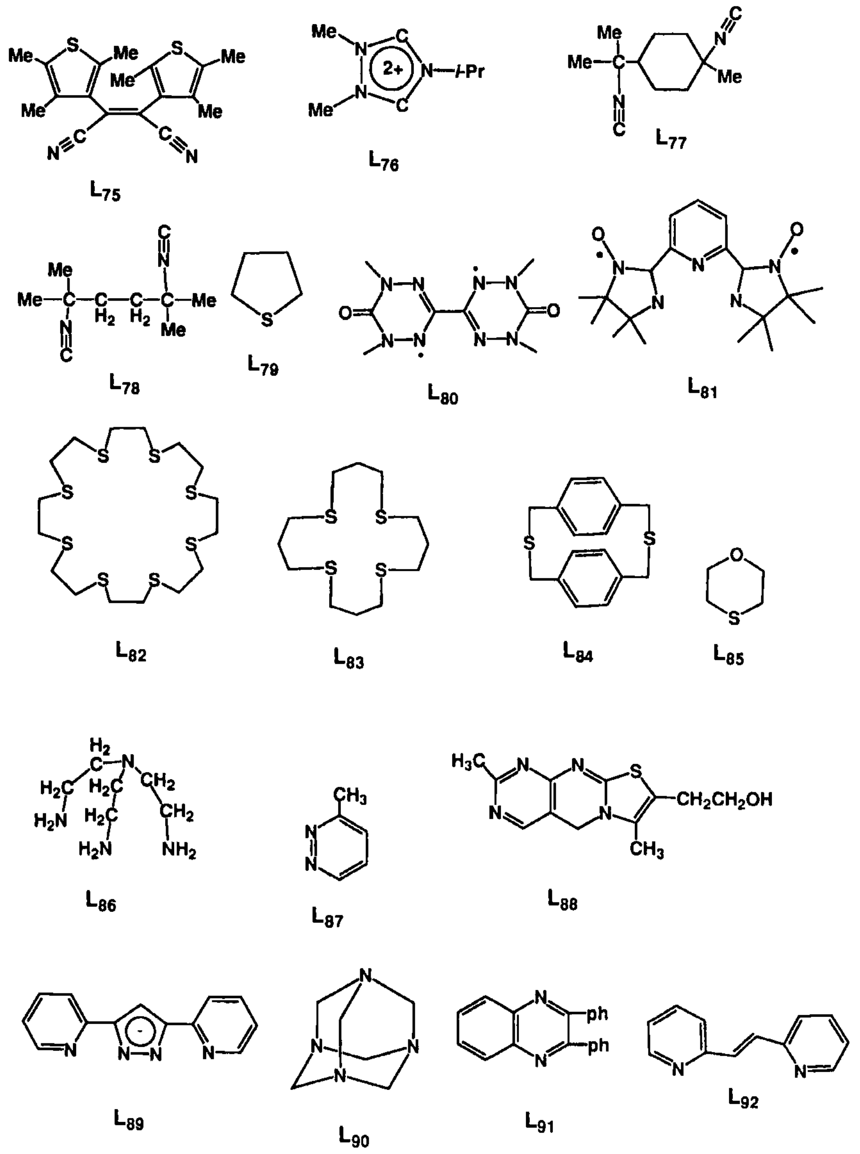
VIII. Other Frameworks Based on Covalent Bonds

Apart from several of the classes of intermolecular forces based in supramolecules described earlier, coordination polymers with extended frameworks based mainly on covalent bond forces represent another well characterized class of transition metal supramolecules. One might anticipate that application of the strategies that have worked so well for the preparation of copper(I) and silver(I) coordination polymers with a diversity of novel frameworks based on intermolecular forces would allow a similar easy access to formation of the covalent-force-based frameworks by the selection of suitable ligands and spacers and the introduction of flexibilizing groups, either in the polymer backbone or in the side-group structure (Fig. 60). Recent publications did reveal several such notable examples of infinite chains, two-dimensional sheets, and three-dimensional networks formed by metal cations linked through multidentate organic ligands.

A. INFINITE-CHAIN STRUCTURES

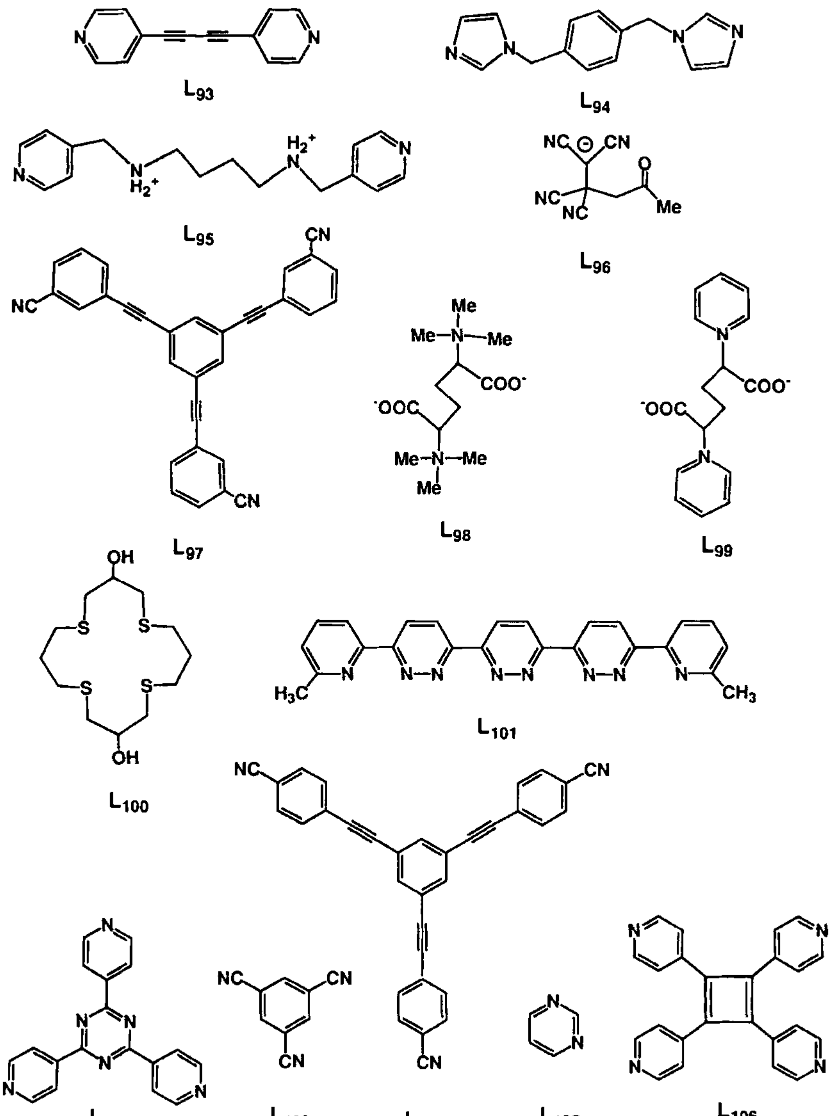
1. Light-Induced Crystal Oscillation

In addition to their novel frameworks, low-dimensional metal-containing coordination polymers are of interest with respect to their electrical, magnetic, and optical properties, and possibly their catalytic behavior. For example, the study of photochromic compounds, which undergo thermal irreversible and fatigue-resistant photochro-



L_{75} L_{76} L_{77} L_{78} L_{79} L_{80} L_{81} L_{82} L_{83} L_{84} L_{85} L_{86} L_{87} L_{88} L_{89} L_{90} L_{91} L_{92}

FIG. 60. List of ligands in copper(I) and silver(I) complexes with linear chain, 2-D and 3-D networks.



L_{93} L_{94} L_{95} L_{96} L_{97} L_{98} L_{99} L_{100} L_{101} L_{102} L_{103} L_{104} L_{105} L_{106}

FIG. 60. (*continued*)

mic reactions, is one of the key points in the current revival of interest in designing light-triggered molecular and supramolecular devices (*209*). Recent work by Munakata and co-workers has yielded a range of interesting and well-characterized materials with intriguing properties (*210, 211*). Reaction of copper(I) perchlorate solution with *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene ($\mathbf{L}_{75}$) yielded single crystals of $[Cu(\mathbf{L}_{75})_2]ClO_4$, the structure of which is composed of noninteracting anions and macrocations in which each metal center is coordinated with one CN group of the four dithienylethene molecules and each $\mathbf{L}_{75}$ in turn bridges two copper(I) ions with two cyano groups, leading to an infinite network of metal cations as illustrated in Fig. 61(a). The most striking feature of the complex is that it shows reversible ring-closed and ring-open transformation under different wavelengths of light when probed by both electrical and NMR spectroscopy. This cycle can be repeated many times, indicating that the reversible cyclization reaction takes place in the crystalline state. The light-induced crystal oscillation is suggested to be one possible pathway to account for the approach and rotation of the two thiophene rings as shown in Fig. 61(b). Such a system may be used as an optical memory.

2. *Organometallic Polymers*

Several organometallic polymers containing copper(I) and silver(I) ions have been reported that, by definition, involve unanimously direct interaction between the carbon atoms of the ligand and the metal ions. The organic ligands studied include alkynyls, isonitriles, and π-conjugated systems. Addition of $AgClO_4$ to *trans*-$[Pt(C{\equiv}CH)_2(PMe_2Ph)_2]$ gave a 1:1 adduct of $[PtAg(ClO_4)(C{\equiv}CH)_2(PMe_2Ph)_2]$ (*212*) in which the *trans* coordination of the Pt is maintained and the Ag atom is coordinated on the same face of each Pt coordination plane, forming a zigzag chain with a perchlorate ion in each cavity along the chain as shown in Fig. 62. Recently Bertrand reported the first bis(carbene)-silver polymer $[Ag(\mathbf{L}_{76})CF_3SO_3$ obtained at −30°C from an acetonitrile/ether solution of 1,2,4-triazole-3,5-diylidene ($\mathbf{L}_{76}$) and $AgCF_3SO_3$ (*213*). In the cation each ligand links two linear silver atoms with C–Ag–C bond angles of 175–180°, and due to the alternation in the orientation of the five-membered rings, the complex is regarded as a one-dimensional polymer in which all the rings are coplanar.

Despite the fact that silver(I)–aromatic complexes of benzene, cyclophane, indene, acenaphthene, naphthalene, and anthracene have been reported, the corresponding organometallic polymers of pyrene ($\mathbf{L}_{68}$) and perylene ($\mathbf{L}_{69}$) have been crystallographically characterized only recently (*187*). X-ray structure determination of the complex with pyrene $[Ag_2(\mathbf{L}_{68})(ClO_4)_2]$ reveals that it exists in the solid state as an

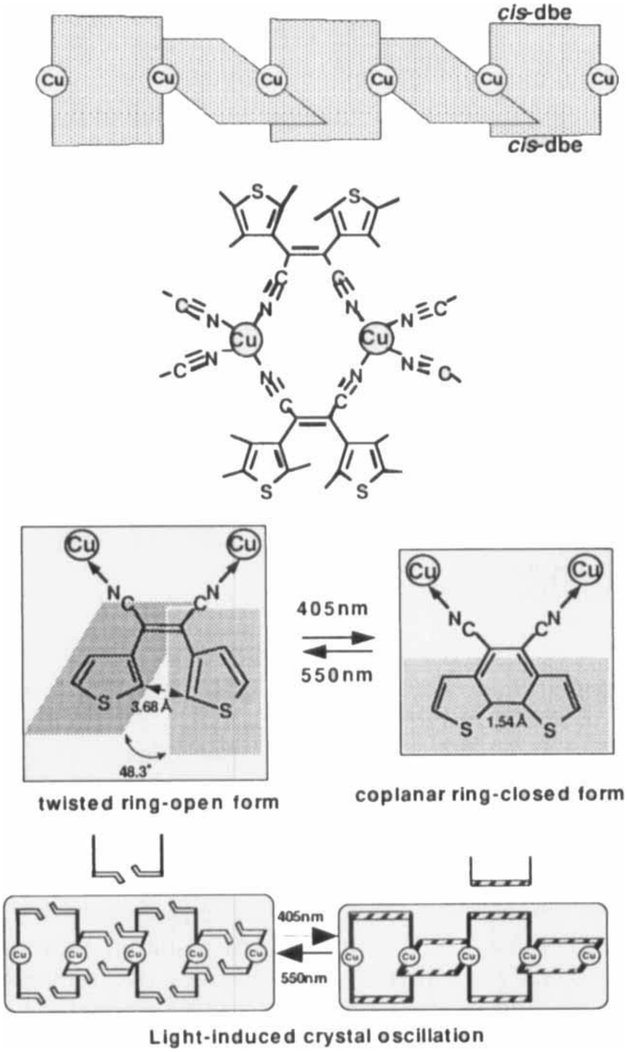


FIG. 61. Schematic presentation of chain structure (a) and the light-induced crystal oscillation model (b) in $[Cu(\mathbf{L}_{75})_2]ClO_4$.

arene-linked polymer of dimers as shown in Fig. 63. Within the dimer, there are two independent Ag(I) ions coupled by one perchlorate–oxygen bridging with Ag(1)···Ag(2) separation of 4.39 Å. Each pyrene moiety exhibits a tetra-η^2-coordination fashion sequentially bridging four metal centers, resulting in a polymeric W-type sandwich

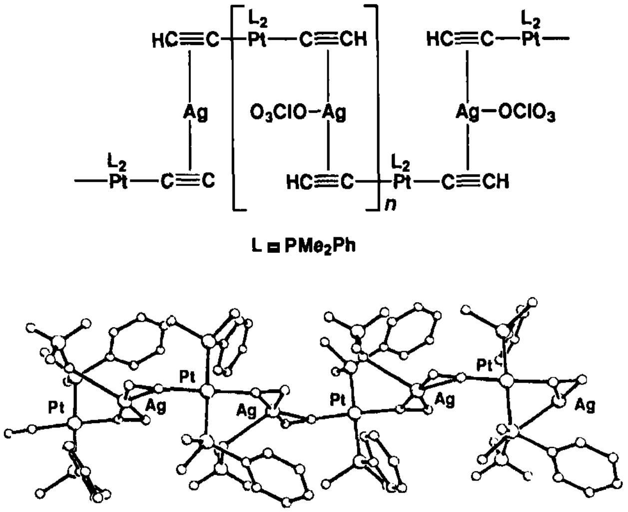


FIG. 62. Structure of the linear $[PtAg(ClO_4)(C{\equiv}CH)_2(PMe_2Ph)_2]$. (From Fig. 3 in Yamazaki, S.; Deeming, A.; Speel, D. M.; Hibbs, D. E.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Chem. Commun.* **1997**, 177.)

of alternating aromatic and silver(I) perchlorate groups running along the *b*-axis as shown in Fig. 63(b).

Several research groups have used isonitriles to prepare organometallic polymers (*214, 215*). End-on coordination at the terminal carbons and linear geometry at the nitrogens impart to these molecular structures the characteristic of association of metal complexes into di-, tri-, and even polymeric species. Harvey has recently reported a series of new organosilver polymers of 1,8-diisocyano-*p*-methane ($\mathbf{L}_{77}$), $[Ag(\mathbf{L}_{77})_2]X$ ($X = BF_4^-$, NO_3^- or ClO_4^-), with tubular structures in the solid state (*214*). Each ligand group bridges two tetrahedral silver atoms, forming zigzag chains that crystallize side by side separated by two rows of the counteranions (Fig. 64). Before this study two series of organosilver polymers with 2,5-dimethyl-2′,5′-diisocyanohexane ($\mathbf{L}_{78}$) had been reported (*215*). Complexes of the first series contain one diisonitrile per metal with the formula $[Ag(\mathbf{L}_{78})]X$ ($X = BF_4^-$, PF_6^-, or NO_3^-). The structures contain infinite chains of silver atoms alternating with bridging ligands. The second series crystallized as $[Ag_2(\mathbf{L}_{78})_3]X_2$, and again, the extended *trans*-conformer of $\mathbf{L}_{78}$ alternating with Ag atoms generates infinite chains. However, the unique structural difference lies in a adjacent pairs of chains cross-linked by extra ligand groups, leading to a ladderlike pattern.

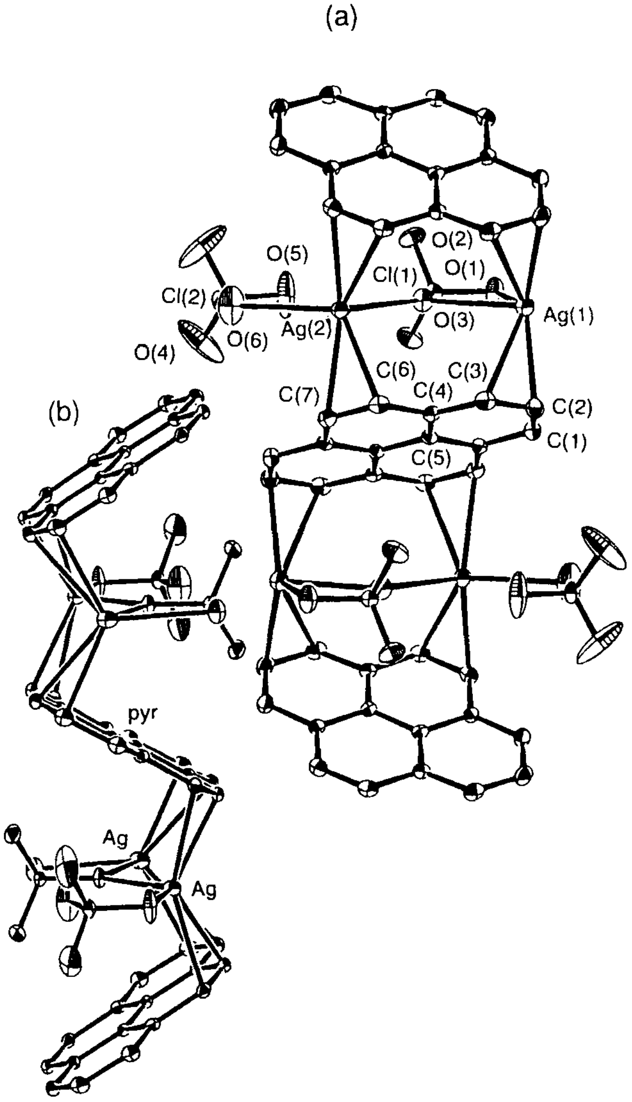


FIG. 63. The W-type sandwich arrangement of an arene-linked polymer of dimers in $[\mathrm{Ag_2(L_{68})(ClO_4)_2}]$. (From Fig. 1 in Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sugimoto, K. *Inorg. Chem.* **1997,** *36,* 4903.)

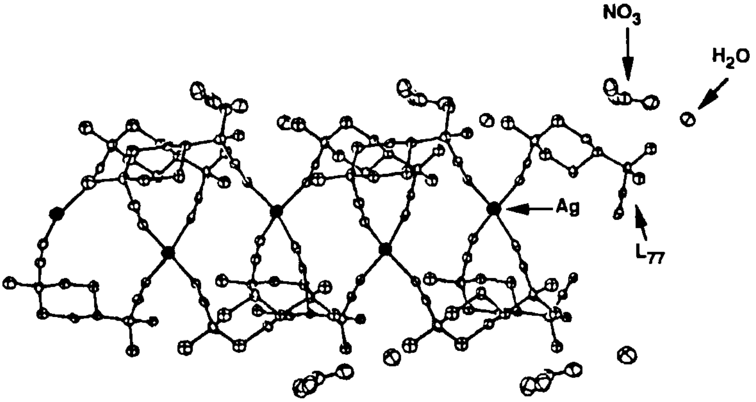


FIG. 64. Structure of the polymeric chain in $[Ag(L_{77})_2]NO_3$. (From Fig. 1 in Fortin, D.; Drouin, M.; Turcotte, M.; Harvey, P. D. *J. Am. Chem. Soc.* **1997,** *119,* 531.)

3. *Heterometallic Cluster Chain*

Heterometallic polymeric cluster compounds have received considerable attention due to their useful properties, which are derived from low-dimensional structures. Haushalter and co-workers recently initiated a study designed to determine the possibility of introducing unpaired electrons to closed-shell, low-dimensional Zintl-phase materials by suitable structural modifications or elemental substitutions, with the aim of increasing their electrical conductivity (*216*). Figure 65 shows the structure of one such example, $(Et_4N)_4[Au(Ag_{1-x}Au_x)_2Sn_2Te_9]$, which contains a semiconductive 8-Å-wide, one-dimensional chain composed of four different elements surrounded by insulating organic material. The magnetic susceptibility of the compound [Fig.

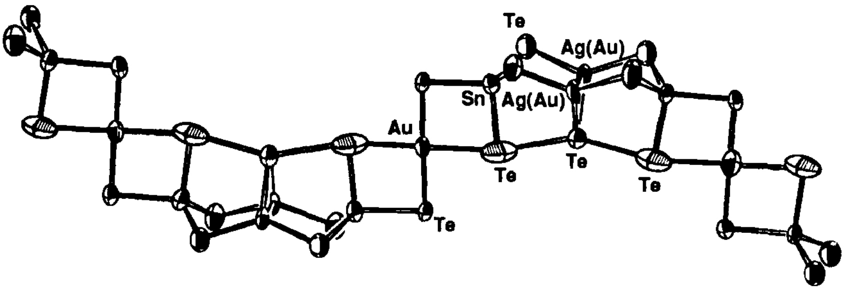
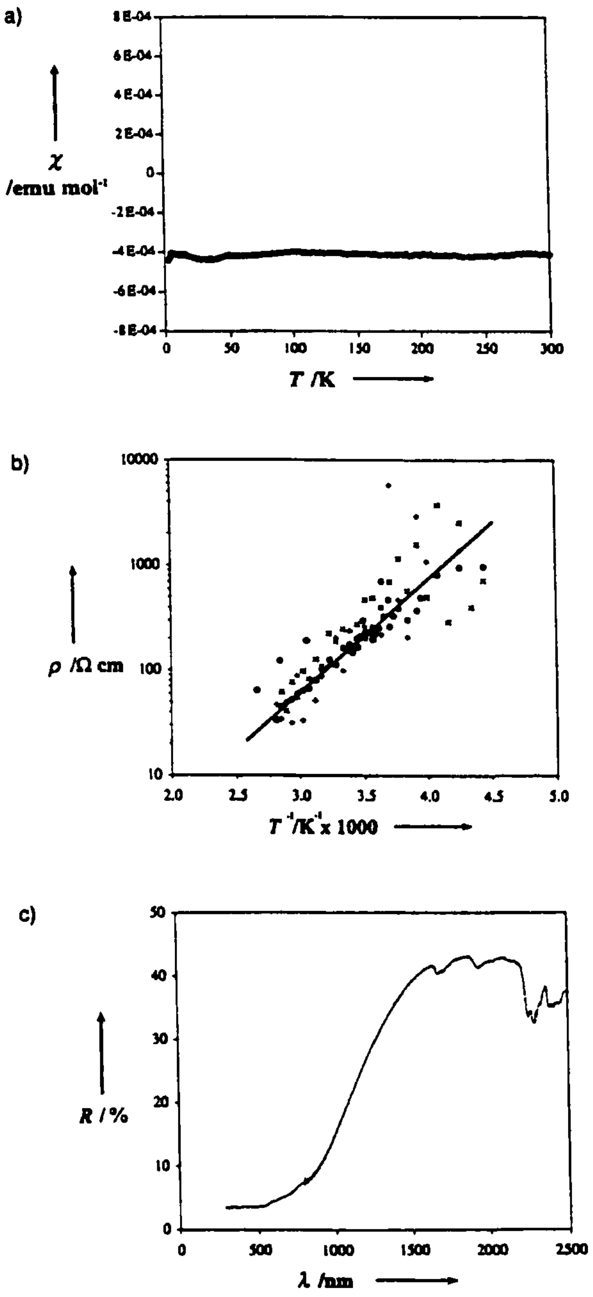


FIG. 65. Structure of the 1-D polymeric chain $[Au(Ag_{1-x}Au_x)_2Sn_2Te_9]^{4-}$. (From Fig. 1 in Dhingra, S. S.; Seo, D.-K.; Kowach, G. R.; Kremer, R. K.; Shreeve-Keyer, J. L.; Haushalter, R. C.; Whangbo, M.-H. *Angew. Chem., Int. Ed. Engl.* **1997,** *36,* 1087.)

66(a)] indicates that the chain is diamagnetic in nature and is nearly independent of temperature down to 4 K. Both resistivity data obtained by the microwave cavity perturbation technique and optical diffuse reflectance measurements as shown in Fig. 66(b) and (c) respectively, support the claim that the compound is a semiconductor and the delocalized one-dimensional band structure undergoes a Peierls distortion above room temperature. Heterometallic polymeric cluster compounds $[W_4Ag5S_{16}][M(dmf)_8]$ (M = Nd or La) derived from tetrathiotunstate and silver(I) have been reported (*217*). The one-dimensional polymeric anion can be regarded as octanuclear cyclic cluster fragments, $[W_4Ag_4S_{16}]^{4-}$, linked through Ag^+ ions as shown in Fig. 67. The significantly short W–Ag bond length of 2.928(1) Å is observed in the analogous compound $[Ag_4WS_4](NH_4)$, suggesting that $Ag^- > WS_4$ electron delocalization and stronger continuous metal–metal interactions are present in this type of heterometallic chains. Reaction of $(NEt_4)_2MS_4$ (M = Mo or W) with CuCl and KSCN (or NH_4SCN) afforded a set of mixed metal–sulfur compounds containing infinite anionic chains $Cu_4(NCS)_5MS_4^{3-}$ and $(CuNCS)_3WS_4^{2-}$ or two-dimensional polymeric dianions $(CuNCS)_4MS_4^{2-}$ (*218*). Short W···Cu distances ranging from 2.62 to 2.70 Å are observed in these compounds. Incorporation of polyoxoanions into one-dimensional coordination polymer matrices, either through direct condensation to form oxo-bridged arrays of clusters or through transition-metal coordination compounds acting as inorganic bridging ligands, provides a route to composite organic/inorganic materials. In this respect, two composite compounds containing Cu(I) complex ions of 4,4′-bipyridine ($\mathbf{L}_{51}$), $[Cu(\mathbf{L}_{51})_4Mo_8O_{26}]$ and $[Cu(\mathbf{L}_{51})_4Mo_{15}O_{47}] \cdot 8H_2O$, have recently been prepared by intercalation of molybdenum oxide clusters into the void space in the Cu–$\mathbf{L}_{51}$ subunits (*219*). By comparison, in a new mixed-ligand Cu(I) polymer containing $\mathbf{L}_{51}$, $[(PPh_3)_2Cu_2Cl_2(\mathbf{L}_{51})]$, a different lattice appeared (*220*). This structure consists of $(PPh_3)_2Cu_2Cl_2$ units that are bridged by $\mathbf{L}_{51}$ (Fig. 68). The significance of these studies is that members of the vast family of polyoxoanion clusters may be employed as structural motifs to fill tunable void volumes created by extended cationic frameworks, and it would appear that this synthetic approach provides a method for structural modification of metal oxide and, consequently, tuning of electronic, magnetic, and optical properties of the oxide phases.

4. Mixed-Valence Copper Complex with Chain Structure

The mixed-valence copper complexes with polymeric chain structures have been described. Reaction of the cyclic thioether ligand tet-


a)
χ /emu mol⁻¹
8E-04
6E-04
4E-04
2E-04
0
-2E-04
-4E-04
-6E-04
-8E-04
0
50
100
150
200
250
300
T /K
b)
ρ /Ω cm
10000
1000
100
10
2.0
2.5
3.0
3.5
4.0
4.5
5.0
T⁻¹/K⁻¹ x 1000
c)
R / %
50
40
30
20
10
0
0
500
1000
1500
2000
2500
λ /nm

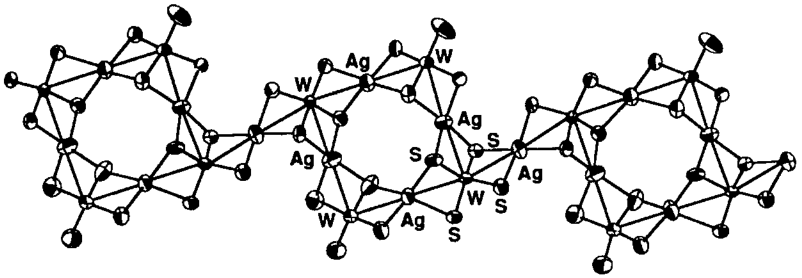


FIG. 67. Structure of the 1-D polymeric anion $[W_4Ag_4S_{16}]^{4-}$. (From Fig. 1 in Huang, Q.; Wu, X.; Wang, Q.; Sheng, T.; Lu, J. *Angew. Chem., Int. Ed. Engl.* **1996,** *35,* 868.)

rahydrothiophene ($\mathbf{L}_{79}$) with $CuCl_2 \cdot 2H_2O$ in acetone yielded the polymeric, mixed-valence complex $[Cu^I_3Cu^{II}(\mathbf{L}_{79})_3Cl_5]$ (*221*). The structure contains two distinct types of copper atoms: The divalent copper atoms involve an intemediate geometry between square planar and tetrahedral, comprising four chlorine atoms, and the monovalent copper atoms have distorted tetrahedral S_2Cl_2 donor sets. The magnetic susceptibility data, ESR, and electronic reflectance spectra for the compound indicate that no intervalence interactions occurred between two Cu(I) and Cu(II) sites.

5. *Diradical Ligand Complex with Chain Structure*

Polymeric transition metal complexes of organic radical ligands have received recent attention in magnetic systems. The ligands concerned include the diradical 1,1′,5,5′-tetramethyl-6,6′-dioxobis(verdazyl) ($\mathbf{L}_{80}$). Reactions of $\mathbf{L}_{80}$ with copper(I) halides in acetonitrile or copper(II) halides in methanol gave copper(I) complex $[Cu_2X_2(\mathbf{L}_{80})]$ (*222*), whose structure is found to be a polymeric chain with the tetrahedral copper atoms alternately bridged by two halide ions and two verdazyl diradicals [Fig. 69(a)]. Magnetic susceptibility measurements indicate that the spins couple in one-dimensional chains with alternating exchange parameters [Fig. 69(b)]. Although the intraligand electronic exchange is still antiferromagnetic in the system, the triple excited state is considerably stabilized compared with the free ligand as a result of an increasingly important superexchange through the cop-

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FIG. 66. Physical properties of $[Au(Ag_{1-x}Au_x)_2Sn_2Te_9]^{4-}$. (a) Temperature dependence of the magnetic susceptibility χ; (b) temperature-dependent resistivity ρ; (c) optical diffuse reflectance R versus wavelength λ of incident light. (From Fig. 4 in Dhingra, S. S.; Seo, D.-K.; Kowach, G. R.; Kremer, R. K.; Shreeve-Keyer, J. L.; Haushalter, R. C.; Whangbo, M.-H. *Angew. Chem., Int. Ed. Engl.* **1997,** *36,* 1087.)

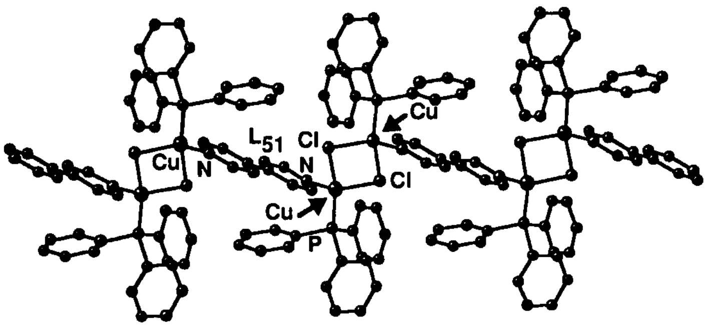


FIG. 68. View of the $[(PPh_3)_2Cu_2Cl_2(L_{51})]$ chain. (From Fig. 2 in Lu, J.; Crisci, G.; Niu, T.; Jacobson, A. J. *Inorg. Chem.* **1997,** *36,* 5140.)

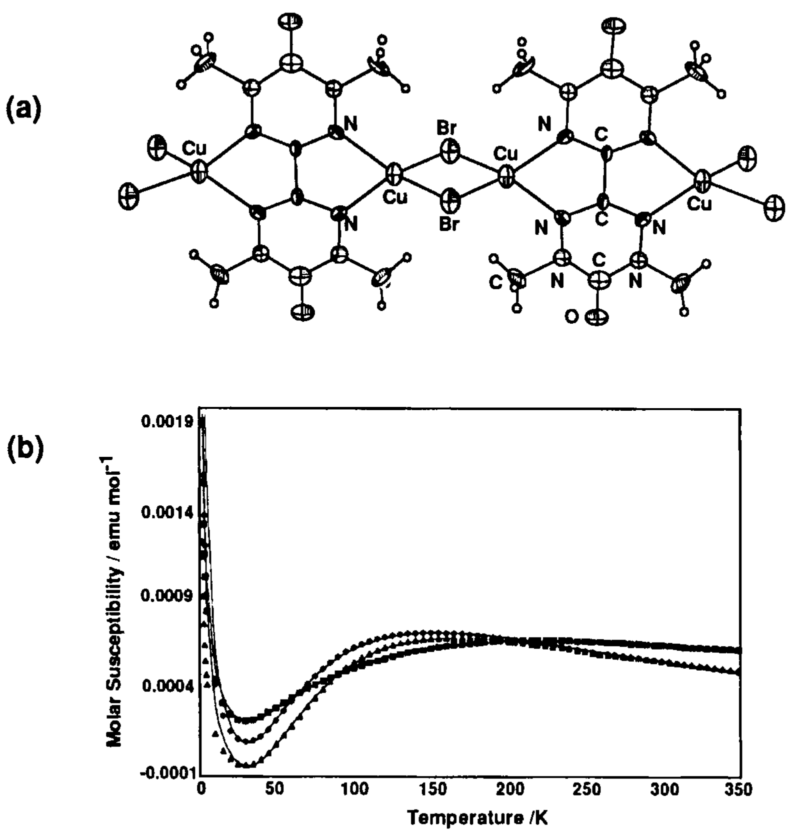


FIG. 69. View of the chain structure (a) and temperature dependence of magnetic susceptibility (b) in $[Cu_2X_2(L_{80})]$. (From Fig. 3 and Fig. 7 in Brook, D. J. R.; Lynch, V. Conklin, B.; Fox, M. A. *J. Am. Chem. Soc.* **1997,** *119,* 5155.)

per(I) center. Another example of coordination of diradical with copper metal is reported by Oshio in a copper(II) complex of imino nitroxide $[Cu^{II}(\mathbf{L}_{81})](PF_6)_2$ obtained from the reaction of $[Cu^{I}(CH_3CN)_4]$ PF_6 with $\mathbf{L}_{81}$ in methanol (*223*), where $\mathbf{HL}_{81}$ is 2-(1′-oxy-4′,4′,5′,5′-tetramethyl-4′,5′-dihydro-1′*H*-imidazole-2′-yl)-6-(1″-oxyl-4″,4″,5″,5″-tetramethyl-4″,5″-dihydro-1″*H*-imidazole-2″-yl)pyridine. In this complex the square planar copper(II) ions are bridged by the imino-hydroxyamino anions to form a one-dimensional helical structure. Here again, the magnetic susceptibility data revealed antiferromagnetic interactions. From the investigation of the coordination chemistry of these unusual diradicals it can be expected that the bridging ligands $\mathbf{L}_{80}$ and the polypyridyl type of imino nitroxide hold great promise as building components for future design and construction of polyradical magnetic materials.

6. *Carboxylate Ligand Complexes*

Although the silver(I) ion is regarded as a typical soft Lewis acid, it forms a variety of coordination compounds with carboxylate ligands. Mak classified the coordination modes of Ag carboxylates into four types, most of which are constructed from either dimeric units or polymeric networks of dimeric subunits (*224*). The same author prepared and characterized two polymeric silver(I) complexes of betaine, $[Ag_2(Me_3NCH_2COO)_2(H_2O)_2(NO_3)_2]$ and $[Ag_2(C_5H_5NCH_2COO)_2(ClO_4)_2]$ (*224*). The two complexes are structurally similar, both consisting of centrosymmetric carboxylato-bridged Ag_2(carboxylato-*O*,*O*′)2 dimers, which extend into a stairlike polymer through the coordination of each metal center by a carboxylate oxygen atom from an adjacent dimer. It is worth noting that both polymers are found to involve very short intradimer Ag---Ag distances of 2.898(1) and 2.814(2) Å, respectively, compared with other dinuclear silver(I) carboxylates.

7. *Thio-Ligand Complexes*

Although both copper(I) and silver(I) metal ions are expected to readily form coordination compounds with thio ligands by covalent bonds, few polymeric structures for thioether crown complexes have been reported. Among these few examples, two silver(I) complexes with thioether macrocyclic ligands are particularly interesting (*225*). Reaction of $[24]aneS_8$ ($\mathbf{L}_{82}$) with 2 molar equivalents of $AgCF_3SO_3$ gave a one-dimensional polymer, $[Ag_2(\mathbf{L}_{82})(CF_3SO_3)_2(MeCN)_2]$, in which each Ag atom is coordinated to four S-donors in a distorted tetrahedral geometry. As illustrated in Fig. 70, the four S-donors come from two different ligand molecules to generate an infinite ladder polymer

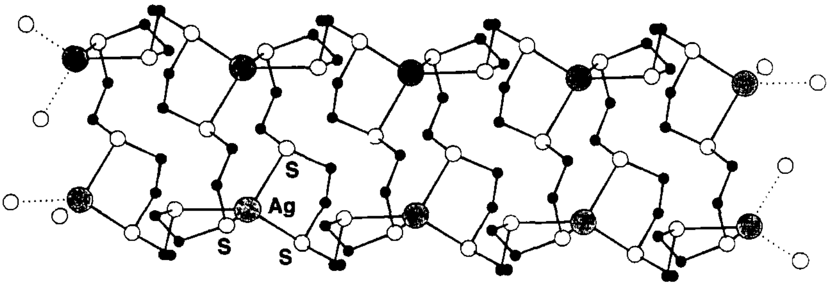


FIG. 70. View of the polymeric chain in $[Ag_2(\mathbf{L}_{82})]^{2+}$. (From Fig. 1 in Blake, A. J.; Li, W.-S.; Lippolis, V.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1997**, 1943.)

along the *b*-axis. A similar reaction with the crown thioether containing four S-donors, [16]aneS_4 ($\mathbf{L}_{83}$), gave a three-dimensional polymer, $[Ag(\mathbf{L}_{83})(BF_4)]$, in which each Ag(I) ion is coordinated by four symmetry-equivalent S-donors in a tetrahedral geometry, and each ligand group in turn bridges four different Ag atoms. The work illustrates the potential of thioether crowns as building blocks for the synthesis of inorganic architectures using their *exo*-orientated S-donors.

The rodlike ligand 2,11-dithia[3,3]paracyclophane ($\mathbf{L}_{84}$) is found to be a particularly versatile organic ligand for the formation of polymeric chains in the presence of bridging anions (*226*, *227*). The arrangement of such chains in the lattice is controlled and modified by the metal ions and coordination of a suitable anion. Two copper(I) and one silver(I) complex of $\mathbf{L}_{84}$ have been reported (*226*), in one of which, $[Cu_2Br_2(\mathbf{L}_{84})(MeCN)_2]$, the two Br atoms bridge pairs of Cu(I) ions to form a rhombic CuBrCuBr ring as shown in Fig. 71 and each ligand molecule links two separate metal cations on each side through two sulfur atoms, resulting in a one-dimensional polymeric chain running parallel to a diagonal axis of the triclinic cell.

Silver(I) complexes of 1,4-thioxane ($\mathbf{L}_{85}$) have been reported (*228*). Both $[Ag(\mathbf{L}_{85})(CF_3SO_3)]$ and $[Ag_2(\mathbf{L}_{85})(CF_3SO_3)_2]$ were isolated from the mixture of $\mathbf{L}_{85}$ and silver triflate at ambient temperature in a 1 : 1 mixture of dichloromethane and acetonitrile. The former involves silver(I) cations tetrahedrally coordinated by two sulfur atoms of two $\mathbf{L}_{85}$ molecules and the oxygen atoms of two bridging triflate anions, giving in the crystal an infinite one-dimensional chain with bridging only through the triflate moieties. Although the immediate coordination environment around the silver(I) ion in the latter complex is similar to that in the former, bridging between Ag^I cations occurs via the participation of both 1,4-thioxane sulfur and triflate oxygen atoms, leading to a two-dimensional lattice.

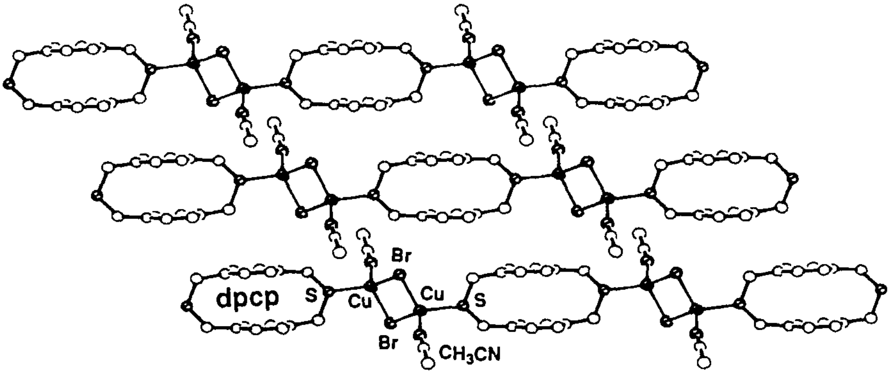


FIG. 71. View of the infinite chains in $[Cu_2Br_2(L_{84})(MeCN)_2]$. (From Fig. 1 in Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Nakagawa, S. *J. Chem. Soc., Dalton Trans.* **1996,** 1525.)

Silver(I) complexes of the nonchelating dithioether ligand have been described (*229*). Crystallographic studies of $[Ag(MeSCH_2CH_2CH_2SMe)]BF_4$ revealed a chain structure involving trigonal $(\mu_2\text{-}S)_2,S$ ligation with one S donor bridging two adjacent Ag cations while another S donor of the dithioether ligand is nonbridging. In contrast, X-ray analysis of $[Ag(PhSCH_2CH_2CH_2SPH)_2]BF_4$ revealed monodentate S ligation of four distinct dithiother ligands to the Ag atom, giving an approximately tetrahedral geometry at the metal ion, with the second S donor of each ligand linking to four other Ag^I ions, hence generating a three-dimensional infinite lattice.

Due to the biological relevance of copper–sulfur coordination compounds to metalloproteins, the copper(I) complex of thiourea, $[Cu\{SC(NHCH_3)_2\}_2]NO_3$, has been prepared from an aqueous solution of copper(II) nitrate and *N,N′*-dimethylthiourea (*230*). The structure contains substantially distorted CuS_4 tetrahedra, each being linked by common edges with two neighbors, resulting in infinite isolated chains parallel to the *c*-axis of the cell. The nitrate anions are not coordinated to the silver(I) ions, but associate the individual chains of edge-sharing CuS_4 tetrahedra together.

8. *Other Nitrogen-Containing Ligand and Mixed-Ligand Complexes*

Mingos and co-workers have recently reported several novel silver(I) complexes with simple polydentate acyclic nitrogen-donor ligands such as diethylenetriamine (dien) and tris(2-aminoethyl)amine

(**L**$_{86}$) (*231*). The dien complex [Ag(dien)]PF_6 is slightly light-sensitive, but may be stored indefinitely under nitrogen at −30°C in the dark. The complex consists of two crystallographically independent silver atoms and two nonequivalent dien ligands, which link adjacent T-shaped silver centers to form a catena structure. The tren complex [Ag(**L**$_{86}$)]PF_6 also has a zigzag chain structure and possesses similar structural features except that the two silver(I) ions involve distorted tetrahedral geometries and tren acts essentially as a tetradentate ligand.

Luminescent coordination compounds continue to attract considerable attention. Zink recently reported a new mixed-ligand copper(I) polymer that shows interesting photoluminescence (*232*). The complex [CuCl(**L**$_{44}$)Ph_3P] consists of a one-dimensional chain lattice of metal ions bridged by both Cl^- ions and pyrazine molecules. The compound shows conductivity of less than 10^{-8} $S \cdot cm^{-1}$. The absorption spectrum of the complex shows a band at 495 nm, which could be interpreted as the promotion of an electron from the valence band to the conduction band. On the basis of resonance Raman spectra, the lowest excited state in the polymer is assigned to the Cu(I)-to-pyrazine metal-to-ligand charge-transfer excited state.

In the previous section, 1-cyanoguanidine (**L**$_{52}$) was quoted as an example of the multifunctional ligands for the formation of H-bonded frameworks (*157*). Because this molecule can act either as a monodentate ligand (nitrile N donor) or as a bidentate bridging ligand (nitrile and amino N donor) a number of 1:1 and 1:2 1-cyanoguanidine–copper(I) halide adducts have been reported (*233*). The complex [CuX(**L**$_{52}$)], where X = Cl^- or Br^-, is characterized by two mutually perpendicular chains of $[CuX(\mathbf{L}_{52})]_n$ and $(CuX_2^-)_n$ joined at a common halogen. Within these two individual chains the copper atoms are found to involve different distorted tetrahedral and trigonal planar stereochemistries, respectively.

Among the mixed-ligand-complexed copper(I) complexes, the one formed by pyrazine (**L**$_{39}$) and 3-methylpyridazine (**L**$_{87}$) deserves to be mentioned (*234*). The compound $[Cu_2(\mathbf{L}_{87})_2(\mathbf{L}_{39})_3](ClO_4)_2$ was prepared by the stepwise reaction of copper(I) with two ligands. The two copper centers involve different coordination environments, one in a three-coordinate Y-shaped form and the other in a typical four-coordinate tetrahedral form. The structure consists of a tetracopper unit bridged alternately by **L**$_{87}$ and **L**$_{39}$ groups (Fig. 72). In addition, the cyclic voltammogram of the complex reveals two reversible redox couples with $E_{1/2}$ = +0.22 and +0.53, which are ascribed to the Cu^ICu^I/Cu^ICu^{II}

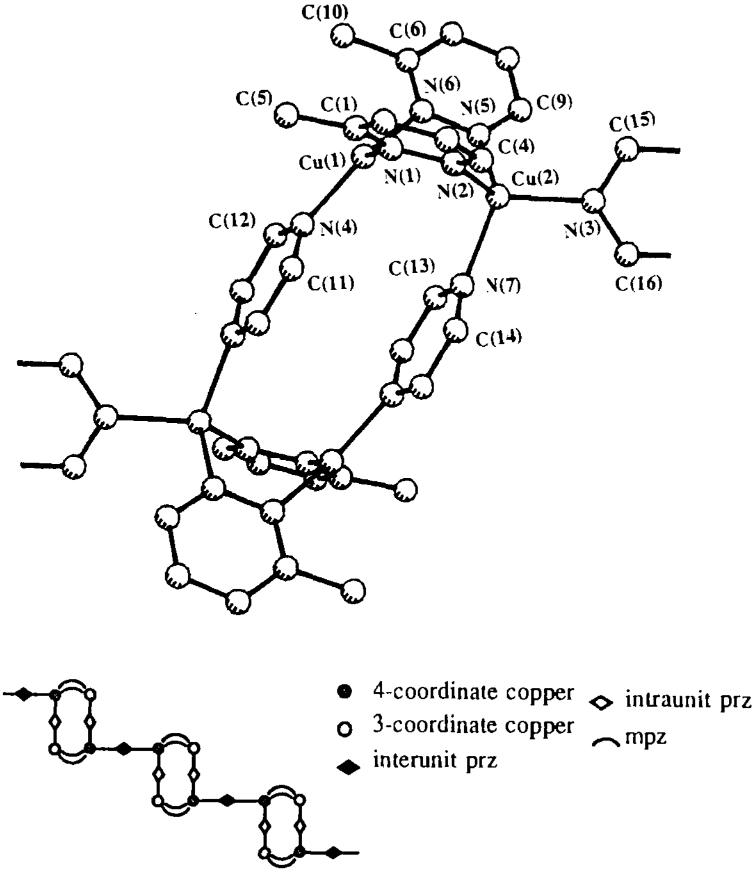


FIG. 72. Structure of an infinite cationic chain in $[Cu_2(L_{87})_2(L_{39})_3](ClO_4)_2$. (From Fig. 1 and Fig. 2 in Kitagawa, S.; Munakata, M.; Tanimura, T. *Chem. Lett.* **1991,** 623.)

and $Cu^{I}Cu^{II}/Cu^{II}Cu^{II}$ reactions of the closely contacting dicopper moiety, respectively.

In an attempt to use dicopper(I) complex unit as building block for synthesis of metal-containing polymers, Kitagawa reported his interesting results in synthesis and structural characterization of an infinite stair-type chain compound (*235*). The complex of thiochrome ($\mathbf{L}_{88}$) $[Cu_2(\mathbf{L}_{88})_2](ClO_4)_2$ was prepared by reduction of copper(II) perchlorate followed by reaction with the ligand. The structure contains a dinuclear cationic unit in which the two T-shaped metal ions are doubly bridged by two thiochrome molecules with extremely short Cu---Cu contact of 2.476(3) Å. The dimeric units are mutually linked by the 2-hydroxyl group of the coordinated ligand group, giving a novel stair-type chain. The cyclic voltammogram in the solid state gives a single quasi-reversible wave, indicating that the dicopper site undergoes redox reactions.

Coordination compounds of biheteroaromatic ligands have been extensively studied (*236*). The nitrogen-rich ligand, 3,5-bis(2-pyridyl) pyrazole ($\mathbf{L}_{89}$), in which the pyrazole ring is attached to bulk nitrogen heterocycles at the 3-and 5-positions, belongs to this class. Polymeric silver(I) complexes containing the uninegative pyrazolate ion had been known for over a century when the formation of an insoluble silver pyrazolate salt Ag(pz) was reported; however, its structure has never been crystallographically established (*237*). Fortunately, the structure of the polymeric silver(I) complex of the pyrazole derivative ligand $\boldsymbol{L}_{89}$ has been determined recently (*238*). Along with it, Munakata has also reported a copper(II) and another silver(I) complex with $\mathbf{L}_{89}$. The reaction of $\mathbf{L}_{89}$ and $AgClO_4$ in different solvents at various molar ratios surprisingly leads to the isolation of two totally different silver(I) complexes, one dimer, $[Ag_2(\mathbf{L}_{89})_4](ClO_4)_2 \cdot 2Me_2CO$, and one polymer, $[Ag(\mathbf{L}_{89})]ClO_4$. In the polymeric structure the coordination around the metal ion involves a distorted trigonal planar core, AgN_3, and each $\mathbf{L}_{61}$ molecule bridges two metal centers, giving an extended zigzag chain as shown in Fig. 73. Between the chains there is no effective interaction present due to the presence of anion column separating the cationic chains.

Like $\mathbf{L}_{89}$, hexamethylenetetraamine ($\mathbf{L}_{90}$) is also a potentially tetradentate ligand. Two silver(I) coordination polymers with this polydentate N-donor base have been reported, and one involves a one-dimensional lattice (*239*). Reaction of $AgSbF_6$ and $\mathbf{L}_{90}$ in a 1 : 1 molar ratio in ethanol–CH_2Cl_2 isolated the compound $[Ag(\mathbf{L}_{90})]SbF_6 \cdot H_2O$. The structure contains a novel type of ribbon formed by hexagonal meshes of alternate Ag^I ions and $\mathbf{L}_{90}$ molecules. The water molecules coordinated to the silver ions form O—H---N hydrogen bonds with the $\mathbf{L}_{90}$ groups of adjacent ribbons, which generate a three-dimensional network of unprecedented topology (Fig. 74).

In terms of Pearson's hard–soft acid–base principle, the soft Lewis acid copper(I) ion is not compatible with the hard base H_2O molecule, but a recent article provided the first example of a copper(I)–water bond (*240*). The novel copper(I) complex with 2,3-diphenylquinoxaline ($\mathbf{L}_{91}$), $[Cu(\mathbf{L}_{91})(H_2O)]ClO_4$, is diamagnetic and indefinitely stable in air in the solid state. Its structure consists of an infinite polymeric cationic chain in which adjacent metal centers are bridged by the aro-

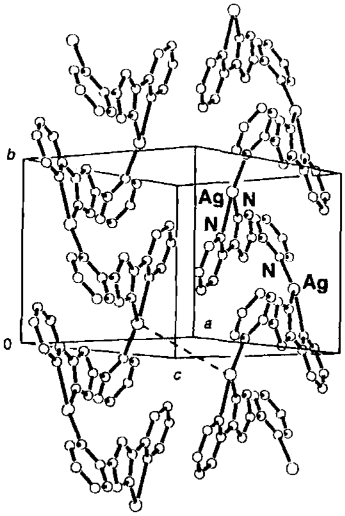


FIG. 73. View of the chain structure in $[Ag(\mathbf{L}_{89})]^+$. The dashed line shows the contact between the nearest silver atoms, Ag---Ag 5.67 Å. (From Fig. 3 in Munakata, M.; Wu, L. P.; Yamamoto, M.; Kuroda-Sowa, T.; Maekawa, M.; Kawata, S.; Kitagawa, S. *J. Chem. Soc., Dalton Trans.* **1995,** 4099.)

matic nitrogens of the bidentate ligand of $\mathbf{L}_{91}$. The Cu–O bond length of 2.154(6) Å is longer than the calculated distance of 1.99 Å based on the bond-valence-sum models. Therefore, the coordination of the copper is best described as distorted trigonal planar CuN_2O with a weak interaction with the water molecule.

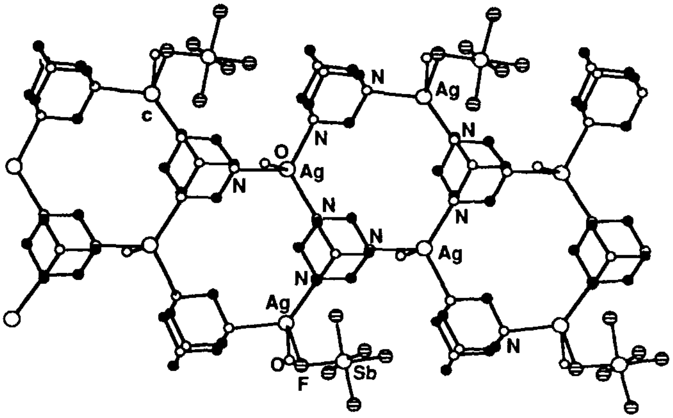


FIG. 74. One-dimensional ribbon in $[Ag(\mathbf{L}_{90})]SbF_6 \cdot H_2O$. (From Fig. 2 in Bertelli, M.; Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Mater. Chem.* **1997,** *7,* 1271.)

Several copper(I) and silver(I) complexes with *trans*-1,2-bis(2-pyridyl)ethylene (L_{92}) have been reported (*241*). In [M(L_{92})]X, where M = Cu or Ag and X = PF_6^- or ClO_4^-, a distorted linear coordination geometry completed by the nitrogen atoms of two different ligands is observed for both Cu^I and Ag^I ions. Both complexes have a similar chain structure, and they only differ in the mode of polymerization, being of rectangular and triangular wave chain types, respectively (Fig. 75). Additionally, the pyridine ring contact between the adjacent chains in the copper complex is 3.46 Å, indicative of π–π interactions present. In another copper(I) complex, [Cu(L_{92})(CO)(CH_3CN)]PF_6, an infinite

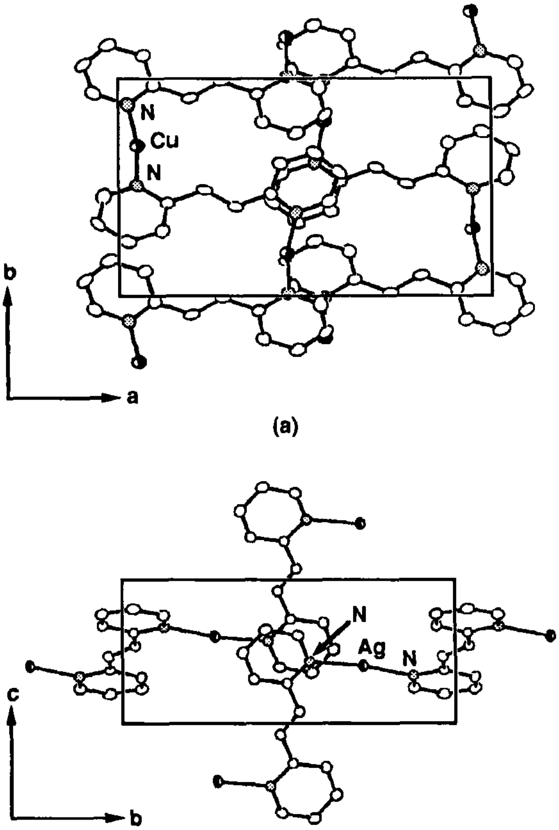


FIG. 75. ORTEP views of the cationic chains in [Cu(L_{92})]PF_6 (a) and [Ag(L_{92})]ClO_4 (b). (From Fig. 1 in Powell, J.; Horvath, M. J.; Lough, A. *J. Chem. Soc., Dalton Trans.* **1996**, 1669.)

one-dimensional chain based on bridging of **L_{92}** between two metal ions is also observed. However, with additional coordination of carbonyl and acetonitrile, each metal center involves a tetrahedral core $CuN_2N'C$.

Coordination compounds containing simple alkyl and aryl halides have been structurally characterized (*242*, *243*). Novel examples include silver(I)–iodocarbon complexes obtained from the reaction of $AgPF_6$ and $AgNO_3$ with diiodomethane, 1,3-diiodopropane, and simple aryl iodides (*243*). The compound $[Ag(NO_3)(1,2\text{-}I_2C_6H_4)]$ is composed of spiral chains of $[Ag(\mu\text{-}NO_3)]_n$ as shown in Fig. 76, in which the nitrate uses only one oxygen atom to bridge two silver ions. In $[Ag\{I(CH_2)_3I\}_2]PF_6$, $[Ag(ICH_2I)_2]PF_6$, $[Ag(1,2\text{-}I_2C_6H_4)_3]PF_6$, and $[Ag(1,2\text{-}BrIC_6H_4)_4]PF_6$, the structure consists of tetrahedrally coordinated Ag^+ ions and bridging iodocarbon ligands, giving rise to a chain polymer array.

B. TWO-DIMENSIONAL STRUCTURES

1. *Polycatenane and Polyrotaxane Complexes*

Catenanes are a group of interlocked or catenated molecules, and rotaxanes are a class of molecules in which a dumbbell-shaped compo-

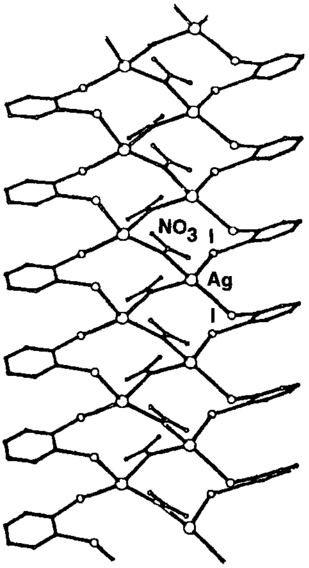


FIG. 76. Structure of the spiral chains in $[Ag(NO_3)(1,2\text{-}I_2C_6H_4)]$. (From Fig. 8 in Powell, J.; Horvath, M. J.; Lough, A. *J. Chem. Soc., Dalton Trans.* **1996**, 1669.)

nent is encircled by a macrocycle. The efficient synthesis of such systems fascinated and inspired many scientists in the 1960s and 1970s (*244*). Due to the introduction of metal templating and supramolecular approaches for molecular threading and interlocking, this area has experienced a renaissance in recent years (*245*, *246*). Multicomponent polycatenane and polyrotaxane molecular systems incorporating metal-ion templates represent a particularly interesting class of supramolecular species that might exhibit intriguing chemical topology and display some fascinating electronic, optical, and magnetic properties (*247–251*).

Schröder and co-workers have successfully isolated a unique polycatenated undulating molecular ladder that forms interwoven two-dimensional sheets (*252*). The reaction of $[Cu(MeCN)_4]PF_6$ with 1,4-bis(4-pyridyl)butadiyne ($\mathbf{L}_{93}$) in $MeCN-CH_2Cl_2$ yielded the complex $[Cu_2(MeCN)_2(\mathbf{L}_{93})_3](PF_6)_2$. The compound exists as a network of molecular ladders in which the two independent Cu^I centers are each coordinated in a tetrahedral geometry to three $\mathbf{L}_{93}$ groups and one MeCN molecule. The lattices are polycatenated to give a remarkable two-dimensional layer structure (Fig. 77). The sheets of interwoven molecules are separated by PF_6^- counteranions and solvent molecules. The structure is further stabilized by the $\pi-\pi$ interactions between adjacent, symmetry-related ladders.

Robson has constructed a two-dimensional polyrotaxane sheet from the rodlike ligand 1,4-bis(imidazol-1-yl-methyl)benzene ($\mathbf{L}_{94}$) (*253*). The compound $[Ag_2(\mathbf{L}_{94})_3(NO_3)_2]$ was obtained by reaction of $\mathbf{L}_{94}$ and silver nitrate in aqueous methanol. The coordination polymer consists of one-dimensional chains in each of which the metal center is located

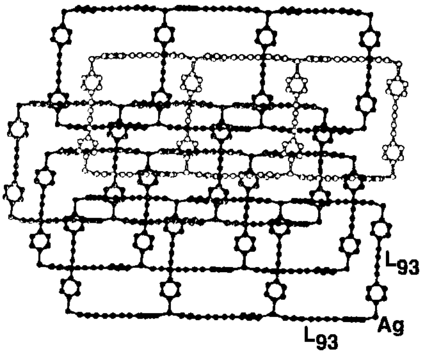


FIG. 77. View of the polycatenated sheet structure in $[Cu_2(MeCN)_2(\mathbf{L}_{93})_3](PF_6)_2$. (From Fig. 3 in Blake, A. J.; Champness, N. R.; Khlobystov, A.; Lemenovskii, D. A.; Li, W.-S.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1997**, 2027.)

within the plane of the N_3 donor set. The individual chains are associated to produce the polyrotaxane sheets as shown in Fig. 78, in which the $\mathbf{L}_{94}$ moiety provides both the rodlike segments and two half-loops for each of the rings.

Kim and Whang have constructed a polyrotaxane containing cyclic beads threaded on two-dimensional coordination polymer networks (*254*). The compound $[Ag_2(\mathbf{L}_{95})_3(\text{cucurbituril})_3](NO_3)_8 \cdot 40H_2O$, where $\mathbf{L}_{95}$ = *N*,*N*′-bis(4-pyridylmethyl)-1,4-diaminobutane dihydronitrate and cucurbituril = $C_{36}H_{36}N_{24}O_{12}$, was prepared by the route shown in Fig. 79. The compound is a polyrotaxane in which the cyclic beads of cucurbituril are threaded on a two-dimensional coordination polymer network. The two-dimensional polyrotaxane network forms layers stacked on each other, which in turn fully interlock with themselves.

2. *Two-Dimensional Network Comprising Copper Clusters*

Copper(I) thiolate complexes show remarkable diversity of structure, and the most common structural unit in the known thiolate is a three-coordinate copper atom bonded to μ_2-bridging thiolates (*15*). Parish has recently reported a novel compound in which the thiolate sulfur atom involves unusual four-way bridging (*255*). The compound with composition $[Cu_{13}Cl_{13}(SR)_6] \cdot H_2O$ (R = $CH_2CH_2NH_3$) was obtained by reaction of CuCl and cysteamine hydrochloride in an aqueous solu-

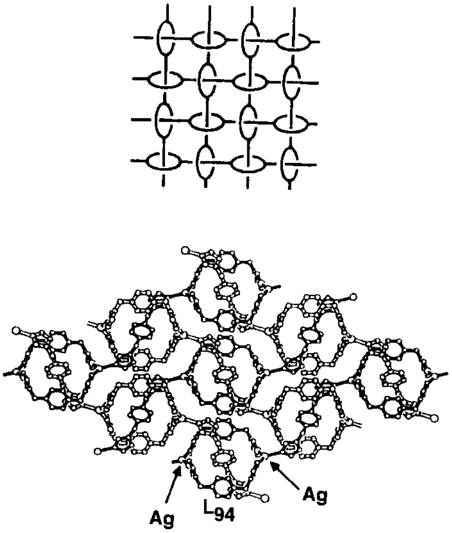


FIG. 78. A 2-D polyrotaxane network in $[Ag_2(\mathbf{L}_{94})_3(NO_3)_2]$. (From Insertion Fig. V and Fig. 2 in Hoskins, B. F.; Robson, R.; Slizys, D. A. *J. Am. Chem. Soc.* **1997,** *119,* 2952.)

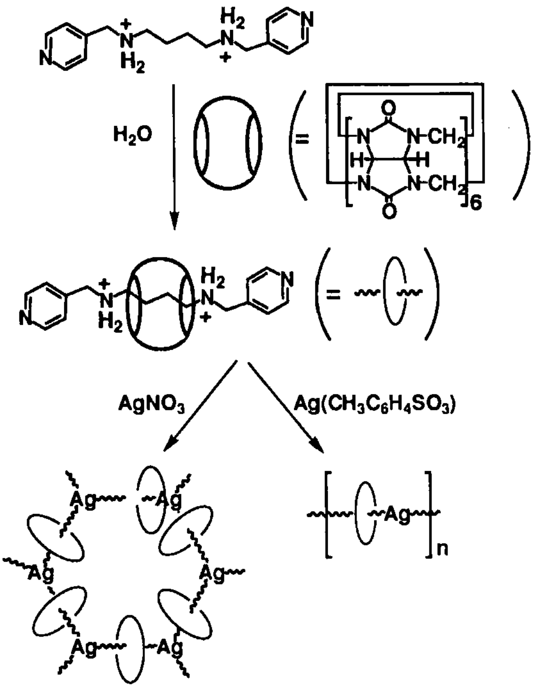


FIG. 79. Construction scheme for the 2-D polyrotaxane network of $[Ag_2(L_{95})_3(\text{cucurbituril})_3](NO_3)_8 \cdot 40H_2O$. (From Scheme 1 in Whang, D.; Kim, K. *J. Am. Chem. Soc.* **1997,** *119,* 451.)

tion. X-ray analysis revealed a polymeric structure containing a centrosymmetric Cu_{12} cubo-octahedron unit. A regular octahedron of sulfur atoms, bearing organic chains pointing outward, has each edge bridged by a CuCl unit. There are thus three mutually perpendicular, planar, eight-membered $[(CuCl)(\mu_2\text{-}SR)]_4$ rings intersecting at the sulfur atoms, giving a gimba-like "Atlas-sphere" configuration (Fig. 80). The $Cu_{12}Cl_{12}(SR)_6$ clusters are further linked to form two-dimensional sheets with different linkages in the two directions.

3. *Two-Dimensional Network Containing Hexagonal Meshes and a Zeolite-like Framework*

Ciani and co-workers have reported the self-assembly of two remarkable polymeric networks based on an anionic acetonyl derivative of tetracyanoethylene (*256*). The attempts to obtain novel extended frameworks of Ag ions bridged by the neutral tetracyanoethylene

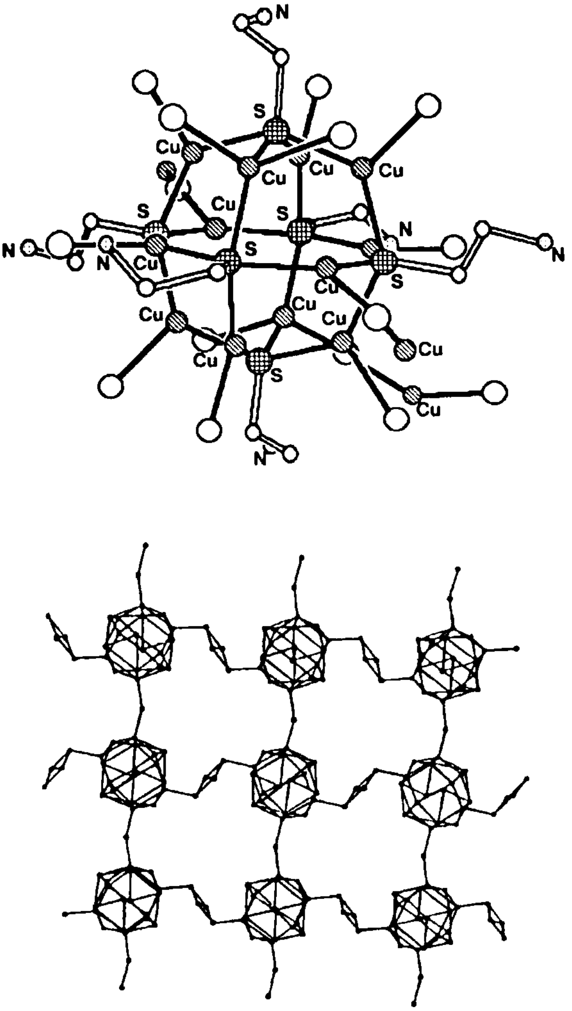


FIG. 80. Structure of the basic $[Cu_{13}Cl_{13}(SR)_6]$ unit and the layers of clusters forming sheets. (From Fig. 1 in Parish, R. V.; Salehi, Z.; Pritchard, R. G. *Angew. Chem., Int. Ed. Engl.* **1997,** *36,* 251.)

have led to the unexpected formation of $[Ag(\mathbf{L}_{96})]$, where $\mathbf{L}_{96}$ = 1,1,2,2-tetracyanopentan-4-one-1-ide. The structure consists of two-dimensional undulated nets of hexagonal meshes formed by alternate three-coordinate silver ions and tridentate anion $\mathbf{L}_{96}$ (Fig. 81). Two independent nets of this type interpenetrate to give a layer structure. The targeted synthesis of $[Cu(MeCN)_4]PF_6$ with the preformed conju-

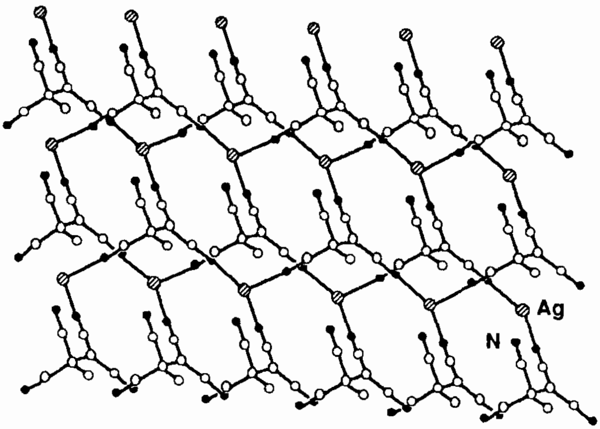


FIG. 81. View of the twofold interpenetrated layer of [Ag($\mathbf{L}_{96}$)]. (From Fig. 1 in Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Angew. Chem., Int. Ed. Engl.* **1996,** *35,* 1088.)

gated acid of $\mathbf{L}_{96}$ in acetone gave the corresponding copper(I) polymer [Cu($\mathbf{L}_{96}$)] · Me_2CO. Although the compound holds the same stoichiometry as the silver complex, its structure consists of a three-dimensional neutral network of four-coordinate copper(I) ions linked by anions $\mathbf{L}_{96}$. The framework resembles a honeycomb with large channels that include guest acetone molecules. The large difference between the two structures can be related to the higher tendency of Cu^I ions over Ag^I ions to achieve a tetrahedral coordination. Therefore, by using this methodology it should be possible to generate other topologies with different metal ions and/or with similar polycyano anions.

The assembly of a long-range solid-state superstructure with a zeolite-like framework has been exploited by a number of research groups (*118, 127*). Recently, it has proven possible to synthesize coordination networks with microporous structures that maintain crystal integrity upon loss of guest species. Such zeolite-like behavior of a coordination network represents a new challenge for chemists to look for new class of microporous substances. Reaction of silver triflate and the tritopic ligand 1,3,5-tris(3-ethynylbenzonitrile)benzene ($\mathbf{L}_{97}$) yielded solid [Ag($\mathbf{L}_{97}$)(CF_3SO_3)] · $2C_6H_6$ (*257*). The compound contains a two-dimensional network in which the coordination geometry around silver is trigonal pyramidal, with three nitriles of the network in the basal plane and a trilate counterion in the apical position as shown in Fig. 82. The sheets are stacked, creating a channel structure in which solvent benzene molecules reside in the micropores. The com-

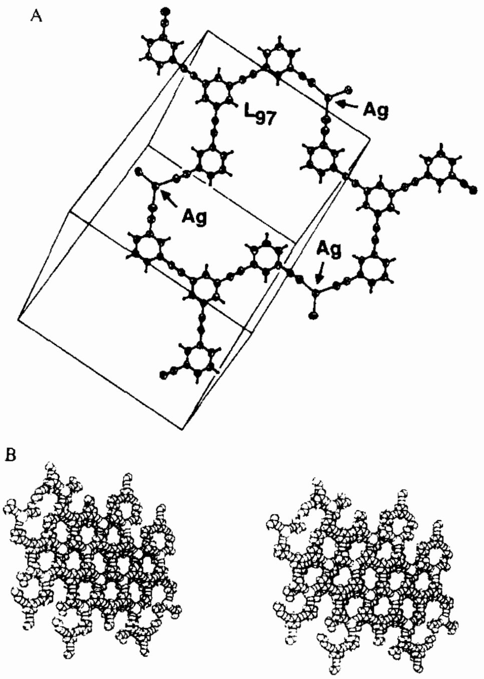


FIG. 82. Structure and coordination network in $[\mathrm{Ag}(\mathbf{L}_{97})(\mathrm{CF_3SO_3})]$. (From Fig. 1 in Venkataraman, D.; Gardner, G. B.; Lee, S.; Moore, J. S. *J. Am. Chem. Soc.* **1995,** *117,* 11600.)

pound shows stability toward partial loss of inclusion molecules. The TGA trace of the compound reveals two discrete mass losses at 110 and 145°C (Fig. 83), corresponding to the removal of distorted benzene molecules. At 145°C, a solid-to-solid phase transition occurs concomitant with the loss of the remaining benzene molecules. DSC and optical microscopy indicate no evidence of a phase change associated with the first mass loss. Further observations demonstrate that the sample can reversibly remove and reabsorb benzene molecules without collapse of the channel network analogous to that of zeolite-type materials.

4. *Two-Dimensional Network Containing an Undulated Wave Layer Structure*

In the Section VIII.A, "Infinite-Chain Structures," we noted that Mak *et al.* characterized a number of carboxylato-bridged silver(I) complexes with chain structures (*224*). The same research group has

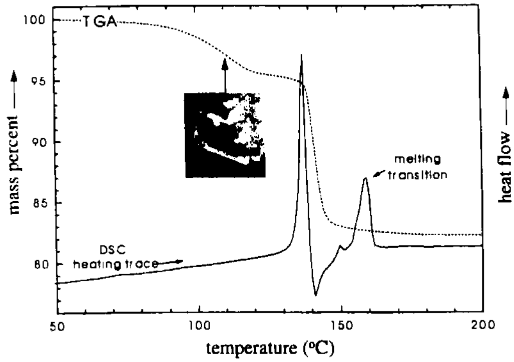


FIG. 83. Overlay of TGA and DSC traces for [Ag($\mathbf{L}_{97}$)(CF_3SO_3)]. (From Fig. 2 in Venkataraman, D.; Gardner, G. B.; Lee, S.; Moore, J. S. *J. Am. Chem. Soc.* **1995,** *117,* 11600.)

also employed dicarboxylate-like ligands *meso*-2,5-bis(trimethylammonio)adipate ($\mathbf{L}_{98}$) and *meso*-2,5-bis(pyridinio)adipate ($\mathbf{L}_{99}$) to synthesize silver(I) complexes with two-dimensional networks (*258*). Structure analysis revealed that in each of the four complexes [$Ag_2(\mathbf{L}_{98})$](ClO_4)$_2$, [$Ag_2(\mathbf{L}_{99})$](ClO_4)$_2$, [$Ag_2(\mathbf{L}_{98})$](NO_3)$_2$, and [$Ag_2(\mathbf{L}_{99})$](NO_3)$_2$, a dimeric unit is involved in which each pair of adjacent metal atoms is doubly bridged by coplanar *syn-syn* μ-carboxylate-*O,O′* groups. The dimeric subunits are extended into a step polymer through the linkage of each metal center to a carboxylate group of an adjacent dimer. The basic coordination environment for the metal is completed by three carboxylato oxygen atoms in a T-shaped geometry, if the interaction between the anion and the metal center is ignored, as occurred in two perchlorate complexes. Because the nitrate anion functions as a unidentate and *O,O′*-bridging mode in the third and the last complex, respectively, it leads correspondingly to a distorted tetrahedral and unusual square pyramidal five-coordination at Ag^I ion. Figure 84 shows the structure and packing drawing of the layer structure of the five-coordinate silver complex. All compounds exhibit short Ag---Ag separation in the dimeric unit, ranging from 2.794(1) Å to 2.878(2) Å, substantially smaller than that in metallic silver (2.89 Å). It is debatable whether these distances are a result of the bridging ligand or suggestive of strong metal–metal interactions present.

Crown thioether can not only form a one-dimensional chain structure, it can also form two-dimensional sheet frameworks (*225*). The crown thioether ligand $(OH)_2[16]aneS_4$ ($\mathbf{L}_{100}$) reacted respectively with silver nitrate and silver acetate, giving two polymeric silver(I) com-

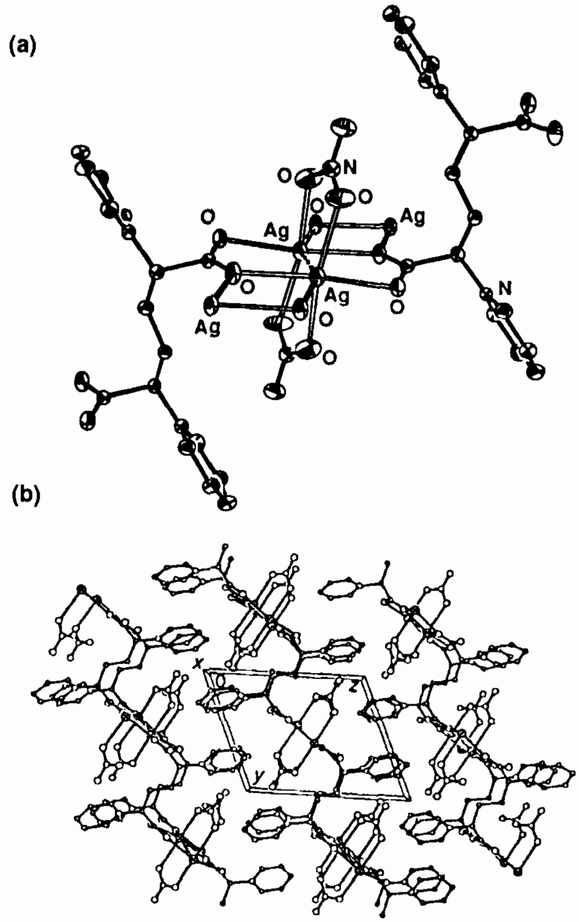


FIG. 84. Structure skeleton of the asymmetric unit (a) and packing drawing of the layer structure (b) in $[Ag_2(\mathbf{L}_{99})(NO_3)_2]$. (From Fig. 5 in Wu, D.-D.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1995,** 2671.)

plexes, $[Ag(\mathbf{L}_{100})]O_2CMe$ and $[Ag(\mathbf{L}_{100})]NO_3$ (*259*). The two compounds are not isostructural, but their structures and dimensionality seem to be controlled by change of the anions. In the complex with silver acetate, each metal center is bound to four thioether sulfur atoms in a rather distorted tetrahedral fashion. The silver atoms are in a two-dimensional sheet arrangement interconnected by the macrocycle in which two crystallographically independent Ag^I ions are stacked alternately along a diagonal to the *a*- and *c*-axes of the unit cell (Fig. 85). By contrast, the complex with silver nitrate consists of a three-

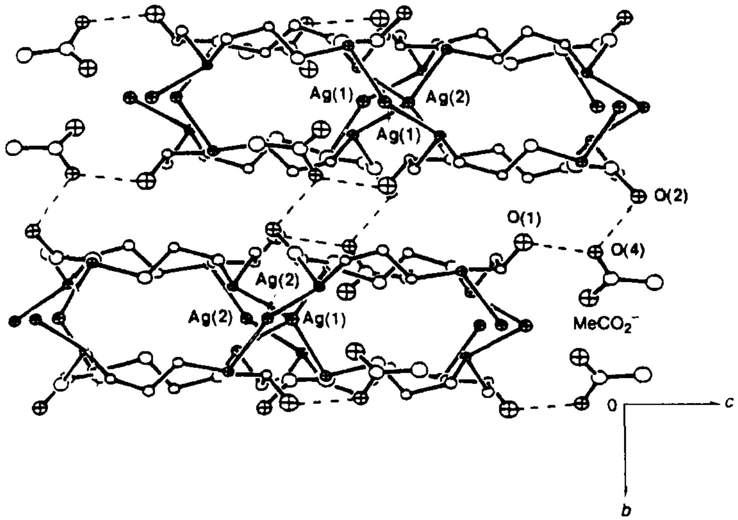


FIG. 85. Packing diagram for $[Ag(L_{100})]O_2CMe$ with dashed lines showing the hydrogen bonds. (From Fig. 4 in Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M. *J. Chem. Soc., Dalton Trans.* **1995,** 3215.)

dimensional tetrahedral network linked by an exodentate coordination of the thioether.

5. *Conductive π-Complex*

Although the silver(I)-pyrene complex $[Ag_2(L_{68})(ClO_4)_2]$ is found to display a chain structure as already mentioned, a similar complex with perylene, $[Ag_2(L_{69})(ClO_4)_2]$, consists of a two-dimensional framework of the metal ions bridged by the bidentate counterions and the tetra-η^2-arene groups shown in Fig. 50 (*187*). Such two-dimensional sheets are further connected by the superposed intersheet aromatic π–π stackings at an average distance of 3.31 Å, generating a three-dimensional network structure. The physicochemical property measurements of two complexes show that at room temperature no strong ESR spectrum was observed for each case, but the light-irradiated samples show a characteristic *g* value attributable to the aromatic radicals, suggesting that upon irradiation electron transfer partially takes place from the aromatic donor to the silver (I) ion, giving an organic radical cation and silver(0). In addition, both compounds are electrically nonconducting, whereas their I_2-doped samples display semiconducting behavior at ambient temperature, which is presumed to connect mainly with the nonintegral formal oxidation state of the crystallized organic radicals. These conducting radical cation complexes might constitute new functional materials among low-dimensional molecular solids similar to polymetallocenes and multidecker metallacarboranes. A further example of a silver(I) π-complex with a two-dimensional sheet framework is found in a silver(I)–iodocarbon complex, $[Ag_2(O_2PF_2)_2(p\text{-}IC_6H_4Me)]$ (*243*). The solid-state structure of the compound is composed of an infinite two-dimensional sheet array of $[Ag(O_2PF_2)]_n$ in which each *p*-iodotoluene bonds to two Ag^I ions via one I–Ag bond and an η^2-arene bond involving two of the carbons not bonded to I or Me.

6. *Inorganic Polymers*

The development of inorganic polymer chemistry based on incorporation of transition metals into a polymer main chain has resulted in diverse arrays of interesting structures in recent years. These polymers are expected to constitute a new type of inorganic functional material. It is not the aim in this section to undertake a comprehensive treatment of this field; for this, the reader is directed to the recent reviews and the references herein (*260, 261*). Here we just list a few examples of inorganic polymers that incorporate copper(I) or silver(I) ions with two-dimensional sheet frameworks. Pfitzner has carried out a systematic investigation on new adducts of copper(I) halides with neutral chalcogen fragments or polychalcogenide anions (*262*). One of them, $(CuI)_3Cu_2TeS_3$, was found to contain layers of the complex thioanion $[TeS_3]^{2-}$ embedded between layers of iodide ions. Copper atoms are distributed in the arrangement of iodine and sulfur atoms.

Kanatzidis and Zhang have utilized sulfur-rich mixed polysulfide/telluride fluxes in combination with transition metals to synthesize novel solid-state materials (*263*). Thus, six new quaternary copper(I) and silver(I) compounds with composition $AMTeS_3$, where A = K, Rb, or Cs and M = Cu or Ag, were prepared. The structure consists of anionic $[MTeS_3]_n^{n-}$ layers and charge-compensating alkali ions between the layers. Each layer is composed of tetrahedrally coordinated Cu^I or Ag^I centers and trigonal pyramidal TeS_3^{2-} units, joined together via bridging S atoms. Similar low-dimensional quaternary compounds, KCu_2AsS_3 and KCu_4AsS_4, have also been reported, and a unique layered framework was observed in both compounds in which the Cu(I) ions are linked in a complex manner by a series of trigonal AsS_3^{3-} groups or AsS_3^{3-} groups as well as S^{2-} ions (*264*).

7. *Inorganic Grid and Heterobimetallic Aggregates*

Inspired by the idea that an n-topic ligand would form an $n \times n$ inorganic grid based on n^2 metal ions and $2n$ ligand components, Lehn and co-workers have reported the self-assembly of the inorganic 3 × 3 grid consisting of an array of nine silver(I) metal ions and six tritopic ligands (*265*). The complex $[\mathrm{Ag_9}(\mathbf{L}_{101})_6](\mathrm{CF_3SO_3})_9$, where $\mathbf{L}_{101}$ = 6,6′-bis[2-(6-methylpyridyl)]-3,3′-bipyridazine, contains an arrangement of a 3 × 3 grid of nine $\mathrm{Ag^+}$ ions chelated by six bidentate ligand molecules as shown in Fig. 86. Such an architecture opens the way to a whole family of polynuclear inorganic $m \times n$ grids, which represent a new facet in the controlled arrangement of metal ions into specific arrays and patterns.

Among the previously discussed heterobimetallic aggregates of copper(I) with thiotungstates and thiomolybdates, those containing the two-dimensional polymeric dianions $(\mathrm{CuNCS})_4\mathrm{MS}_4^{2-}$ are noteworthy (*218*). X-ray diffraction results show that four edges of the tetrahedral MS_4^{2-} (M = Mo or W) core are coordinated by copper atoms forming $\mathrm{WS_4Cu_4}$ aggregates linked by eight-membered rings of $-\mathrm{Cu(NCS)_2Cu}-$ (Fig. 87).

8. *Two-Dimensional Sheets Containing Cu$_6$ Hexagons*

The rodlike ligand $\mathbf{L}_{84}$ was also found to form a polymeric complex with copper(I) (*226*), but the complex obtained by reaction of $\mathbf{L}_{84}$ with 1 molar equivalent of CuI in thf, $[\mathrm{Cu_2I_2}(\mathbf{L}_{84})_2]\cdot$thf, is surprisingly not isostructural of the corresponding complex of the bromide. Instead, it

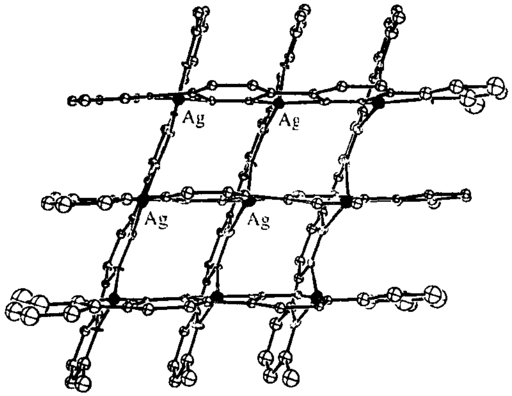


FIG. 86. Crystal structure of the self-assembled 3 × 3 inorganic grid $[\mathrm{Ag_9}(\mathbf{L}_{101})_6](\mathrm{CF_3SO_3})_9$. (From Fig. 3 in Baxter, P. N. W.; Lehn, J.-M.; Fischer, J.: Youinou, M.-T. *Angew. Chem., Int. Ed. Engl.* **1994,** *33,* 2284.)

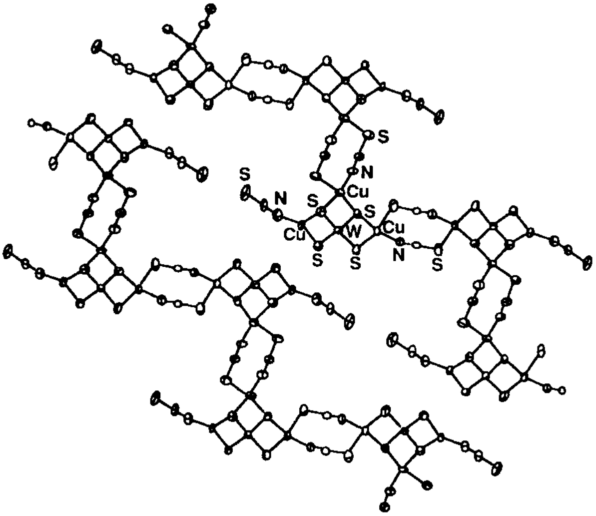


FIG. 87. Perspective view of zig-zag anionic chains in $(CuNCS)_4MS_4^{2-}$. (From Fig. 2 in Manoli, J. M.; Potvin, C.; Secheresse, F.; Marzak, S. *Inorg. Chem. Acta* **1988,** *150,* 257.)

is composed of a two-dimensional framework in which a large ring containing six copper atoms includes a thf molecule as guest inside the open cavity (Fig. 88). As in the bromide, the rhombic CuICuI ring formed by bridging the two iodide ions between pairs of copper atoms leads to a Cu---Cu distance of 3.18 Å and an I---I distance of 4.30 Å. Each $\mathbf{L}_{84}$ fragment bridges two separate metal cations through two sulfur donors, resulting in a two-dimensional sheet arrangement of copper(I) ions. The framework contains six-membered rings of Cu_6 hexagons incorporating the thf molecule in the open cavity. In contrast to the formation of the rhombic ring by copper(I) halide ions, the one-nitrate oxygen bridging two metal ions in the silver(I) complex $[Ag(\mathbf{L}_{84})(NO_3)]$ yielded a unique three-dimensional channel framework of silver(I) ions (*226*). For these reasons, both metal ions and counteranions are considered to be the fundamental factors controlling crystallization and variation of frameworks.

C. THREE-DIMENSIONAL STRUCTURES

1. *Construction of Channeled Frameworks*

The rational design of multidimensional coordination compounds incorporating large cavities or channels capable of hosting small mol-

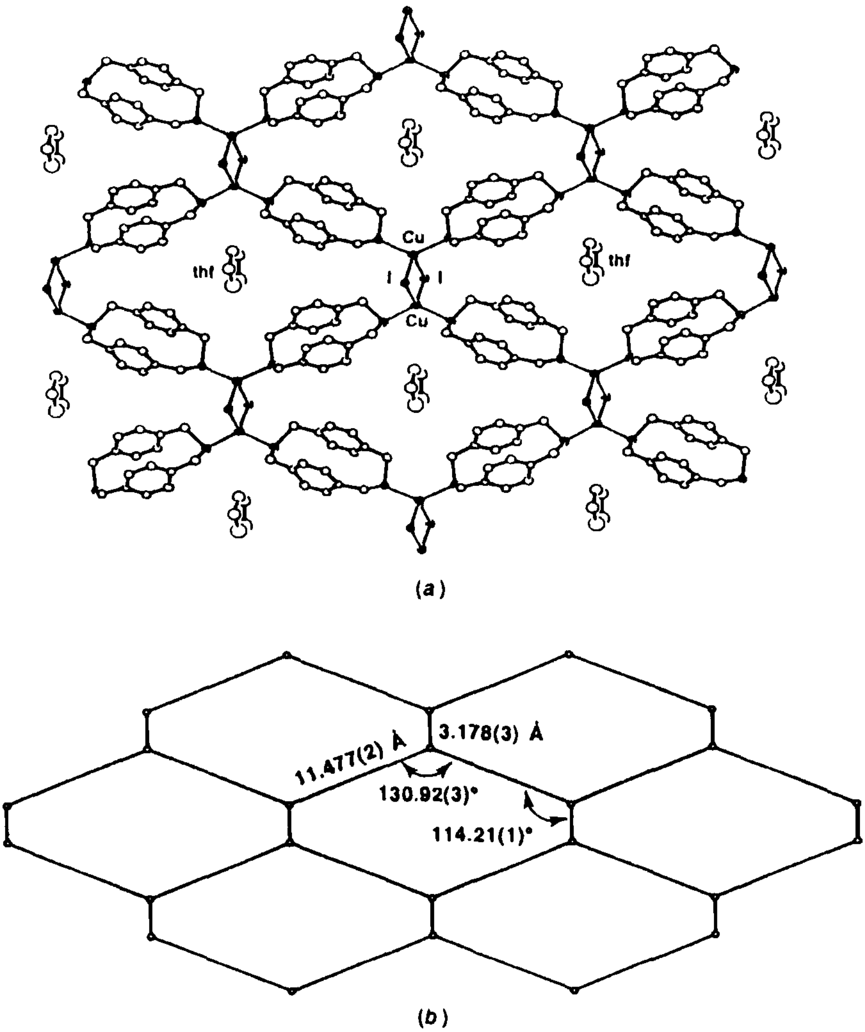


FIG. 88. Molecular packing diagram of complex $[Cu_2I_2(L_{84})_2] \cdot$ thf (a) and a view of the 2-D sheet consisting of Cu_6 hexagons (b) where only the metal centers are presented as open circles. (From Fig. 3 in Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Nakagawa, S. *J. Chem. Soc., Dalton Trans.* **1996,** 1525.)

ecules is currently recognized as one of the most important issues in the synthesis of functional materials for molecular sieves, shape-selective catalysis, ion exchangers, and many other applications (*4, 266–270*). The approach generally employs rigid and highly symmetric organic units as building blocks via intermolecular forces such as hydrogen bonds (*159–163*) or coordination to metals. Such zeolite-like behavior of the coordination network in copper(I) and silver(I) complexes is not limited to two-dimensional structures (*257*). In fact, the majority of examples are found in three-dimensional copper and silver complexes of nitrogen ligands derived from organocyanides (*121–128, 271*), 4,4′-bipyridyl, and hexamethylenetetraamine.

The simple ligand 4,4′-bipyridyl ($\mathbf{L}_{51}$) has been chosen by many groups as a rod linking together metal centers to give extended solids with diverse topologies (*272–275*). Reaction of $AgNO_3$ and $\mathbf{L}_{51}$ in MeCN gave the silver(I) polymer $[Ag(\mathbf{L}_{51})]NO_3$ (*273, 274*). The crystal structure reveals a triple interpenetrated cationic network schematically shown in Fig. 89, each consisting of linear $[Ag(\mathbf{L}_{51})]_\infty$ chains cross-linked by Ag–Ag bonds of 2.970(2) Å. The resultant open framework contains large interconnected cavities that form stairlike microchannels of approximate cross section 6 × 23 Å. Rather small channels are observed in the corresponding complex of copper(I) chloride, $[Cu(\mathbf{L}_{51})Cl]$, obtained by diffusing solutions of CuCl and $\mathbf{L}_{51}$ into ethylene glycol (*275*). The structure contains chloro-bridged Cu^I dimers, which form a sheet framework with 4,4′-bipyridyl molecules. The overall structure thus formed is a neutral three-dimensional framework, in which the interpenetrating two-dimensional sheets fill up most of the pore space with channels of only small diameter (2 × 4 Å) remaining open, too small to accomodate acetonitrile or DMSO solvent molecules as guests in the crystal.

Paralleling the approach used in supramolecular organic chemistry of adamantyl templates with different synthons (*266–268*), Ciani and

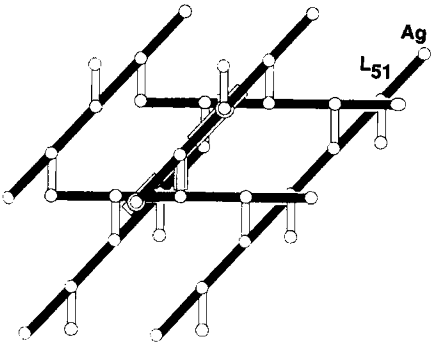


FIG. 89. Schematic representation of the 3-D framework in $[Ag(\mathbf{L}_{51})]NO_3$, with circles representing Ag cations, filled bars representing $\mathbf{L}_{51}$ and empty bars representing Ag–Ag bonds. (From Scheme 1-D in Robinson, F.; Zaworotko, M. *J. Chem. Soc. Chem. Commun.* **1995,** 2413.)

co-workers have developed a scheme using the potentially tetradentate ligand hexamethylenetetraamine ($\mathbf{L_{90}}$) for the preparation of supertetrahedral networks with metallic synthons (*239, 276–278*). They employed reaction of $\mathbf{L_{90}}$ with different silver(I) salts of noncoordinating anions and isolated a number of polymeric silver complexes with three-dimensional frameworks. The first of this series, $[Ag(\mathbf{L_{90}})]PF_6 \cdot H_2O$, was reported in 1995 (*276*). The compound was obtained by slow evaporation of an ethanolic solution of $AgPF_6$ layered on a solution of $\mathbf{L_{90}}$ in CH_2Cl_2. The structure contains a molecular-based framework topologically related to the three-dimensional, three-connected cubic net of highest symmetry as schematically shown in Fig. 90. The PF_6^- anions and the guest water molecules occupy the large octagonal channels and form an extended hydrogen-bonding network. Similar reactions under different conditions afforded three other compounds. The structure of $[Ag_{11}(\mathbf{L_{90}})_6](PF_6)_{11} \cdot 14H_2O$ consists of an open three-dimensional cationic frame, with all the $\mathbf{L_{90}}$ molecules acting as tetradentate ligands while nine silver cations are biconnected and two are triconnected to the ligands per formula unit (*239*). The (3,4)-connected network schematically shown in Fig. 91 is composed of triconnected (silver ions) and tetraconnected ($\mathbf{L_{90}}$) centers in the ratio 1 : 3. Such connection generates two types of parallel channels to host the anions and the water molecules. The compound $[Ag_5(\mathbf{L_{90}})_6](PF_6)_5 \cdot 3CH_2Cl_2$ is an oligomer, whereas $[Ag_4(\mathbf{L_{90}})(H_2O)](PF_6)_4 \cdot 3EtOH$ gives a three-dimensional network with large cavities and channels of the hexagonal sections, including anions and solvent molecules as guest species (*277*).

Reaction of $AgClO_4$ and $\mathbf{L_{90}}$ in a different molar ratio yielded two polymeric complexes (*278*). The crystal structure of $[Ag(\mathbf{L_{90}})]ClO_4$ consists of two-dimensional infinite layers of hexagonal meshes formed by alternate triconnected silver ions and $\mathbf{L_{90}}$ molecules. The structure

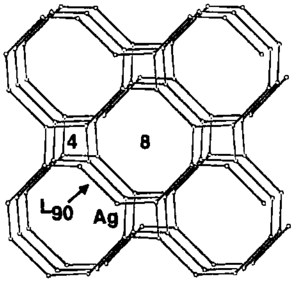


FIG. 90. A schematic view of the 3-D network in $[Ag(\mathbf{L_{90}})]PF_6 \cdot H_2O$. (From Chart 1 in Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.*, **1995**, *117*, 12861.)

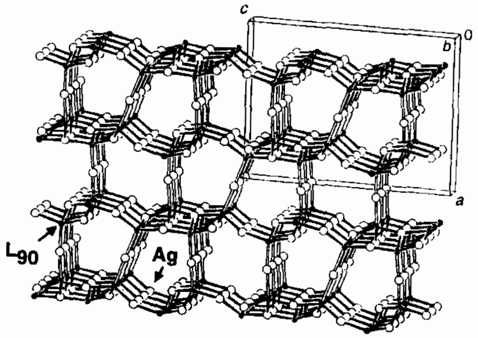


FIG. 91. A schematic view of the 3-D network in $[Ag_{11}(\mathbf{L_{90}})_6](PF_6)_{11} \cdot 14H_2O$. (From Fig. 7 in Bertelli, M.; Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Mater. Chem.* **1997,** 7, 1271.)

of $[Ag_3(\mathbf{L_{90}})_2](ClO_4)_3 \cdot 2H_2O$ contains an open three-dimensional cationic network formed by $[Ag(\mathbf{L_{90}})]$ hexagonal layers, which are joined by biconnected silver ions (Fig. 92). Thus, the three-dimensional framework is a (3,4)-connected net comprising triconnected and tetraconnected centers in the ratio 1 : 1. Guest water molecules occupy the large hexagonal channels and interact with the silver ions of the layers. Thermal analysis has shown that these water molecules can be reversibly removed from the crystals by thermal activation.

Another highly symmetrical coordination polymer was formed in the reaction of $[Cu(CH_3CN)_4]ClO_4$ and 2,4,6-tri(4-pyridyl)-1,3,5-triazine ($\mathbf{L_{102}}$). The compound formulated as $[Cu_3(\mathbf{L_{102}})_4](ClO_4)_3$ has a cu-

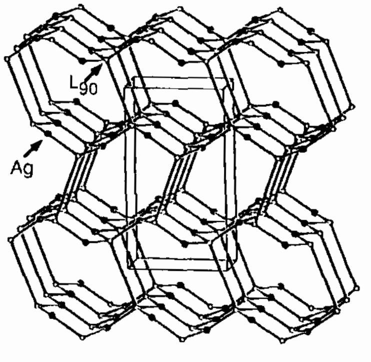


FIG. 92. A schematic view of the 3-D network in $[Ag_3(\mathbf{L_{90}})_2](ClO_4)_3 \cdot 2H_2O$. (From Fig. 2 in Carlucci, L.; Ciani, G.; v. Gudenberg, D. W.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1997,** 631.)

bic (3,4)-connected net with large cavities (*279*). All the ligand groups are equivalent and are attached to three copper centers at the corners of an equilateral triangle, and each copper ion is coordinated by four pyridine donors in a distorted tetrahedral arrangement. This results in an infinite (3,4)-connected three-dimensional network containing large octahedral chambers of diameter 18.241(4) Å. Each chamber is connected by its six copper vertices to six others whose centers are arranged octahedrally around, generating an infinite cubic collection of chambers (Fig. 93).

Reid has extended the investigation of channeled frameworks to the methylene-bridged bidentate ligands $MeECH_2EMe$ (E = S, Se, or Te) on the expectation that such ligands would disfavor chelation and might therefore promote formation of ordered extended networks (*280*). X-ray diffraction studies show that in $[Cu(MeSeCH_2SeMe)_2]PF_6$ each copper ion is tetrahedrally coordinated to one Se donor of four diselenoether ligands and the second Se donor of each ligand is ligated to a different adjacent Cu^I ion to give an infinite three-dimensional cationic network (Fig. 94). The network contains cylindrical channels of diameter *ca.* 12.5 Å incorporating the PF_6^- counteranions. The silver(I) complex $[Ag_4(MeSeCH_2SeMe)_8](BF_4)_4$ contains a similar three-dimensional lattice with rectangular-shaped channels of cross section *ca.* 12.6 × 4.1 Å to fill in the anions.

A large number of host–guest structures are known, but a reversible guest exchange or chemical transformation of the guest inside a coordination polymer framework has been described for only a few (*257*, *281–283*). In most cases the integrity of the inclusion lattice cannot be effectively maintained in the absence of guest molecules

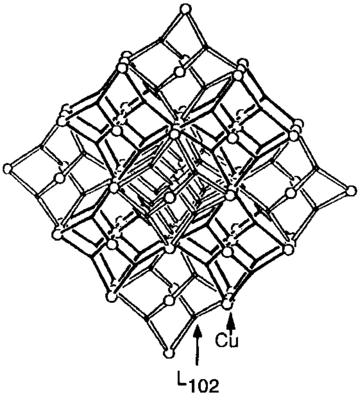


FIG. 93. Schematic representation of two interpenetrating, identical frameworks in $[Cu_3(L_{102})_4](ClO_4)_3$. (From Fig. 3 in Abrahams, B. F.; Batten, S. R.; Hamit, H.; Hoskins, B. F.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1996,** *35,* 1690.)

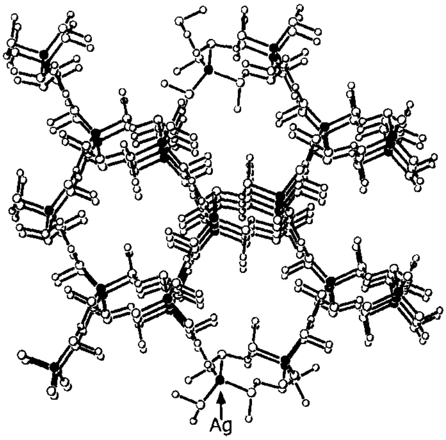


FIG. 94. View of the 3-D network in $[Cu(MeSeCH_2SeMe)_2]PF_6$. (From Fig. 1 in Black, J. R.: Champness, N. R.: Levason, W.; Reid, G. *Inorg. Chem.* **1996,** *35,* 4432.)

(*166*). By using the trigonal ligands, 1,3,5-tricyanobenzene ($\mathbf{L}_{103}$) and 1,3,5-tris(4-ethynylbenzonitrile)benzene ($\mathbf{L}_{104}$), to make networks joined at the vertices by metal ions, Moore and Lee have obtained two silver(I) complexes $[Ag(\mathbf{L}_{103})(CF_3SO_3)]$ and $[Ag(\mathbf{L}_{104})(CF_3SO_3)]$ by mixing the constituent molecules in benzene (*281*, *282*). The crystal structure of the compound with $\mathbf{L}_{103}$ consists of honeycomb sheets based on alternating $\mathbf{L}_{103}$ and the trigonal Ag^I units. The honeycomb sheets create cavities of diameter 10.03 Å to accommodate $CF_3SO_3^-$ ions which are weakly bound to the silver at the axial position of a trigonal pyramid. By contrast, the complex with the larger ligand $\mathbf{L}_{104}$ generates larger channels of diameter 15 × 22 Å and consequently involves interpenetration of lattices (Fig. 95). The three-dimensional (3,3)-connected net is based on the end-on coordination of $\mathbf{L}_{104}$ to the trigonal pyramidal silver cations. The interpretation of the networks generates hexagonal channels in which the benzene molecules from the crystallization process are located. Investigation of exchange properties within a host crystal were carried out in solution and in vapor with a variety of guest molecules. The process was monitored by powder X-ray diffraction and thermogravimetric analyse (TGA)/differential scanning calorimetry (DSC) studies, and the results show that the host adduct can be repeatedly voided of and filled with guest molecules without the destruction of the channel framework.

2. *Feldspar Structure Without Void Space*

The term “mineralomimetic chemistry” was proposed to denote the chemistry of the build-up of mineral-like structures using materials

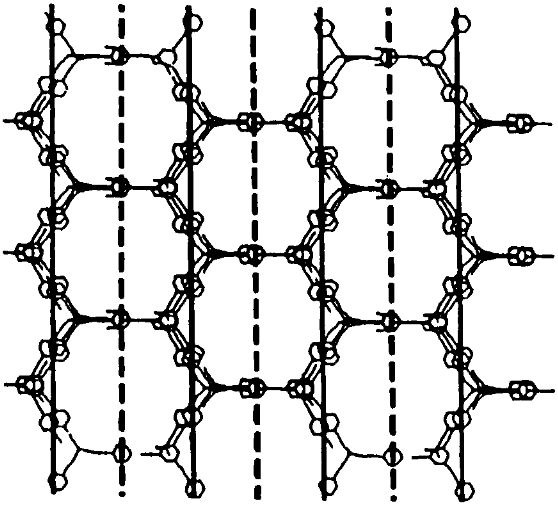


FIG. 95. View of $[Ag(L_{104})(CF_3SO_3)]$ down the *a*-axis with plane waves corresponding to the 002 reflection highlighted. Triflate anions are omitted. (From Fig. 1c in Gardner, G. B.; Kiang, Y.-H.; Lee, S.; Asgaonkar, A.; Venkataraman, D. *J. Am. Chem. Soc.* **1996,** *118,* 6946.)

that never give stable minerals in nature (*270*). The topologic similarities observed between the well-defined coordination geometries and in natural minerals prompted many chemists to mimic the structures of simple minerals (*121*). The copper(I) complex of pyrimidine ($\mathbf{L}_{105}$), $[Cu(\mathbf{L}_{105})_2]BF_5$, was found to have a three-dimensional structure related to that of the natural mineral feldspar (*284*). The complex, obtained by reaction of $[Cu(CH_3CN)_4]BF_4$ and pyrimidine, contains two independent copper centers in the unit cell, each coordinated in a slightly distorted tetrahedral geometry by four nitrogen atoms from four different ligand molecules. Each $\mathbf{L}_{105}$ in turn bridges two copper ions, leading to a three-dimensional framework. The structure is related to that of feldspar in such that the corner-shared network consists of eight-rings of tetrahedral connected together with four-rings to form elliptical channels (Fig. 96). Due to interpenetration of neighboring layers, such channels are almost completely constricted, leaving no void space in the structure. This phenomenon has been previously described in $[Cu(\mathbf{L}_{51})Cl]$, where the interpenetrating of the two-dimensional sheets resulted in small channels (*275*). Thus, it would be possible to increase the volume of the channels by lengthening the spacer ligands that connect the metal centers.

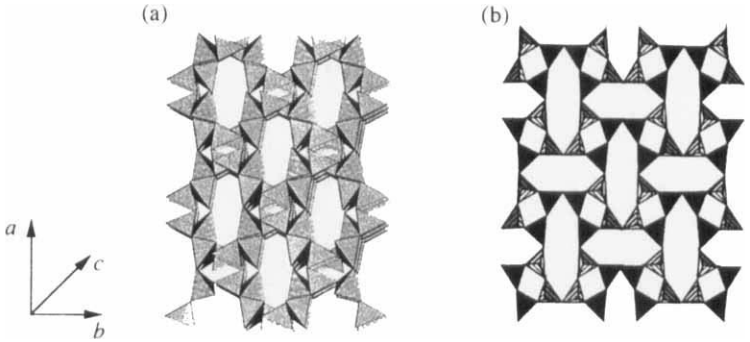
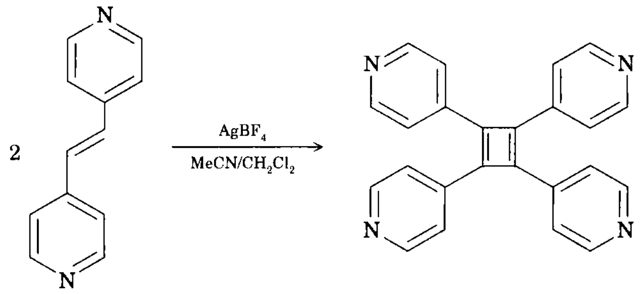


FIG. 96. Polyhedral packing diagram of $[Cu(\mathbf{L}_{105})_2]BF_4$ (a) and schematic view of the feldspar structure viewed down the *a*-axis (b). (From Fig. 2 in Keller, S. W. *Angew. Chem., Int. Ed. Engl.* **1997,** *36,* 247.)

3. *Channel Structure Through Silver(I)-Promoted in Situ Ligand Synthesis*

Successful construction of multidimensional frameworks largely relies on ligand design to suit different geometries and coordination numbers of the metal ions. A recent report on isolation of an unexpected three-dimensional metal complex by *in situ* cyclization of the ligand aroused tremendous interest among ligand designers (*285*). Reaction of 1,2-*trans*-(4-pyridyl)ethene ($\mathbf{L}_{70}$) and $AgBF_4$ in MeCN and CH_2Cl_2 in the presence of light yielded $[Ag(\mathbf{L}_{106})]BF_4$, where $\mathbf{L}_{106}$ = 1,2,3,4-tetrakis(4-pyridyl)cyclobutane. The complex exists as a three-dimensional cationic polymer in which each Ag^I ion is coordinated to one pyridyl group of four different $\mathbf{L}_{106}$ groups. Each $\mathbf{L}_{106}$ bridges four tetrahedral metal centers leading to a three-dimensional array of silver atoms containing channels to fill in the BF_4^- anions and MeCN solvent molecules (Fig. 97).



L_{70} L_{106}

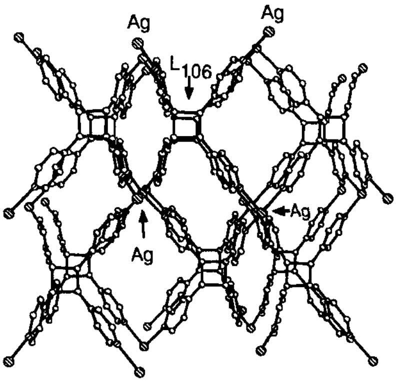


FIG. 97. View of the polymeric array formed by $[Ag(\mathbf{L}_{106})]^+$ illustrating the channels formed. (From Fig. 3 in Blake, A. J.; Champness, N. R.: Chung, S. S. M.; Li, W.-S.; Schröder, M. *J. Chem. Soc. Chem. Commun.* **1997,** 1675.)

X-ray structural determination results revealed that the ligand $\mathbf{L}_{70}$ had undergone a [2 + 2] cyclization to form a tetrapyridyl-substituted cyclobutane ring. The light-induced dimerization is found to be promoted by the presence of Ag^I ions. Although the detailed mechanism of the cyclodimerization reaction is not clear, such *in situ* formation of the ligand nevertheless represents a new approach to future inorganic crystal engineering.

IX. Concluding Remarks

The design and synthesis of new functional polymeric coordination complexes through intermolecular interactions or coordination bonds is a continuing challenge. Our aim in this review has been to show what this development has achieved recently in copper(I) and silver(I) chemistry. Throughout we have employed relatively straightforward ideas covering the latest references and reviews. The concept of supramolecular chemistry is not new, but in order to keep this review within bounds, we have had to severely restrict the number of references. Most of these can be traced via a recent comprehensive review (*286*). In the present review we have tried to emphasize three aspects toward the construction of functional solid-state supramolecular metal complexes, illustrating them by reference to a variety of topological systems. The first point is that the coordination number and stereochemistry of metal ions play an important role in construction of multidimensional networks. Most polymeric frameworks encountered, such as diamondoid, are based upon linear, trigonal, and tetrahedral metal templates. Therefore, the 4-coordinate tetrahedral copper(I) ion and the 2–4-coordination of silver(I) ion are likely to be the best candidates to produce diverse architectures. Second, designing ligands is an important step in making new functional solids. We must realize that the study we are undertaking today is not just limited to appreciation of novel frameworks for the aesthetics that the system can offer. We have already explored a number of functional ligands such as the conductive molecule TTF and derivatives, the photochromic compound *cis*1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl) ethane ($\mathbf{L}_{75}$), and the linear exodentate spacer 4,4′-bipyridine. We also have noted that in the metallic conductive compound $[\mathrm{Cu}(\mathbf{L}_{71})_2]$, matching of metal d-orbitals with π-orbitals of ligand may be responsible for the observed extremely high electrical conductivity (*197–200*). Thus, in striving for functional coordination materials with potential applications as inorganic devices, the search for functional ligands constitutes a new challenge. Finally, X-ray diffraction in combination with other physical methods has proven to be the dominant means of structure determination of inorganic polymers. To obtain single crystals in the polymeric phase, the art of synthesis must undergo a constant modification. On the other hand, application of newer experimental techniques for structural analysis of the powder sample may provide further advances in the study of polymeric structures.

The structural chemistry of coordination compounds continues to pose challenging problems, but a combination of physical methods and revolutionized synthetic techniques should clarify the picture and provide a real opportunity for those involved in this research. It should be encouraging. Such a prospect provides a major impetus to discover other coordination polymers with unexpected frameworks.

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