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Molecular architecture of copper (I) coordination polymers towards crystal lattice design

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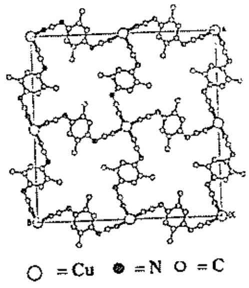
I. Introduction

The infinite chain and sheet structure of metal complexes are of substantial interest in understanding the solid state chemistry of metal complexes. The recent advent of copper coordination polymers, which have very good conductivity, have added an intriguing dimension to group 11 metal complex chemistry, prompting one to prepare a well-ordered assembly of copper complexes. $[Cu(Me_2dcnqi)]_\infty$ (Me_2dcnqi = 2,5-dimethyl-*N,N'*-dicyanoquinondiimine) (Fig.1(b)) (Aumueller, Erk, Klebe, Huenig, Schuetz, & Werner, 1986; Erk, Huenig, Schuetz, Werner, & Wolf, 1988) has a sheet structure of dcnqi-bridged tetrahedral copper atoms, which take mixed-valence oxidation state of +1.3. $[(ET)_2(Cu(NCS)_2)]_\infty$ (ET = bis(ethylenedithio)tetrathiafulvalene) (Urayama, Yamochi, Saito, Nozawa, Sugano, Kinoshita, et al., 1988)(Fig.1(b)) is a superconductor and the conducting column of ET molecules are sandwiched in the two sheets of $[\{Cu(SCN)_2\}]_\infty$. The layered copper polymers are essential for the superconducting properties and the critical temperature (Tc) greatly depends on the polymer structures. The similar compounds $[(ET)_2\{Cu(N(CN)_2)\}X]_\infty$ (X = Cl or Br)(Kini, Geiser, Wang, Carlson, Williams, Kwok, et al., 1990; Williams, Kini, Wang, Carlson, Geiser, Montgomery.L.K., et al., 1990) and $[(ET)_2\{Cu_2(CN)_3)\}]_\infty$(Geiser, Wang, Carlson, Williams, Charlier, Heindel, et al., 1991) have been prepared by modifying the infinite sheet structure of copper.

On the synthetic point of view, there are sparse literatures, which have elucidated the relationship between structures of polymers and monomers, toward rational synthesis of copper complex polymers in the single crystal phase. One field of this synthetic chemistry concerns the choice of linking ligands, which have at least two donor atoms or a donor atom with bridging capability. Inorganic ligands such as halide ions are used for complexes known for three decades(Hathaway, 1988), while the polymer compounds having organic ligands are still sparse.

This review focuses on the structure of one- to three-dimensional copper(I) polymers in relation to the bridging ligands, unique interactions to build up crystal lattice, and choice of linking ligands for rational synthesis.

(a) $[Cu(2,5\text{-}Me_2dcnqi)_2]_\infty$



(b) $\{(ET)_2[Cu(NCS)_2]\}_\infty$

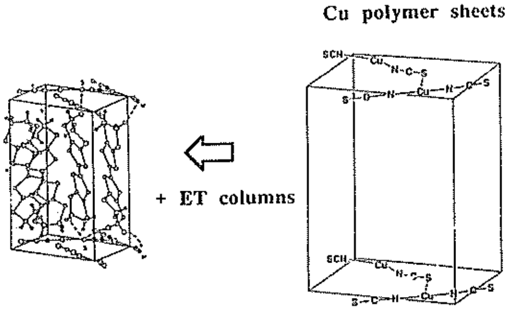


Figure 1. Coordination copper polymer structures found in conducting compounds. Two-dimensional layered structure of (a) $[Cu(2,5\text{-}Me_2dcnqi)_2]_\infty$ and (b) k- $(ET)_2[Cu(NCS)_2]_\infty$.((a)Aumueller, A.;Erk,P.; Klebe, G.;Huenig, S.;Schuetz, J.U.v.; Werner, H.-P .*Angew.Chem.Int.Ed.Engl.*1986,*25*, 740-741. (b)Urayama, H.; Yamochi, H.; Saito, G.;Nozawa, K.;Sugano, T.;Kinoshita, M.;Sato, S.;Oshima, K.;Kawamoto, A.;Tasaka, J.*Chem.Lett.*1988,55.)

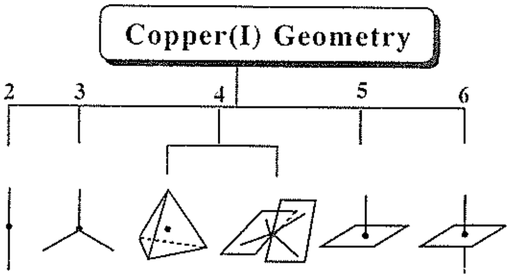


Figure 2. A variety of copper (I) geometries.

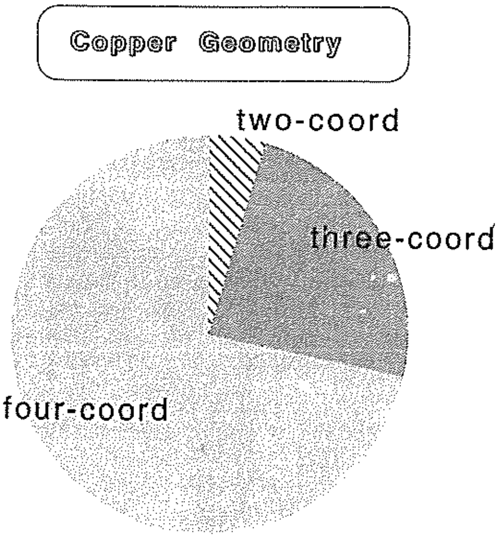


Figure 3. Distribution of copper (I) geometries found in copper (I) coordination polymers.

II. Structures of Copper(I) Geometries in Coordination Polymers

Crystalline copper(I) polymers provide various unique structures. This is associated with the copper(I) coordination geometry. Copper(I) can have a wide variety of geometrical structures(Cotton & Wilkinson, 1988), from two- to six-coordinate(Fig.2), affording various types of solid structures as relevant building blocks. Especially, the low coordination numbers such as 2, 3, and 4 mostly occur in the usual copper complexes, attributable to spherical d^{10} configuration. Fig.3 shows

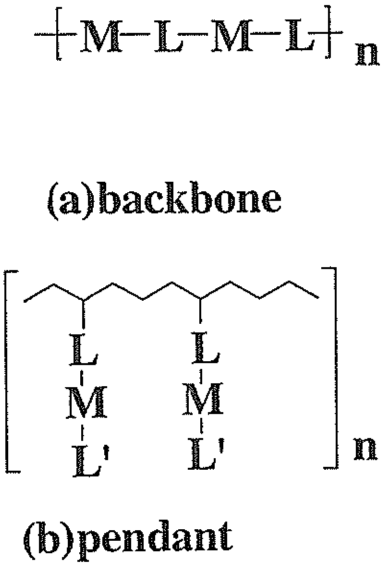


Figure 4. Types of coordination polymers

the distribution of copper geometries in the copper(I) polymers, which have so far synthesized and characterized crystallographically. It is evident that a four-coordinate copper, usually taking tetrahedral geometry, is preferred while a two-coordinate form is not popular in the crystalline polymers. The spatial dimensionality is also an important factor to understand polymer structures and crystal lattices. In this review the dimensionality is defined as the spatial structure of copper backbone built by coordinate bond(Fig.4(a)). Thus, the polymers in which copper atoms are attached to the polymeric ligand as a pendant are excluded(Fig.4(b)). Figure 5 exhibits the distribution and occurrence of low-dimensional structures in copper(I) coordination compounds. One- and two-dimensional complexes cover most of copper(I) polymers. There are two ways to realize high dimensionality by cross-linking of low dimensional polymer motifs. One is to use coordinate bond, by which copper atoms in chains or sheets are linked. In this case multi-site coordination ability of ligands are required. The other is to utilize interactions such as hydrogen bonding and aromatic stacking. There are many linking ligands used for copper(I) polymers. Halide ions, CN^-, and SCN^- are representative of simple ligands, while carboxylates and diazines are organic-type ligands. Typical structures are listed in Figure 6. In the following sections the polymer structures are listed, which, in certain cases, are characteristic of linking ligands or common in all complexes.

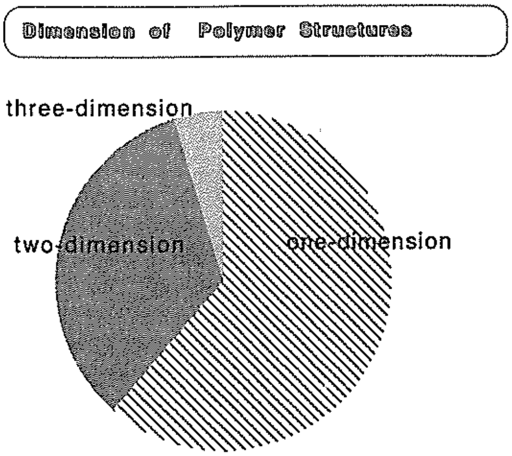


Figure 5. Distribution of polymer structural dimensionality found in copper (I) coordination polymers.

III. Classification of Linking Ligands and Their Polymers

(A)Inorganic ligands

(1)halide ions

Copper(I) prefers halide anions to

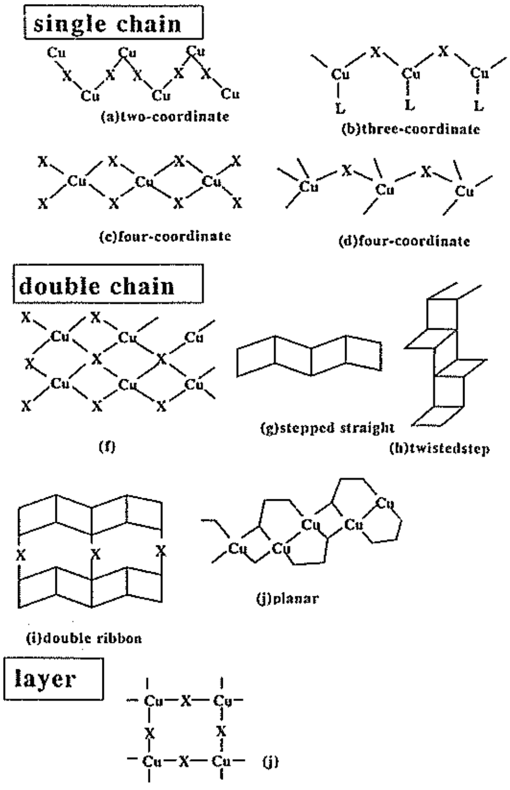


Figure 6. Typical polymer structures.

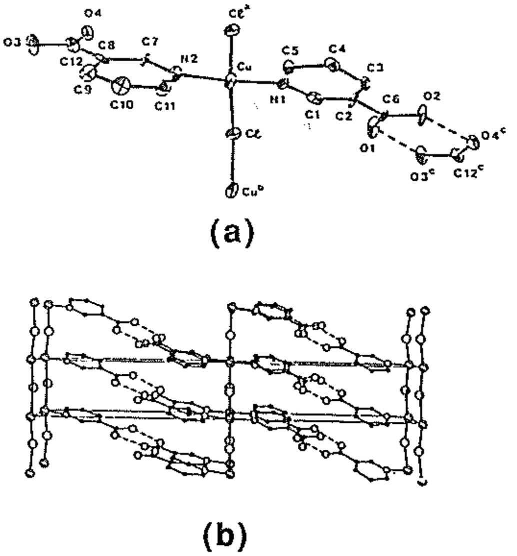


Figure 7. Monomer unit(a) and polymeric structure (b) of $[CuCl(Hna)_2]_\infty$ having hydrogen bond networks, which are represented by broken lines. Hna = nicotinic acid. (Goher, M.A.S.; Mak, T.C.W. *Inorg.Chim.Acta* 1987, *127*, L13–L16)

form infinite backbone of polymers. Halide anions are usually two- or three-coordinate. The simplest polymeric structure is a zigzag chain of repeating (CuX) units (Fig.6(a)-(d)). $[CuCl(Hna)_2]_\infty$ (Hna = nicotinic acid)(Goher & Mak, 1987) has a typical zigzag chain comprising a tetrahedral CuN_2Cl_2 unit(Fig.7). The nicotinic acids joint two neighboring chains through hydrogen bonding between metal-free carboxyl groups. The details will be mentioned in the following section. $[CuI(collidine)]_\infty$ (Campbell, Raston, & White, 1977) takes an infinite zigzag chain comprising a tetrahedral CuN_2Cl_2 unit (Fig.7). $[CuI(acridine)]_\infty$ (Healy, Pakawatchai, Raston, Skelton, & White, 1983) has the similar infinite zigzag structure of (CuI) backbone, where acridine molecules are aligned on the same side of the chain(Fig.8). In $[CuCl((C_2H_5)_2S_2)]_\infty$ (Braenden, 1967) dimeric parts of $(Cu_2(\mu\text{-}Cl)(\mu\text{-}(C_2H_5)_2S_2)_2)$ are linked by chloride anions to form an infinite zigzag chain (Fig.9(b)).

Successive CuCl steps in a zigzag ladder are found in $[CuCl(pyridine)]_\infty$ (Campbell, et al., 1977). This structure is considered as "stairs" or ribbon (Fig. 9(c)). The similar ribbon structure is also found in $[CuBr(CH_3CN)]_\infty$ (Massaux, Bernard, & Bihan, 1971) and $[Cu_2Cl_2(azomethane)]_\infty$ (Brown & Dunitz,

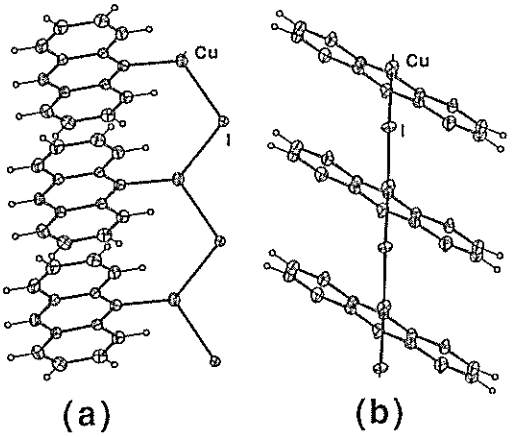


Figure 8. Chain structure of $[\mathrm{CuI(acridine)}]_\infty$ (Healy, P.C.;Pakawatchai, C.;Raston, C.L.Skelton, B.W.; White, A.H.*J.Chem.Soc.Dalton Trans.*1983, 1905-1916.)

1960). In the case of $[\mathrm{Cu_2Cl_2(azomethane)}]_\infty$ these ribbons of $(\mathrm{CuCl})_n$ are jointed by the azomethane molecules to form infinite layers.

A typical chain structure in Fig.9(d), which is characterized as $(\mathrm{Cu_2X_2})$ parallelograms sharing copper corners, is found in $\{[\mathrm{CuCl_2}](N,N'$-dimethyl-4,4'-bipyridylium$)\}_\infty$ (Prout & Murray-Rust, 1969). The double chain structure is prepared as anionic polymer, $\{\mathrm{Cs[Cu_2Cl_3]}\}_\infty$ (Brink, Binnendijk, & Linde, 1954), where $(\mathrm{CuCl_4})$ tetrahedra sharing edges. $\mathrm{CuX_4}$ tetrahedra gives infinite chains with the corners or edges shared: the corner-sharing type is $\{\mathrm{K_2[CuCl_3]}\}_\infty$ (Brink & MacGillavry, 1949) while the edge-sharing type is $\{\mathrm{(C_6H_5N_2)[Cu_2Br_3]}\}_\infty$ (Roemming & Waerstad, 1965) and $\{(\text{N-methyl-pyridinium})[\mathrm{Cu_2I_3}]\}_\infty$ (Hartl & M-H-Abadi, 1984). Fig.10 reveals typical structures of linked tetrahedra. The

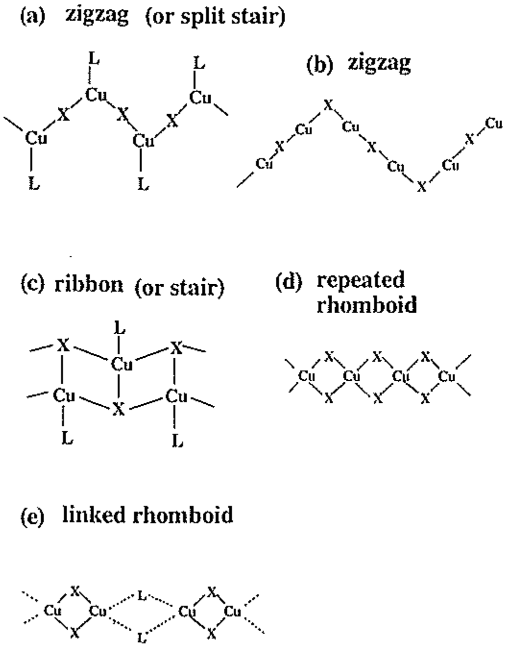


Figure 9. Typical backbone structures of copper (I) compounds having halide ions.

face-shared type is also found in $\{\mathrm{(L)[Cu_3I_4]}\}_\infty$ (L = $\mathrm{(C_6H_5)_3CH_3P}$ and $\mathrm{(C_3H_7)_4N}$) (Hartl & M-H-Abadi, 1984). $\{\mathrm{(R)[Cu_3I_4]}\}_\infty$ (R = $\mathrm{(C_2H_5)_4N}$ and $\mathrm{(CH_3)_2N{=}CH\text{-}N{=}CH\text{-}(CH_3)_2}$) (Hartl & M-H-Abadi, 1981) shows that $\mathrm{CuI_4}$ tetrahedra linked alternatively *via* common edges and faces into a single chains. Other types of double chains are found in $[\mathrm{CuI(CH_3NC)}]_\infty$ (Fisher, Taylor, & Harding, 1960), which has two types of tetrahedral $\mathrm{CuI_4}$ and $\mathrm{CuI_2C_2}$ units. $[\mathrm{Cu_2I_2((C_2H_5)_2S_2)}]_\infty$ (Boorman, Kerr, Kydd, Moynihan, & Valentine, 1982) takes double chains containing (I and S)-bridged copper and I-bridged copper atoms. There are several infinite chains or sheets, in which rhomboid units of

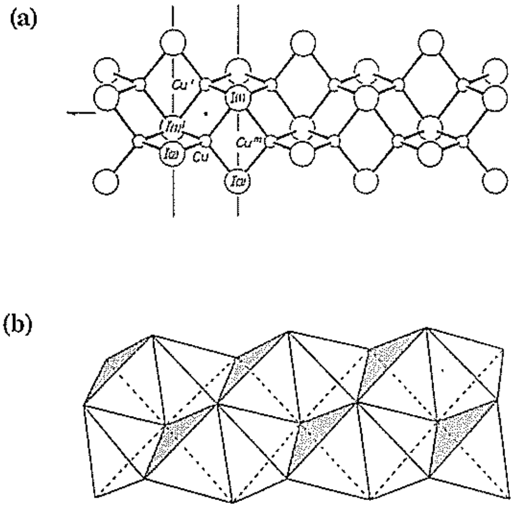


Figure 10. Edge-shared tetrahedra-linked chains. (a) ($[Cu_2I_3]^-$) chains and (b) polyhedra model. (H.Hartl and F.M.-H.-Abadi,Z.*Naturforsch.*, 39b, 149 (1984).)

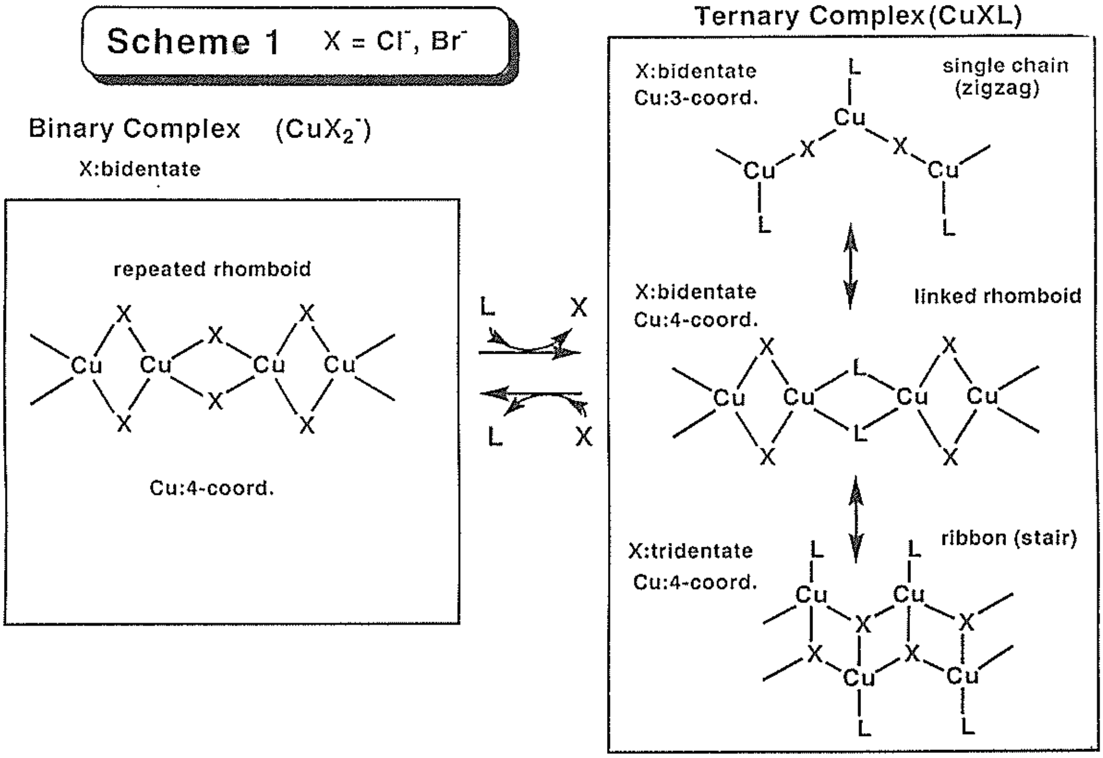
(Cu_2X_2) are linked together by ligands. $[CuBr((C_2H_5)_4P_2)]_\infty$ (Hartung, 1970) has diphosphine bridges(μ,η^2-type) to link the (Cu_2X_2) units, giving an infinite chains. In $[CuBr(C_4H_8OS)]_\infty$ (Barnes & Paton, 1982) oxathiane sulfur bridges the copper atoms of the two (Cu_2X_2) units to afford an infinite chain. The (Cu_2Cl_2) units are linked by cubanes of $(Cu_3MS_3)S$ (M = Mo and W) to form an infinite chain, $\{N(CH_3)_4[MS_4(CuCl)_5Cl_2]\}_\infty$ (Secheresse, Robert, Marzak, Manoli, & Potvin, 1991).

Interestingly, two dimensional layered sheets have been found in $[CuBr(S(CH_3)_2)]_\infty$ (Lenders, Grove, Smeets, Sluis, Spek, & G.van, 1991) and $\{[CuCl\text{-}(C_8H_6N_4S_2)](H_2O)\}_\infty$ (Simmons, Lundeen, & Seff, 1979). The Cu-N distance of 1.966(3) Å is one of the shortest ones in tetrahedral copper(I)-aromatic nitrogen atom.

There are several cases, in which different types of copper geometries give an unique infinite structures. In the case of I-bridged infinite chains, $\{[S_2C_3(SCH_3)_3]\text{-}[Cu_2I_3]\}_\infty$ (Asplund & Jagner, 1984b) consists of copper atoms of $[CuI_3]$ and $[CuI_4]$, which are connected alternatively. $\{[N(C_2H_5)_4]_3[Cu_7Cl_{10}]\}_\infty$ (Asplund & Jagner, 1984a) has six three-coordinate and one two-coordinate copper atoms: the repeating units, in which two six-membered ring of Cu_2Cl_3 are connected by two chlorine atoms, are linked by the $CuCl_2$ unit. The closest Cu...Cu distances are 2.890(20 - 3.447(3) Å. A columnar one-dimensional structure is found in $\{[(N\text{-}methylpyrazinium\ iodide)CuI]^+\}_\infty$ (Adam, Herrschaft, & Hartl, 1991), in which the copper and iodine atoms are also arranged to Cu_3I_3 rings. Two-dimensional layer of $[Cu_2Cl_2(isoprene)]_\infty$ (Hakansson, Jagner, & Walther, 1991) is constituted by chlorine atoms and isoprene molecules: the isoprene exhibits s-trans conformation and bridges two copper(I) atoms through coordination involving both C=C bonds. This is the first example of a complex in which a conjugated diene is bonded to copper(I) through both C=C bonds. The Cu-C distances range from 2.076(5) to 2.244(4) Å.

Mixed-metal polymer chain backbone is isolated as $\{[Cu_3Br_3][Co(S_2CNR_2)_3]\}_\infty$ (Healy, Skelton, & White, 1989), in which six-membered ring Cu_3Br_3 units are linked by $[Co(S_2CNR_2)_3]$.

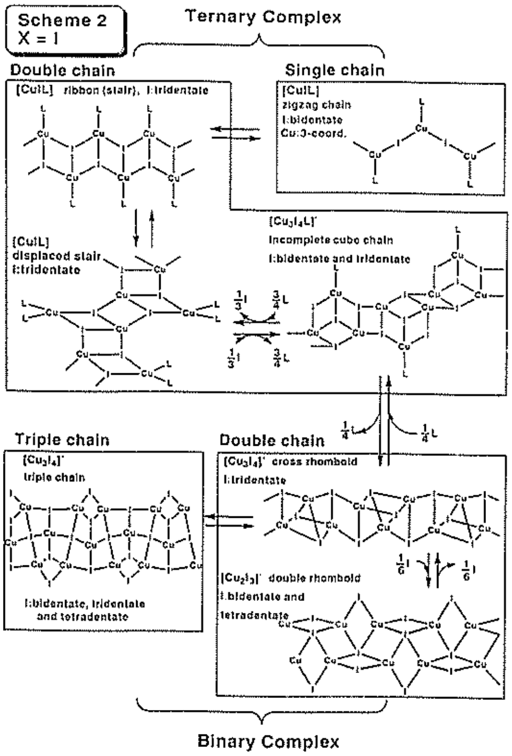
Before closing this section it is worthwhile to describe the coordination mode of halide ions, which usually act as a two-coordinate donor in low-molecular-weight copper(I) complexes.



The higher coordination number of three or four occurs in polymer copper(I) complexes. For Cl^- and Br^- ions the chain type structures form with the stoichiometry of CuX_2 or CuXL(X = Cl^- and Br^-; L = another ligand) and their polymerization modes depend on the coordination number of X, which is summarized in Scheme 1. Iodide ion provides a variety of polymer structures more than chloride and bromide ions. The apparent complication comes from the presence of the four-coordination mode. Scheme 2 represents the relationship between chain structures and iodide ion coordination mode. On these bases halide ions are very convenient linking ligands, , and the rational synthesis of the polymers is dependent on the control of the coordination mode of halide ions.

(2)cyanide ion

Cyanide ion is a good bridging ligand for copper(I) to provide an infinite chain. Simple copper complex is $\{K[Cu(CN)_2]\}_\infty$ (Cromer, 1957), which takes spiral polymer chains containing three-coordinate copper atoms: Cu-C distances are 1.92(2) Å while Cu-N 2.05(2) Å. The Cu...Cu distance is 4.984(6) Å. There are two types of cyanide coordination modes, one bridging and one terminal-CN. When the terminal type contributes to bridging of neighboring chains, two-dimensional sheet structure is built. This is $\{K[Cu_2(CN)_3]H_2O\}_\infty$ (Cromer, 1957), in which $Cu_3(CN)_3$ ring is a basic unit.



Scheme 2
X = I

Interestingly, H_2O molecule is occupied in the cavity of $Cu_3(CN)_3$ ring. This type of structure is also found in $\{[(CH_3)_2(C_6H_5)S][Cu_2(CN)_3]\}_\infty$ (Cernak, Gyoeryova, Sabolova, & Dunaj-Jurco, 1991), which is obtained from the reaction between $K[Cu_2(CN)_3]$ and $[(CH_3)_2(C_6H_5)S]$-ClO_4 in aqueous solution. The polymer sheets consist of distorted hexagons in which two different copper atoms (vertices) are joined with the bridged cyano groups (edges). One copper atom is trigonal while the other is distorted tetrahedral. The distance between the tetrahedral Cu atoms (in adjacent planes) is short, i.e. 2.655(2) Å. Very recently, this infinite sheets are used to sandwich face-to-face ET dimers. $\{\kappa$-$(ET)_2[Cu_2(CN)_3]\}_\infty$ (Geiser, et al., 1991) shows superconductivity at 2.8 K and 1.5 Kbar.

$[Cu(dmphen)CN]_\infty$ (dmphen = 2,9-dimethylphenanthroline (Morpurgo, Dessy, & Fares, 1984) and $[Cu_3(biq)_2(CN)_3]_\infty$ (biq = 2,2'-biquinoline (Dessy, Fares, Imperatori, & Morpurgo, 1985)) consist of zigzag chains of tetrahedral copper atoms(Fig.11). Pairs of biL molecules (biL = dmphen or biq) belonging to parallel chains stack with an interplanar spacing of 3.26 (dmphen) and 3.35 (biq) Å. The polarized crystal electronic spectra show metal-to-ligand charge transfer bands (Cu -biL), which are influenced by the stacks. A SCN anion also provides infinite chain structures similar to a CN anion (Dessy, et al., 1985; Morpurgo, et al., 1984). In addition to the CN bridge hydrazine molecules afford an infinite puckered layers. $[Cu(CN)(N_2H_4)]_\infty$ (Cromer, Larson, & Roof, 1966) has planar zigzag chains, which are jointed by the hydrazine molecules, thus copper atom taking tetrahedral geometry. Polymer sheets of $[Cu(CN)(NH_3)]_\infty$ (Cromer, Larson, & Roof, 1965) results from a bridging coordination mode of a CN group: the carbon atom of a CN group bridges two copper atoms with the Cu-C distances of 2.090 and 2.129 Å, giving a very short Cu...Cu contact (2.417 Å). Sulfur donor atom also bridges Cu-CN zigzag chains to produce an infinite sheet. $[Cu(mimtH)(CN)]_\infty$ (mimtH = 1-methyl-imidazoline-2-thione) (Raston, Walter, & White, 1979) has copper atoms tetrahedrally coordinated by S_2CN donor set and the dimeric Cu_2S_2 units are extended into a two-dimensional array by CN groups. The nitrogen atom of mimtH is metal-free in this compound. Mixed-metal polymer is prepared by the

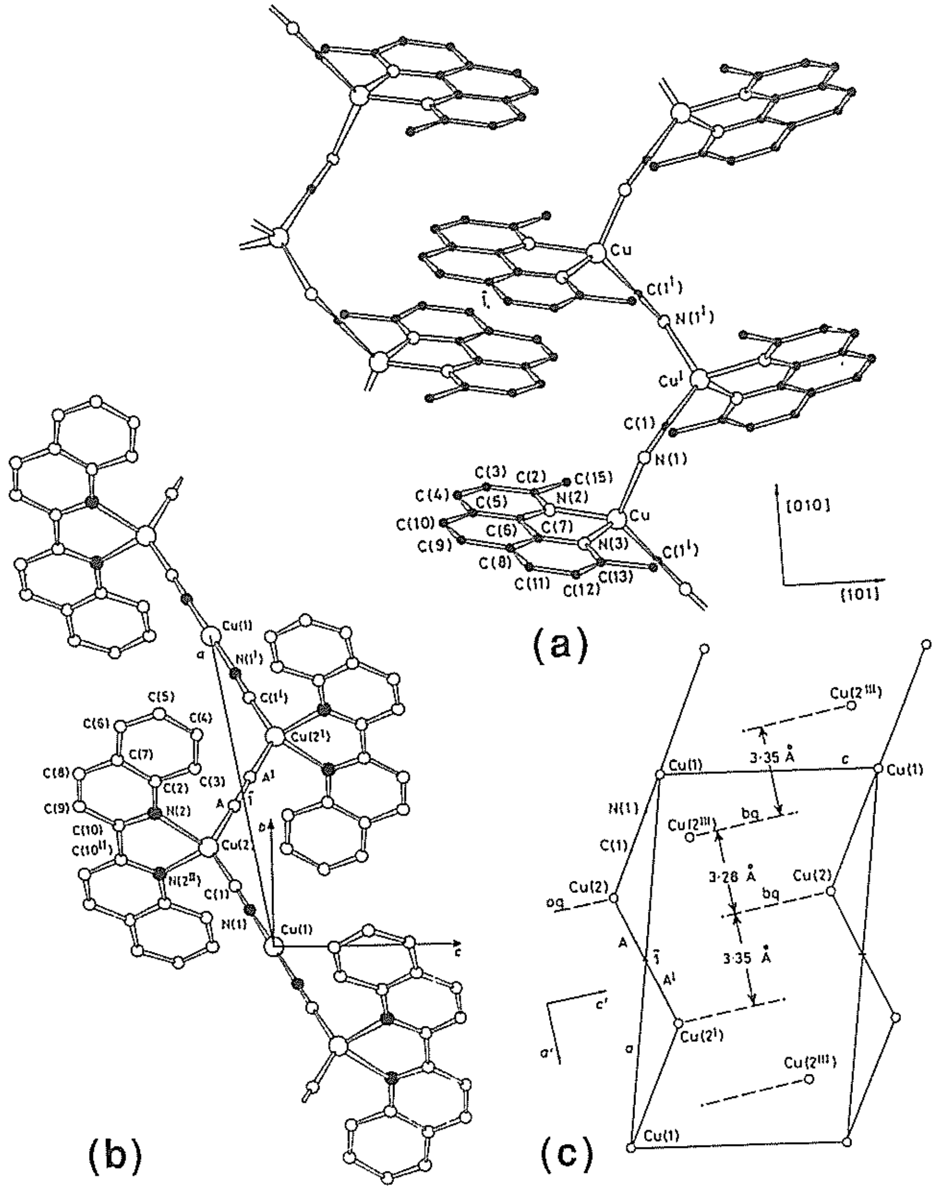


Figure 11. Projection of the structures of [Cu(CN)(dmphen)]∞ (a), [Cu$_3$(CN)$_3$(biq)$_2$)∞ (b), and schematic view of the crystal packing (c) of [Cu$_3$(CN)$_3$(biq)$_2$]∞. dmphen=2,9 -dimethy-1, 10-phenanthroline, biq=2,2'-biquinoline. (Dessy, G.; Fares, V.; Imperatori, P.; Morpurgo, G.O. *J.Chem.Soc.Dalton Trans.* 1985. 1285-1288.)

addition of $(MoS_4)^{2-}$ ligand to CuCN zigzag chain. In $\{((C_6H_5)_4P)_2[Cu(CN)(MoS_4)]_\infty$ and $\{((CH_3)_4N)_2[Cu(CN)(MoS_4)]_\infty$ (Mueller, Dartmann, Roemer, Clegg, & Sheldrick, 1981) there are two types of copper geometries, one is a tetrahedral $CuCNS_2$ in the chain backbone and the other is a trigonal $CuCS_2$ in a pendant-like branch. The Cu-Mo distance is 2.603(1) Å.

Finally, a three-dimensional network is built by use of sodium-CN nitrogen electrostatic forces. $\{Na_2[Cu(CN)_3](H_2O)_3\}_\infty$ (Kappenstein & Hugel, 1978) has a trigonal $(Cu(CN)_3)^{2-}$ anion, whose nitrogen atoms are bonded to three sodiums. Each complex anion is surrounded by nine sodium cations and these bondings shape up the network in which channels appear parallel to the ternary axes. Strictly speaking, this is not a coordination polymer mentioned in this review.

(3)thiocyanate ion

Thiocyanate ion can bridge two copper atoms via both ends: the sulfur

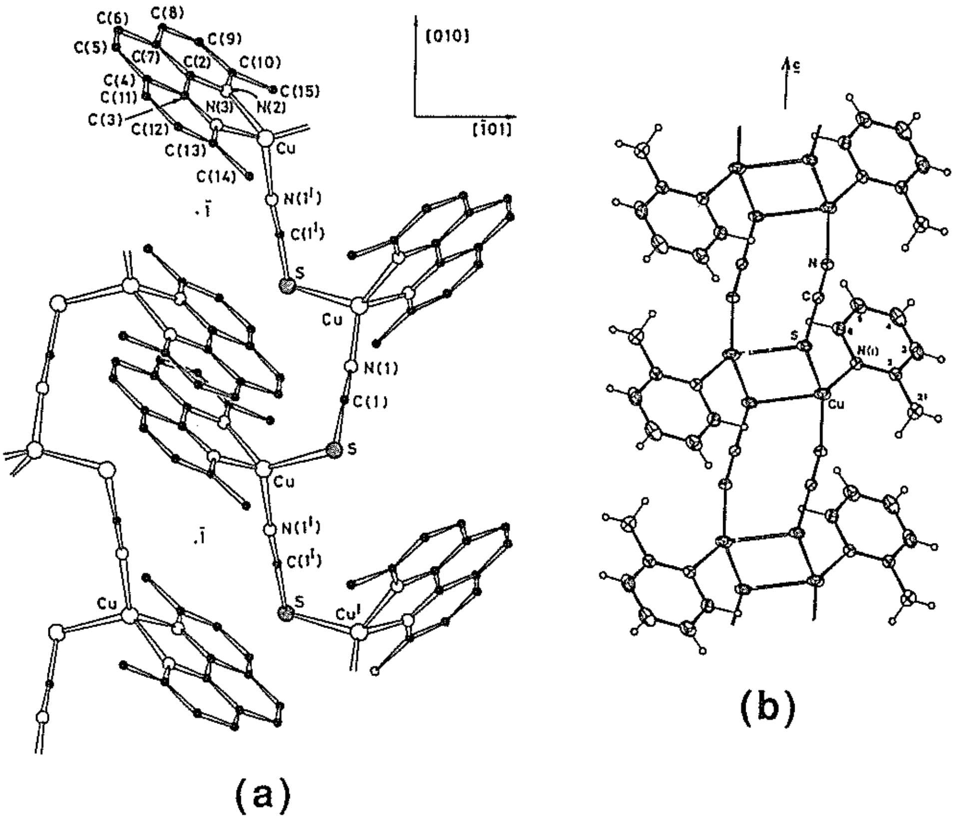


Figure 12 Projection of the structures of $[Cu(SCN)(dmphen)]_\infty$ (a) and $[Cu(SCN)(2\text{-}Me\text{-} py)]_\infty$ (b). (Morpurgo, G.O.; Dessy, G.;Fares, V.*J.Chem.Soc.Dalton Trans.*1984, *1984*, 785-791.)

and nitrogen atoms. Zigzag chains with Cu-SCN-Cu backbone are found in $[Cu(biL)SCN]_\infty$ (biL = 2,9-dimethylphenanthroline (dmphen) (Morpurgo, et al., 1984) and 2,2'-biquinoline (bq) (Dessy, et al., 1985)), $[Cu(SCN)L]_\infty$ (2,6-dimethylpyridine), and $[Cu(SCN)L_2]_\infty$ (2-, 3-, and 4-methylpyridine, and quinoline) (Healy, Pakawatchai, Papaserigo, Patrick, & White, 1984)(Fig.12). Typical instances are shown in Fig.12. The similar polymers are also isolated by using CN-bridge, which is mentioned in section "(2) cyanide ion". The pyridine derivatives are useful ligands to control polymer backbones. Fig.13 summarizes the effect of pyridines, indicating that the number and position of methyl substituents are important factors for polymer structures. The methyl group on α-position hinders the coordination of the two pyridine molecules to copper atom, while methyl groups on 3- and 4-position afford a $CuL_2(SCN)_2$ coordination, which is an unit of zigzag chains. The Cu(SCN)L geometry takes an infinite stairs having eight-membered $Cu(SCN)_2Cu$ rings as shown in $[Cu(SCN)(2\text{-dimethylpyridine})]_\infty$ whereas further addition of methyl group on the α-position results in a splitted stairs, i.e. zigzag chain of Cu(SCN)Cu.

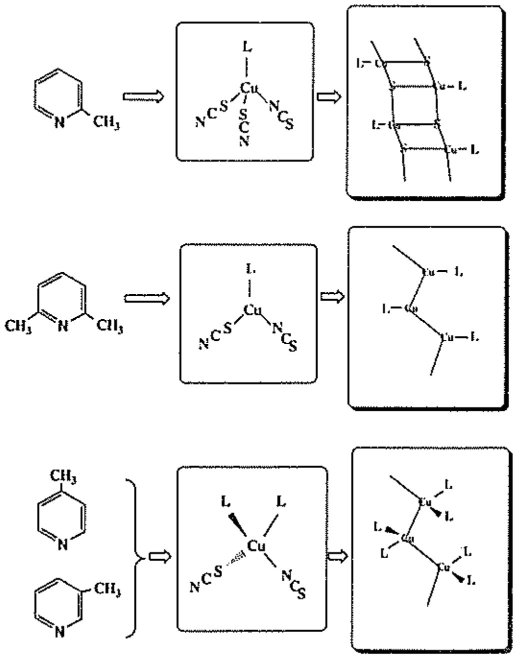


Figure 13 Relationship between methyl substituents of pyridine and the polymeric structures.

Three-dimensional polymer structures are built in $\{(C_5H_6N)[Cu_2(SCN)_3]\}_\infty$ (Raston, et al., 1979) and $\beta\text{-}[Cu(SCN)]\}_\infty$ (Smith & Saunders, 1982). The former contains tetrahedral CuS_2N_2 and CuS_3N to give network cavities, in which pyridinium cations are occupied without short contacts to any atoms.

(4)others

Poly chalcogenide becomes a good ligand to give infinite polymer structures. Two types of infinite chains are prepared by use of S_4^{2-}: in $\{\alpha\text{-}[Cu(S_4)]\}_\infty$ sulfur atoms in α and β position of the S_4 chain are involved in coordination while only sulfur atoms on α-position are bonded to copper atoms in $\{\beta\text{-}[Cu(S_4)]\}_\infty$ (Kanatzidis & Park, 1989). The latter is a kind of chain structures having rhomboid Cu_2S_2 unit. There is an infinite chain containing selenium atoms together with niobium atom. $\{K_2[CuNbSe_4]\}_\infty$ (Kanatzidis & Park, 1989) shows infinite linear chains separated from the K+ ions, consisting of edge-sharing of alternating $NbSe_4$ and $CuSe_4$ tetrahedra. In the case of $\{K_3[CuNb_2Se_{12}]\}_\infty$ (Kanatzidis & Park,

1989) the units forming the infinite chain are unclear because there are two types of the formulation: (CuNb$_2$(Se)$_2$(Se$_2$)$_3$(Se$_4$)$^{3-}$) or (CuNb$_2$(Se)$_3$(Se$_2$)$_3$(Se$_3$)$^{3-}$), whose structure depends on the choice of a cutoff for the length of an Se-Se bond.

(B)Organic ligands

(1)Pyrazine, pyridazine and its derivatives

Diazine family is a very useful ligand, which has given a variety of metal complexes with unique coordination modes such as monodentate, bidentate, and bridging. The ligand is classified into three types according to the relative position of the two nitrogen atoms: pyrazine(1,4-diaza), pyrimidine(1,3-), and pyridazine (1,2-). Among these ligands pyrazine (pz) is well-known to act as a bridging ligand, especially in low-dimensional polymeric compounds. Coordination chemistry of copper(I) pyrazine has been relatively neglected although a large amount of information is available on their copper(II) complexes (Darriet, Haddad, Duesler, & Hendrickson, 1979; Klein, Majeste, Trefonas, & O'Connor, 1982; Morosin, Hughes, & Soos, 1975; O'Conner, Klein, Majeste, & Trefonas, 1982; Richardson, Wasson, & Hatfield, 1977; Santoro, Mighell, & Reinmann, 1970; Valentine, Silverstein, & Soos, 1974), where polynuclear structures including infinite chains have been well characterized. On the other hand, infinite chain copper(I) compounds were few until 1992, in which we have published a series of copper(I) pyrazine polymers. Figure 14 shows the substituted pyrazines, by which copper(I) coordination polymers have been synthesized.

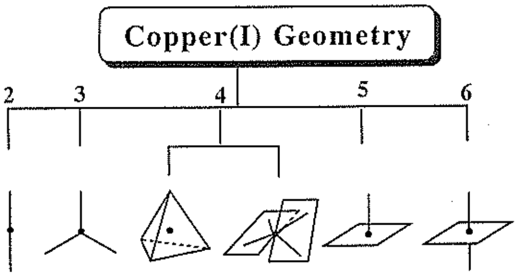


Figure 14. Pyrazine derivatives for linking ligands

$[Cu(pz)_{1.5}(CH_3CN)](PF_6)\cdot 0.5\text{-}C_3H_6O\}_\infty$ (Kitagawa, Munakata, & Tanimura, 1992) is a two-dimensional sheet comprising of hexagonal motif of Cu$_6$(pz)$_6$. This hexagonal motif has a chair-like skeleton as shown in Fig.15. The copper geometry is a four-coordinate tetrahedron, having nitrogen atoms of three pz and acetonitrile. In the case of NH$_2$pz an infinite planar sheet structure crystallizes as $[Cu(apz)_{1.5}]PF_6\}_\infty$ (Kitagawa, 1993) in which copper has three-coordinate geometry without another ligand, making a flat Cu$_6$ motif. 2,6-Substituted pz gives similar trigonal copper environment, and planar sheet. On this basis, substitution hinders the coordination of the forth ligand such as acetonitrile. From this reason four-coordinate Cu(pz)$_4$ motif for infinite polymer appears not to occur. However, in the case of monosubstituted pz the factors governing the structure are not simple. Clpz leads to complicated polymer structure (Kitagawa, Kawata, Kondo, Nozaka, & Munakata, 1993a) : copper takes a four-coordinate tetrahedron. This means that mono-substituted pz can provide three copper geometries, Cu(pz)$_3$, Cu(pz)$_3$L, and Cu(pz)$_4$, all of which generate polymer structure. Attachment of two methyl groups on an either side of pz affords

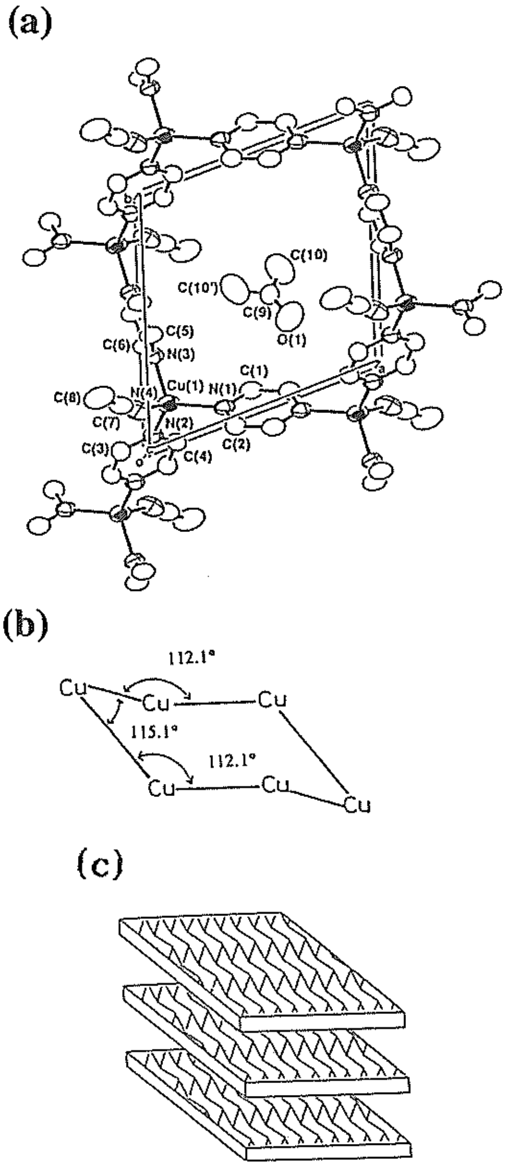


Figure 15. Structure of $[Cu(pz)_{3/2}(CH_3CN)](PF_6)\cdot 0.5C_3H_6O)$. (a) Hexagonal motif, (b) Cu6 skeletone, and (c) layered structure. (Kitagawa, S.; Munakata, M.; Tanimura, T. *Inorg.Chem.* 1992,1714-1717.)

pleated sheets having three-coordinate copper motif. $\{[Cu_2(2,3\text{-}Me_2pz)_3](ClO_4)_2\}_\infty$ (Turnbull, Pon, & Willett, 1991). In the case of $\{[Cu_2(quinoxaline)_3(ClO_4)]ClO_4\}_\infty$ (Lumme, Lindroos, & Lindell, 1987), a planar two-dimensional structure is not formed but three-dimensional network appears accompanying with distorted tetrahedral copper geometry, CuN_3O, ($Cu\text{-}N_{av.} = 2.026(7)$ Å) having semi-coordination of perchlorate anion to copper atom (Cu-O = 2.536(8) Å). This is due to steric hindrance caused by the large quinoxaline molecules. Finally, introduction of substituents in all the four position affords lower-dimensional polymer structure. Four methyl substituents on pz ring prevent the formation of $Cu_6(Me_4pz)_6$ hexagonal motifs and built an linear chain structure of $[Cu_2(Me_4pz)_3](ClO_4)_2\}_\infty$ (Kitagawa, et al., 1992). There are two types of copper environment: one is a three-coordinate copper atom and incorporated into the zigzag backbone while the other two-coordinate copper atom is attached to the backbone like a pendant. Figure 16 summarizes the formation of one- and two-dimensional polymers depending on derivatives on pz ring.

To our best knowledge, there are two infinite chain polymers of pyridazine (pd), $\{[Cu_2(3\text{-}Mepd)_2(pz)_3](ClO_4)_2\}_\infty$ (Kitagawa, Munakata, & Tanimura, 1991c) and $[Cu(CN)(pd)]_\infty$ (Cromer & Larson, 1972). The former is a tetranuclear copper-based infinite one-dimensional system, where 3-Mepd is used to form a dinuclear Cu unit (Cu...Cu = 2.971(2) Å). Thus, the infinite structure is essentially afforded by pz-linking. The latter polymer is built up by pd-linking of CuCN zigzag chains. No copper(I) coordination polymers having

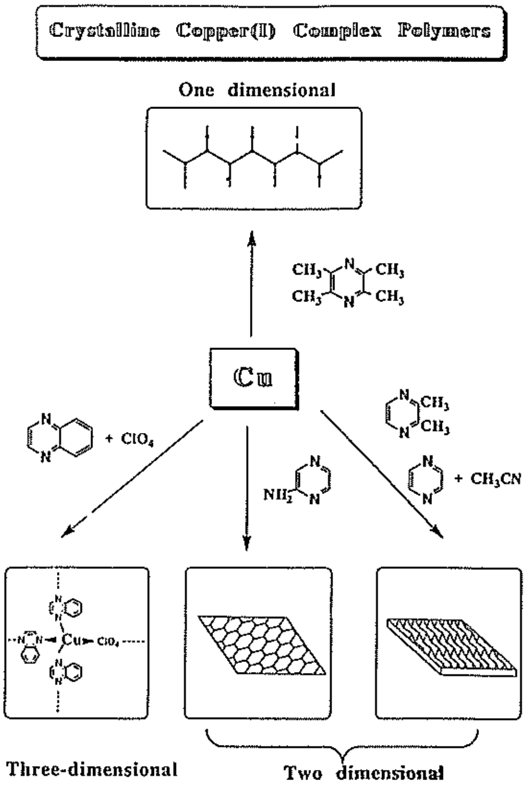


Figure 16. Relationship between pyrazine derivatives and copper(I) polymer structures.

pyrimidine-link have been synthesized except for sulfur-containing purine mentioned below.

(2)Sulfur-containing ligands

Sulfur-containing ligands are considered to be relevant to polymeric structure of copper because of matching of hard-soft criteria and its bridging ability. Among many copper polymer compounds containing sulfur donor atom (Raper, 1993), the linking ligands in the polymer backbone are simple ones such as SCN⁻ mentioned above. In order to expand the coordination polymer chemistry it is of significance to use organic sulphur-containing ligands and to find factors governing electronic and geometric structures for the rational synthesis of coordination polymer.

The ligands containing thioamide structure have considerable coordination potential. The flexibility based on the tautomerism, thionate (-N=C(-SH)-) ↔ thione(-NH-C(=S)-), can afford various coordination modes. Copper(I) prefers a bridged thione form to give discrete polynuclear forms, among which dimers are most common. An additional new dimension is added to the thioamide copper(I) chemistry by preparation of coordination polymer. $\{[Cu(2\text{-quinolinethione})_2]X\}_\infty$ (X = ClO_4 and PO_2F_2) (Kitagawa, Kawata, Nozaka, & Munakata, 1993b) has one-dimensional polymer of CuS_2 backbone. This has two-type of chain-chain interaction: one is aromatic stack interaction of the ligands in neighbouring chains. The other is hydrogen bonding between tetrahedral counter anion (ClO_4 and PO_2F_2) and uncoordinated NH moiety, the anion bridging two NH in neighbouring chains. The large ring system of 8-mercaptopurine also affords an infinite chain of S-Cu-S-Cu backbone. The structure of $[Cu(C_6H_5N_4S)Cl_2]_\infty$ (Caira & Nassimbeni, 1976) consists of infinite columns of 8-mercaptopurine units which are protonated and bonded to copper chloride via their sulfur atoms(Fig.17). There are two NH...Cl hydrogen bonds within any polymer chain, ranging from 3.08(1) to 3.13(1) Å

Rubeanic acid (ra, $C_2N_2S_2H_4$) acts as a bidentate bridging ligand through the two sulfur atoms to provide infinite polymer structures. Infinite zigzag chain is found in $[CuCl(ra)]_\infty$ (Mosset & Glay, 1983). The coordination of copper atom

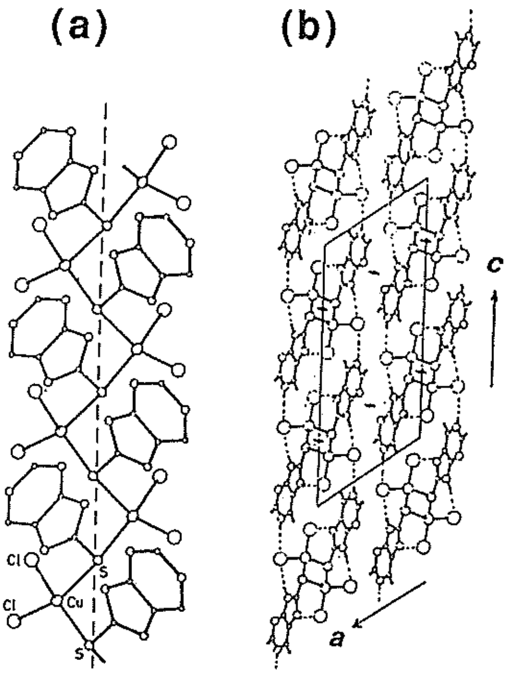
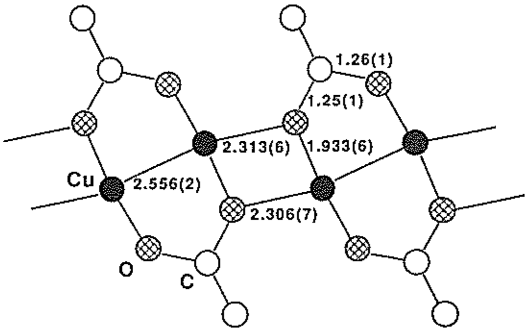


Figure 17. A single column of the polymeric $[CuCl_2(8\text{- mercaptopurine})]_\infty$ (a),illustrating the helical arrangement, and its projection (b). Hydrogen bonds are represented by broken line. (Caira, M.R.; Nassimbeni, L.R.*J.Chem.Soc.Dalton Trans.* 1976, 4-7.)

is described as [3+1] with two S_2Cl and S donors for Cu-S = 2.24(1), Cu-Cl = 2.31(1), and Cu-S = 2.68(2) Å, respectively. The weak bonding Cu-S couples the two neighboring chains to give a ribbon structure. A layerd sheet is prepared by use of the same ligands. $\{[Cu_2Cl(ra)_3](H_2O)_{0.9}\}_\infty$ (Mosset & Galy, 1983) contains infinite double helical chains of CuS_2Cl units, which are linked by the third ra.

(3)Carboxylate

Crystallization of copper(I) acetate, $[Cu(CH_3CO_2)]_\infty$ was succeeded simultaneously by two groups (Drew, Edwards, & Richards, 1973; Mounts, Ogura, & Fernando, 1974). The structure consists of infinite planar chains. Figure 18 shows a T-shape geometry of the copper atom having three oxygen atoms, the two Cu-O distances being shorter (1.925(6) av. Å) than that for another bond(average 2.311(7) Å). Hence, the chains are constituted by dicopper units of $Cu_2(O_2CCH_3)_2$. The Cu...Cu distance of 2.556(2) Å is shorter than that (2.56 Å)(Kittel, 1986) of metallic copper, indicating the possibility of direct metal-metal bonding. Then, the copper atom takes an square-planar geometry, very rare in the copper(I) complexes. The metal-metal interaction is discussed in the following section IV.



Structure of $[Cu(O_2CCH_3)]_\infty$

Figure 18. Structure of $[Cu(CH_3CO_2)]_\infty$

(5)Other bidentate ligands

A unique chain compound, $[Cu(bpen)\text{-}PF_6]_\infty$ (bpen = *trans*-1,2-bis(2-pyridyl)-ethylene) (Kitagawa, Matsuyama, Munakata, & Emori, 1991a), is prepared as well as the silver compound. The coordination geometry for the metal atoms is linear, characteristic of d^{10} metal, and the mode of polymerization is

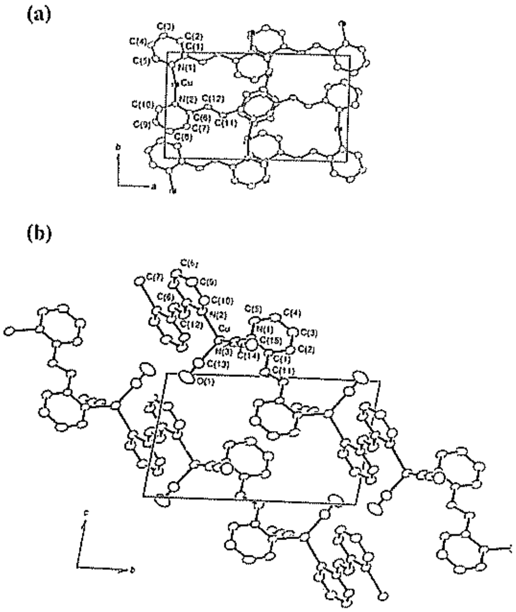


Figure 19. Polymerization modes of (a) $[Cu(bpen)PF_6]_\infty$ (bpen = *trans* 1,2-bis (2-pyridyl)ethylene) and (b) $[Cu(bpen)(CO)(CH_3CN)PF_6]_\infty$ (Kitagawa, S.; Matsuyama, S.; Munakata, M.;Emori,T.*J.Chem.Soc. Dalton Trans.* 1991, 2869-2874.)

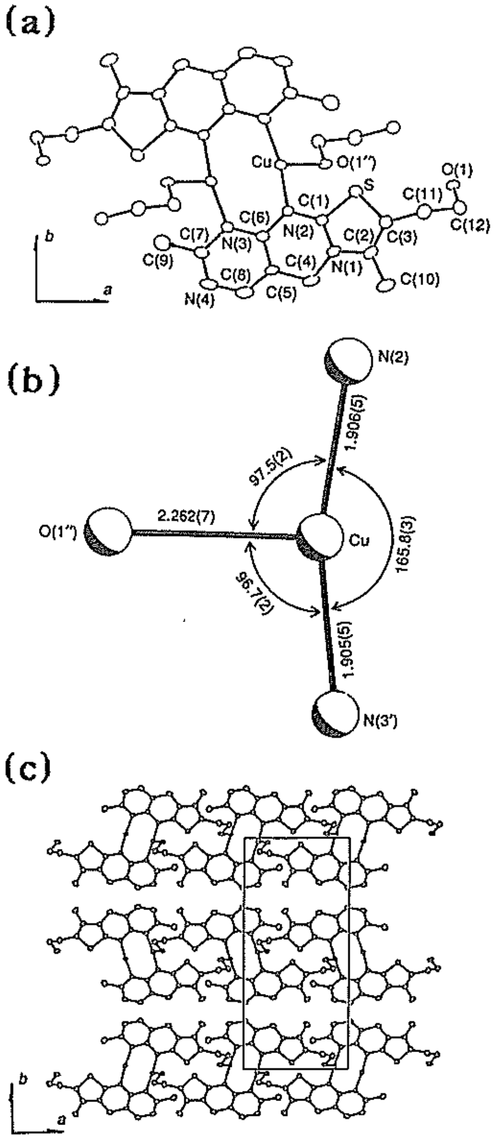


Figure 20. Structure of $[(Cu_2(tc)_2)(ClO_4)_2]_\infty$ (tc = thiochrome). (a) a dimeric unit, (b) coordination geometry of the copper atom, and (c) relationship between chains. (Kitagawa, S.; Matsuyama, S.;Munakata, M.;Osawa, N.;Masuda, H. *J.Chem.Soc.Dalton Trans.* 1991, 1717-1720.)

rectangular wave chain (Fig.19). Moreover, the interesting CO adduct having infinite chain structure is also obtained: $[Cu(bpen)(CO)(CH_3CN)PF_6]_\infty$ consists of tetrahedral copper unit. This is considered to be CO-absorber of copper polymers.

Dinitrile, $NC(CH_2)_nCN$ type, is also a bridging ligand to give polymer structures. A series of nitrate compounds, $\{[Cu(NC(CH_2)_nCN)_2]ClO_4\}_\infty$ (n = 2 ~ 4) (Kinoshita, Matsubara, Higuchi, & Saito, 1959a; Kinoshita, Matsubara, & Saito, 1959b; Kinoshita, Matsubara, & Saito, 1959c) shows infinite structures, whose mode depends on n in spite of common tetrahedral copper geometry: a chain, sheet, and three-dimensional network are built when n = 2, 3 and 4, respectively. In the case of perchlorate anion, $\{[Cu\text{-}(NCCH_2CH_2CN)_2]ClO_4\}_\infty$ (Blount, Freeman, Hemmerich, & Sigwart, 1969) shows infinite puckered sheets of rectangular motifs of $(Cu_4(NCCH_2CH_2CN)_4)$. The ClO_4 ions lie in the cavities. The copper atom has a tetrahedral geometry with four nitrogen atoms at a Cu-N distance of 1.987(5) Å.

Thiochrome(tc) is obtained from the oxidation of thiamine with iodine. The reaction of tc with copper(I) salt gives ladder type one-dimensional polymer, $[\{Cu_2(tc)_2\}(ClO_4)_2]_\infty$, which contains dimetal units of $(Cu_2(tc)_2)$ with short Cu...Cu distance in the unit(2.476(3) Å) (Kitagawa, Matsuyama, Munakata, Osawa, & Masuda, 1991b) Fig.20 shows the details of its polymeric aspect.

IV Specific Interactions in Copper Coordination Polymers

(1)Aromatic stacks (π–π interactions)

Aromatic stacks are one of the effective attractive interactions between polymer chains. The interplanar distances of aromatic moiety are nearly 3.4 Å, similar to that of layers of graphite. Copper(I) polymers with stacks of aromatic ligands have been prepared in order to construct photoactive systems. A large number of copper(I) complexes exhibit intense absorption bands in the visible region, which is ascribed to metal-to-ligand charge-transfer (MLCT) transitions. In the photoexcited state the metal can participate in numerous redox reactions, some of which have practical applications (Ferraudi & Muralidihavan, 1981). 2,9-Dimethyl-1,10-phenanthroline (dmphen) is a particularly suitable ligand because its copper(I) complex $[Cu(dmphen)_2]^+$ can be excited in its low-lying MLCT region, and the complex gives rise to photoluminescence (Buckner & McMillin, 1978). 2,2'-Biquinoline (biq) has higher acceptor properties than dmphen, forming a copper(I) complex with intensely magenta color(Hoste, 1950).

As mentioned in section III, both $[Cu(CN)(dmphen)]_\infty$ (Morpurgo, et al., 1984) and $[Cu_3(CN)_3(biq)_2]_\infty$ (Dessy, et al., 1985) have a stacked-layer arrangement. The crystal structures of $[Cu(CN)(dmphen)]_\infty$ consists of one-dimensional zigzag chains of tetrahedral copper(I) atoms and cyanide groups. Each polymeric sequence in $[Cu(CN)(dmphen)]_\infty$ is 'fitted' with its centrosymmetrical one so that stacks of aromatic systems are formed with alternate dmphen interplanar distances of 3.26 and 3.90 Å as shown in Figure 11(a). Due to steric or packing effects, the Cu-C-N-Cu sequence is not linear, the -N- and -C- angles being 154.8(1) and 169.6(9)°, respectively.

Similarly, $[Cu_3(CN)_3(biq)_2]_\infty$ forms one-dimensional infinite polymer. There are two type copper atoms in the chains (Figure 11(b)). The atom Cu(1) linearly coordinates to two nitrogen atoms of two centrosymmetric CN^- groups. The other atom Cu(2) tetrahedrally coordinates to two nitrogen atoms from a biq molecule and two CN^- groups according to the sequence -C-N-Cu(1)-N-C-Cu(2)- Pairs of biq molecules are formed with an interplanar spacing of 3.28 - 3.35Å (Figure 11(c)), whose degree of superposition is high, the two central phenyl rings being perfectly eclipsed. Unexpectedly, copper polymers of 1,10-phenanthroline (phen) are not found whereas a trinuclear complex,

$[Cu_3(CN)_3(phen)_3]$, is isolated (Dyason, Healy, Engelhardt, Pakawatchai, Patrick, & White, 1985). The formation of the crystalline copper polymers having the stacks is associated with delicate spatial balance.

In contrast with that of phen the following instances indicate the importance of ring size of π systems. Copper(I) cyanide of 4-methylpyridine (4-Mepy) gives an infinite linear polymer, $[Cu_2(CN)_2(4\text{-}Mepy)_3]_\infty$, but has no stacks of pyridine rings. This is possibly due to the flexibility of the geometry of the copper: one of the two copper atoms in the complex is trigonal-planar (C, N(cyanide) and N(4-Mepy) donors) and the other copper atom is pseudo-tetrahedral (C, N(cyanide) and two N(4-Mepy) donors).

Copper(I) polymers linked by SCN^- group, $[Cu(SCN)(dmphen)]_\infty$, analogous to $[Cu(CN)(dmphen)]_\infty$, have been prepared (Morpurgo, et al., 1984). The crystal structure shown in Figure 12(a) is close to that of $[Cu(CN)(dmphen)]_\infty$. (i) NCS^- groups act as a bridge between two metal atoms, and (ii) the dmphen molecules tend to couple by facing each other. There are common features between $[Cu(CN)(dmphen)]_\infty$ and $[Cu(SCN)(dmphen)]_\infty$ due to the stacking at similar distance of the pairs of dmphen planes. The fitting between the centrosymmetric chains is apparently different in the two structures: overlap of each couple of dmphen molecules accounts for 40% of total dmphen area in $[Cu(CN)(dmphen)]_\infty$ and only for *ca* 15% in $[Cu(SCN)(dmphen)]_\infty$ due to the greater inclination of the dmphen molecular plane with respect to the chain vector. The overlap could be one of the main stabilizing factors of these structures (Morpurgo, et al., 1984). This is a key factor to build crystal lattices of the polymers.

In the optical spectra of $[Cu(CN)(dmphen)]_\infty$, $[Cu_3(CN)_3(biq)_2]_\infty$ and $[Cu(SCN)(dmphen)]_\infty$ (Dessy, et al., 1985; Morpurgo, et al., 1984), two bands at 23500 and 19000 cm^{-1} are observed for $[Cu(CN)(dmphen)]_\infty$, and 23200 and 20500 cm^{-1} for $[Cu_3(CN)_3(biq)_2]_\infty$. They are assigned to MLCT bands; the low-energy band is related to d(yz) to φ_π (lowest unoccupied molecular orbital of dmphen), and the high-energy band is $d(z^2)$ or $d(x^2\text{-}y^2)$ to φ_π charge-transfer band. The latter band reflects stacking of monomeric units. Cherry-red $[Cu_3(CN)_3(biq)_2]_\infty$ also exhibits two MLCT bands at 18500 and 21200 m^{-1}.

Although single-stranded polymers $[Cu(NCS)(L)_2]_\infty$ (L=2-methylpyridine (Figure 12(b)), 3-methylpyridine and 4-methylpyridine) have been found and the tetrahedral CuN_3S geometry of the copper is the same as that of $[Cu(SCN)(dmphen)]_\infty$, no π–π stackings of aromatic rings exist (Healy, et al., 1984).

Complexes $[CuI(acr)]_\infty$ (acr=acridine) (Healy, et al., 1983) and $[CuI(coll)]_\infty$ (coll=collidine) (Campbell, et al., 1977) are 'split-stair' polymers with -Cu-I-Cu-I- backbone as illustrated in Fig.8. The copper environment is three-coordinate. The acridine and collidine ligands are aligned so as to hold stacks of aromatic moieties. However, the distance between nearest-neighbours is greater than 4 Å, indicative of no interaction. For derivatives of type $[CuXL]_\infty$ (L=2-methylpyridine (Rath, Maxwell, & Holt, 1986), 2,4-dimetylpyridine (Rath, et al., 1986), benzonitrile(Healy, Kildea, Skelton, & White, 1989)) their structures are 'stair' one-dimensional polymer. The ligand planes are arranged in parallel.

As mentioned in the previous section $\{[Cu(2\text{-quinolinethione})_2]X\}_\infty$ (X = ClO_4 and PO_2F_2)(Kitagawa, et al., 1993b) has aromatic stack interaction of 2-quinolinethione between neighbouring chains. The interplanar distances are 3.206(1) and 3.219(1) Å for X = ClO_4 and X = PO_2F_2, respectively. Stacks of the pyridyl groups joining the neighbouring chains are also found in $[Cu(bpen)PF_6]_\infty$ (Kitagawa, et al., 1991a), in which the interplanar distance is nearly 3.5 Å.

Donor-acceptor complexes of aromatic-electron systems often possess interesting physical properties such as low energy optically allowed intermolecular electronic transition (charge transfer band) which in special cases even occurs thermally to the extent that they may lead to metallic conductivities. Such properties are dependent not only on specific molecular properties of the individual components such as ionization energy of the donor and electron affinity of the acceptor, but also on details of relative arrangement and interactions in the crystal lattice. Therefore the synthetic method, controlling the orientation of molecules in the crystals should be developed.

Phenazine(phz), analogs of acridine and anthracene, has bridging, stacking, and electron-donating capabilities. Copper (I) and silver(I) complexes with phz were synthesized and their molecular packings were determined (Munakata, Kitagawa, Ujimaru, Nakamura, M., & Matsuda, 1993). $[Cu_2(phz)_3(MeOH)_2](phz)(PF_6)_2$ is an infinite stack of alternating metal-free phz molecules and the dicopper complex cations $[Cu_2(phz)_3(MeOH)_2]^{2+}$ with the interplane distance 3.42 Å. This stacks causes an intermolecular CT band from the latter to the former at 710 nm.

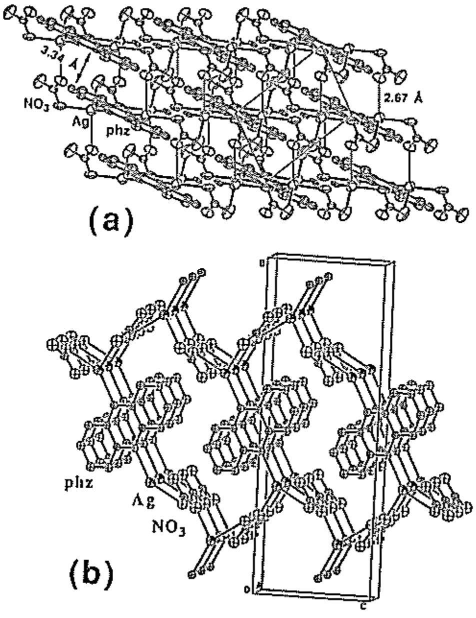


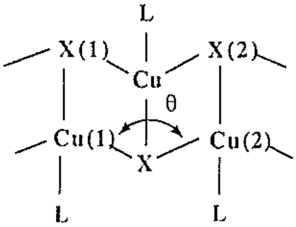
Figure 21. Side view (a) and perspective view (b) of the packing arrangement of $[Ag_2(phz)(NO_3)_2]_\infty$.

Although polymer structures of copper are not synthesized, those of silver are successfully obtained. The molecular packing of $\{[Ag(phz)]ClO_4\}_\infty$ is composed of infinite linear chains of -Ag-phz-Ag-phz- and π–π interaction of the phz molecules between the chains. The interplane distance is 3.35Å. Three-dimensional polynuclear complex $[Ag_2(phz)(NO_3)_2]_\infty$ is made of the framework of six-membered rings of silvers and π–π interaction of phz molecules between the frameworks having the interplane distance of 3.34 Å (Fig.21). Solvents and counter anions play an important role in the molecular packing of metal complexes of phz and by controlling these copper polymers would be prepared. Polymeric and low-molecular-weight copper(I) complexes

Table 1. Comparison[a] of Geometries[b] of Infinite Ribbon Structures in [CuLX] Polymers[a]

	CuCl(py)[c]	$(CuCl)_2(C_2H_6N_2)$[d]	$CuCl(CH_3CN)$[e]	$CuBr(CH_3CN)$[f]	CuI(rhod)[g]
Cu-X	2.530(2)	2.55	2.38	2.50(1)	2.665(2)
Cu-X(1) Cu-X(2)	2.363	2.34	2.42	2.48(1)	2.655
Cu...Cu[h]	2.955(5)	3.01(3)	3.05	3.05(2)	3.008(3)
Cu(1)-X-Cu(2)	109.0(1)	109(2)	107.0	106.2(4)	104.46(6)
dihedral θ	64.4	68.4	69.8	67.9	62.8

a)Table 7 in ref. 10 is modified b)unit in Å. c)ref.10. d)ref. 14. e)ref.104. f)ref. 13.
g) ref. 105. h)Nearest neighbour copper atoms in a ribbon.



with stacks of aromatic molecules are listed in Table 2.

(2)Hydrogen bonds

The hydrogen bonding between X-H (H donor) and Y (H acccepter) is usually found in crystals. Frequently this weak bond has decisive influence on the structure and properties of the substances. It is characterized by the distances between X...Y or H..Y. The ranges in the distances are listed in literatures.(Greenwood & Earnshaw, 1984; Kuleshova & Zorkii, 1981). As mentioned in the previous section there have been found several compounds having hydrogen bonding.

$\{[Cu(2\text{-quinolinethione})_2]X\}_\infty$ (X = ClO_4 and PO_2F_2)(Kitagawa, et al., 1993b) has interchain interaction by hydrogen bonding between tetrahedral counter anion (ClO_4 and PO_2F_2) and uncoordinated NH moiety, the anion bridging two NH in neighbouring chains.

Table 2. Stacks of Aromatic Moieties Found in Copper(I) Polymer Compounds

Compounds	Stacking aromatic molecules	Interplane distances (Å)	ref
$[Cu_2(biq)_2(CN)_2]_n$	2,2'-biquinoline	3.28, 3.35	36
$[Cu(dmphen)(CN)]_n$	2,9-dimethyl-1,10-phenanthroline	3.26, 3.90	35
$[CuCl(PhCN)]_n$	benzonitrile	3.866(1)[b]	106
$[CuBr(PhCN)]_n$	benzonitrile	3.995(1)[b]	106
$[CuI(2\text{-}Me\text{-}py)]_n$	2-methyl-pyridine	3.706(5)[b]	107
$[CuI(acridine)]_n$	acridine	4.117[b]	11
$[Cu(phz)_2(H_2O)]$[a]	phenazine	3.42	78
$[Cu_2(phz)_3(MeOH)_2](phz)$[a]	phenazine	3.39	78
$\{[Ag(phz)](ClO_4)\}_n$[c]	phenazine	3.35	78
$[Ag_2(phz)(NO_3)_2]_n$[c]	phenazine	3.34	78

a)These are not coordination polymers

b)The nearest Cu...Cu distance, to which the interplane distances are considered to be close

c)The corresponding copper(I) complexes were isolated but the X-ray structure could not be determined

Interestingly, octahedral PF_6^- anions included in a starting material are hydrolyzed to be an tetrahedral PO_2F_2 in the products. The crystal lattice favors a tetrahedral anion and the inclusion of the anions makes the crystal structure very stable. Consequently, 2-quinolinethione is an unique ligand having bridging-, hydrogen bonding-, and stacking-capabilities. 8-Mercaptopurine also provides an infinite chain copper(I) complex [$CuCl_2$(8-mercaptpurine)]∞ (Caira & Nassimbeni, 1976), which is obtained as orange color compound from reduction of copper(II) by 8-mercaptopurine. Fig.17(a) illustrates the -S-Cu-S-Cu- backbone forming a helical chain around the two-fold crystallographic axis shown as a broken line. Interestingly there are two N-H···Cl hydrogen bonds within each polymer chains (N···Cl = 3.13 and 3.15 Å) and the polymer chains are cross-linked by a third N-H···Cl interactions (3.08 Å) as shown in Fig.17(b).

Bright red CuCl complex with nicotinic acid is one-dimensional polymer [CuCl$(Hna)_2$]∞ (Goher & Mak, 1987), having hydrogen bondings, which joint two neighboring CuCl chains through metal-free carboxyl groups of the nicotinic acid(Fig.7) (Goher & Mak, 1987). The dimensions of the hydrogen bonds between the nearly planar nicotinic acids are O(1)···O(3)=2.568(2) and O(2)···O(4)=2.64(2) Å. The polymeric [CuCl(Hna)]∞ complex (Goher & Mak, 1985) is also found, whose structure is similar to that of [CuCl$(Hna)_2$]∞.

Bis(*N*, *N'*-dimetylthiourea)copper(I) nitrate, [Cu$(dmtu)_2NO_3$]∞, is synthesized from an aqueous solution of copper(II) nitrate and dmtu (Dubler & Bensch, 1986). The Cu(I) atoms are tetrahedrally coordinated by four thioamido sulfur atoms and form CuS_4 tetrahedra units(Fig.22(a)). Sharing of an edge between two neighboring tetrahedra results in infinite isolated chains of $[Cu(SR)_2^-]$∞, running parallel to the C axis of the cell and separated from

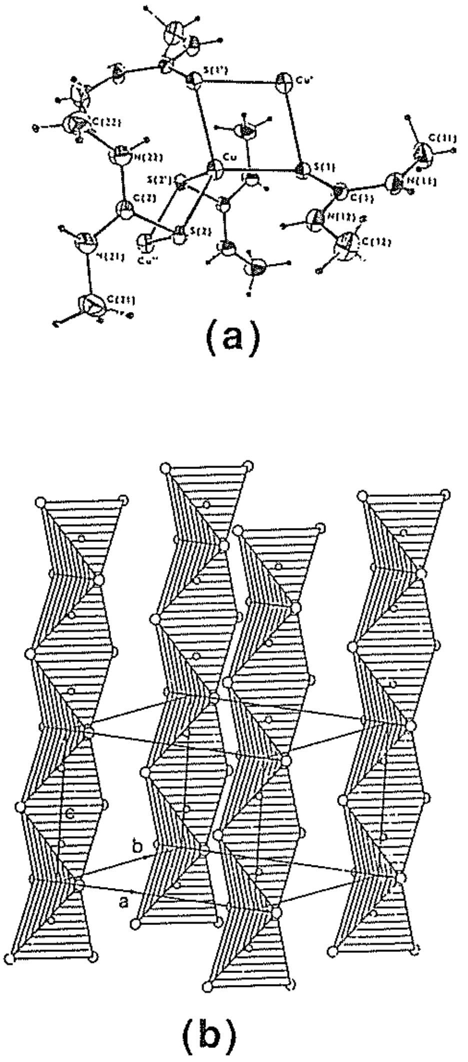


Figure 22. Structure of polymeric [Cu$(dmtu)_2NO_3$]. (a) and alternately stacked CuS_4 tetrahedra in the polymer chains (b).Copper atoms occupy the centers of the tetrahedra. The nitrate ions (omitted for clarity) bridge the individual chains via hydrogen bonds. dmtu-dimethylthiourea. (Dubler, E.;Bensch, W.*Inorg.Chim. Acta* 1986,*125*,37-42).

Table 3 Hydrogen Bondings found in Copper(I) Polymers.

Compounds	X-H Y	X-Y Distance(Å)	ref
$[CuCl(C_6H_5NO_2)_2]_\infty$	O...O	2.52(2), 2.64(2)	9
$[Cu(SC(NHCH_3)_2NO_3]_\infty$	N...O	2.763(3), 2.911(3)	82
$[CuCl_2(C_5H_5N_4S)]_\infty$	N...Cl	3.03(1), 3.13(1), 3.15(1)	60
$[Cu(PPh_3)_2(O_2CCH_2CN)_2H]_\infty$	O...O	2.48(7)	108
$[Cu_2Cl_3(H_2O)(C_7H_{10}N)]_\infty$	N...Cl	3.44	109
$(Na_2[Cu(CN)_3(H_2O)_3)_\infty$	O......O	2.732(14)	41
$([Cu(C_9H_6NS)_2](ClO_4))_\infty$	N......O	2.83(1), 2.85(1)	59
$([Cu(C_9H_6NS)_2](PF_2O_2))_\infty$	N......O	2.74(1)	59

each other by the nitrate anions which do not coordinate to the metal atoms (Fig.22(b)). However, the nitrate ion is fixed by two medium-strong hydrogen bonds of type N-H···O between dmtu and NO_3^-, N···O distances being 2.76 and 2.91 Å. Bridging of the individual chains of edge-sharing CuS_4 tetrahedra occurs through these hydrogen bonds (Dubler & Bensch, 1986). $\{Na_3[Cu(CN)_3]3H_2O\}$ (Kappenstein & Hugel, 1978) has a three-dimensional ordered network with the sodium cations in which channels appear parallel to the ternary axes. The sodium ions are octahedrally surrounded by nitrogen and oxygen(water) atoms. The distances of Na-N range from 2.510(2) to 2.723(6) Å. The water molecules exhibit a hydrogen bond (O...O = 2.73(1) Å). Polymeric and low-molecular-weight copper(I) complexes with hydrogen bondings are listed in Table 3.

(3)Inclusion of Small Molecules

There are several two- and three-dimensional networks composed of cavities which can include small molecules or ions. They are tetragonal (Blount, et al., 1969), hexagonal (Cromer & Larson, 1962; Kitagawa, et al., 1992), and octagonal (Raston, et al., 1979). $\{[Cu(NCCH_2CH_2CN)_2]ClO_4\}_\infty$ (Blount, et al., 1969) has infinite puckered sheets of rectangular motifs of Cu_4, in which ClO_4 ions are lying. No special interaction between ClO_4 ion and the $Cu_4(NCCH_2CH_2CN)_4$. In $\{K[Cu_2(CN)_3]\text{-}H_2O\}_\infty$ (Cromer & Larson, 1962) the water molecules lie within the hexagons and apparently are present only to fill up space within the structure. The nitrogen σ electrons are used for bonding with copper and, therefore, are not available to form hydrogen bonds. The hexagon cavities are prpepared by use of pyrazine. The acetone molecules are included in the hexagons of $[Cu(pz)_{1.5}(CH_3CN)](PF_6)\cdot 0.5C_3H_6O\}_\infty$ (Kitagawa, et al., 1992). All the copper atoms are four-coordinate and the acetone molecules have no interactions with the copper and the ligands. The three-dimensional network of $\{(C_5H_6N)\text{-}[Cu_2(SCN)_3]\}_\infty$ (Raston, et al., 1979) contains cavities, which include pyridinium ions as counterions. In both $[Cu(pz)_{1.5}(CH_3CN)](PF_6)\cdot 0.5C_3H_6O\}_\infty$ and $\{(C_5H_6N)[Cu_2(SCN)_3]\}_\infty$ the included molecules are disordered in the cavities. The perchlorate couterions are included in the cavities of puckered sheets of $\{[Cu(NCCH_2CH_2CN)_2]\text{-}ClO_4\}_\infty$ (Blount, et al., 1969). In cavities of $Cu_4(NCCH_2CH_2CN)_4$ the succinonitrile molecules are disordered while the perchlorate anions are not disordered. All of these complexes there are no special interactions, besides ionic ones, between small included molecules and cavities. The synthesis of polymer compounds with inclusion phenomena displaying the special interactions appears in future issues.

(4)Short Cu-Cu Contact

There have been many copper(I) complexes having short metal-metal contact(Beck & Strachle, 1985; Do, Kang, Knobler, & Hawthorne, 1987a; Do, Knobler, & Hawthorne, 1987b; Doyle, Eriksen, & Van Engen, 1985; Doyle, Eriksen, & Van Engen, 1986; Gambarotta, Floriani, Chiesi-Villa, & Guastini, 1983; Goeden, Huffman, & Caulton, 1986; Hartl & Mahdjour-Hassan-Abadi, 1984; Jarvis, Kilbourn, & Pearce, 1973; Lemmen, Folting, Huffman, & Caulton, 1985; Lemmen, Huffman, & Caulton, 1986; Munakata, Maekawa, Kitagawa, & Adachi, 1990; Papasergio, Raston, & White, 1983) and the possibility of direct bonding between the two copper atoms has been often considered by comparing with the nearest-neighbor distance (2.56 Å) in metallic copper. However, the d^{10} configuration of copper(I) does not form direct bond so much as to dimetal compounds of group 6 - 9 elements (Cotton & Walton, 1982). Thus the attractive interaction between two copper atoms has been considered (Mehrotra & Hoffmann, 1978; Merz & Hoffmann, 1988). The recent molecular orbital calculations(Cotton, Feng, Matusz, & Poli, 1988; Lee & Trogler, 1990) reproduce no metal-metal bondings nor support attractive interaction. The copper-copper interaction in dimetal units are still controversial.

There are also several copper(I) polymers, whose metal-metal distance is significantly short. As shown in section III, $[Cu(CH_3CO_2)]_\infty$ (Drew, et al., 1973; Mounts, et al., 1974) has T-shape copper atoms with short Cu...Cu distance of 2.556(2) Å. On the other hand, the corresponding dimer molecule $[Cu_2(CH_3CO_2)_2]$ has shorter distance of Cu...Cu = 2.491(3) Å (Iijima, Itoh, & Shibata, 1985) obtained from electron diffraction study in the gas phase. The reverse instances that the Cu...Cu distance is shorter in a polymer than in dimer are also found: the dimer molecule of $[Cu_2(1,8\text{-naphthyridine})_2]^+$ has Cu...Cu distance of 2.506(2) Å(Munakata, et al., 1990) while the polymer having analogous dimer units $\{[Cu_2(tc)_2]ClO_4\}_\infty$ gives 2.476(3) Å (Kitagawa, et al., 1991b). Table 4 lists the copper(I) coordination polymers with short Cu...Cu distances. Most of copper geometries are tetrahedral, indicating that the complexes are coordinatively saturated. Even though the metal-metal distance is very short (less than 2.5 Å), there are no rational reasons for the metal-metal bondings or attractive interactions in the complexes with the coordination number more than four. The ligand bite appears to be important in these systems (Cotton, et al., 1988). On the other hand, there would be expected somewhat attractive interaction between the copper atoms in the complexes with the coordination number, such as two to three. To prove this interaction the simple dicopper complexes should be explored in advance.

Table 4 Short Metal-Metal Contact Found in Copper(I) Coordination Polymers

compounds	coordination donor set (geometry)[a]	distance (Å)	ref
$\{[S_2C_3(SCH_3)_3][Cu_2I_3]\}_\infty$	CuI_4(td) , CuI_3(tg)	2.331(3), 2.657(3)	28
$[CuCN(NH_3)]_\infty$	CuC_2N_2(td)	2.417	38
$\{(C_3H_7)_4N[Cu_3I_4]\}_\infty$	CuI_4(td)	2.461(5), 2.503(5)	19
$\{[Cu_2(tc)_2](ClO_4)_2\}_\infty$	CuN_2O(tg)	2.476(3)	71
$[Cu(CH_3CO_2)]_\infty$	CuO_3(tg)	2.544	63
		2.556(2)	64
$[(Cu_2I_2)(C_2H_5)_2S_2]_\infty$	CuI_3S(td)	2.612(3), 2.756(3)	22
$\{R[Cu_2I_3]\}_\infty$[b]	CuI_4(td)	2.507(1), 2.679(1)	20
$\{R'[Cu_2I_3]\}_\infty$[b]	CuI_4(td)	2.491(2), 2.699(2)	20
$\{[C_5H_6N][Cu_2(SCN)_3]\}_\infty$	CuS_3N(td) CuS_2N_2(td)	2.801(2)	39
$\{[N(C_2H_5)_4]_3[Cu_7Cl_{10}]\}_\infty$	$CuCl_3$(tg), $CuCl_2$(dg)	2.890(2) - 3.447(3)	29
$[CuI(CH_3NC)]_\infty$	CuI_4(td), CuC_2I_4(td)	2.89	21

a)td = tetrahedral, tg = trigonal, and dg = digonal.

b)R = $(CH_3)_4N^+$; R' = dimethyl(3-dimethylamino-2-aza-2-propenylidene)ammonium

Recently, it is reported(Kutal, 1990) that the short Cu...Cu contact influences the photochemical properties of the copper(I) complexes. The short copper-copper contact in the polymers would provide new photo-physicochemical properties of the solids. Hence, the synthesis of copper(I) polymers having short copper-copper contact is one of the most intriguing targets.

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