COPPER(I) COMPLEXES

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I. Introduction

A very large number of stable copper(I) complexes exist in a variety of stoichiometries. In few of these complexes does the formal coordination number of the metal atom exceed four. Indeed, along with silver(I) and gold(I), it is one of the few oxidation states to exhibit regularly the low coordination numbers two and three. The simple amine and halo complexes isolated from aqueous solution fortuitously contain linear copper(I) ions. As a result, coordination number two is erroneously considered to be a common coordination number for this oxidation state. In fact, two-coordinate complexes are probably outnumbered by the trigonally coordinated complexes, whereas against the vast host of tetrahedral complexes the two- and three-coordinate complexes are numerically insignificant.

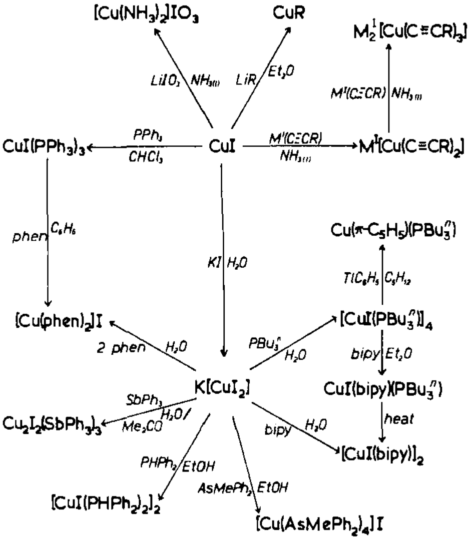


FIG. 1. Complexes derived from copper(I) iodide.

Most of the nonradioactive elements of Groups V, VI, and VII coordinate with the metal in this oxidation state, and there is also quite an extensive organometallic chemistry as befits an element of such importance in synthetic organic chemistry. An indication of the diversity of complexes [in this instance all derived from copper(I) iodide] is given in Fig. 1.

The thermodynamic factors involved in the relationship among

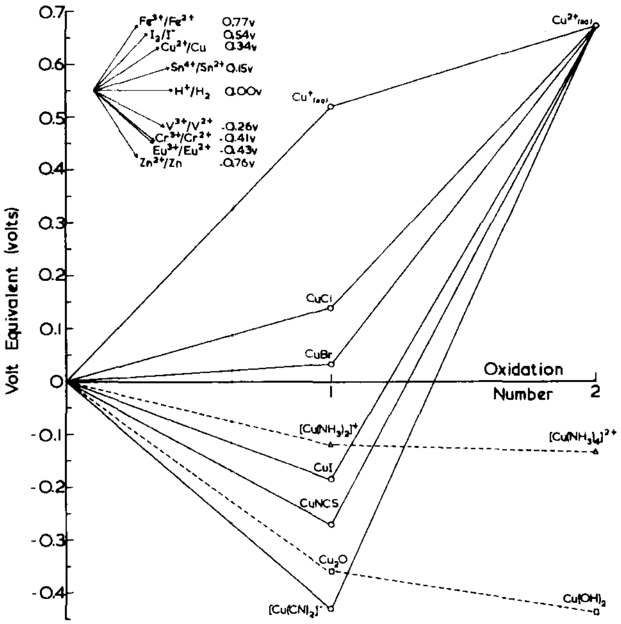


FIG. 2. Oxidation state diagram (*285*) for copper. (Data from Ref. *207*.)

copper(I), copper(II), and copper(0) (*207*) are shown in Fig. 2. From this it can be observed that it is possible for copper(I) complexes to disproportionate:

$$2\text{Cu}^{+}(\text{aq}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu}^{0} \qquad (1)$$

The equilibrium constant of reaction (1), $K = [\text{Cu}^{2+}][\text{Cu}^0]/[\text{Cu}^+]^2$, is of the order of 10^6; thus, only vanishingly small concentrations of aquocopper(I) species can exist at equilibrium. However, in the absence of catalysts for the disproportionation—such as glass surfaces, mercury, red copper(I) oxide (*7*), or alkali (*311*)—equilibrium is only slowly attained. Metastable solutions of aquocopper(I) complexes may be generated by reducing copper(II) salts with europium(II) (*113*), chromium(II), vanadium(II) (*113*, *274*), or tin(II) chloride in acid solution (*264*). The employment of chromium(II) as reducing agent is best (*113*), since in most other cases further reduction to copper metal is competitive with the initial reduction (*274*).

Aquocopper(I) complexes are fairly powerful reducing agents and the kinetics of their reactions with iron(III) (*275*), vanadium(IV) (*312*), cobalt(III), and mercury(II) (*113*) have been studied. Further, the role of copper(I) species in the copper(II)-catalyzed reduction of cobalt(III) by vanadium(II) (*112*) has been confirmed with the reduction of

$[Co(NH_3)_5Br]^{2+}$ by copper(I) (*277*). Similarly Cu(I) species catalyze the reduction of cobalt(III) complexes by vanadium(III) (*276*).

Solutions of many simple copper(I) compounds are easily oxidized by air, and the reactions proceed via peroxo species which, in turn, form hydrogen peroxide from the solvent (*157*, *261*, *353*, *362*).

Polarographic behavior of copper(II) and copper(I) species in the presence of various ligands has been investigated (*154*, *215*, *258*, *279*, *343*). In some instances, however, no copper(I) intermediate was observed in the reduction to copper amalgam at the electrode, e.g., at low concentrations of 1,2-diaminoethane (*270*) or similar diamines (*205*); this is in keeping with a value of 4×10^5 for the equilibrium constant (*33*, *291*) of the reaction

$$[Cu(en)_2]^{2+} + Cu + 2en \rightleftharpoons 2[Cu(en)_2]^+ \qquad (2)$$

In other solvents, particularly those that are capable of solvating copper(I) ions more effectively than water, copper metal can be used to reduce copper(II) species to copper(I) complexes. Such is the case in acetonitrile (*197*), liquid ammonia (*314*), or in the molten eutectic $AlCl_3$–NaCl–KCl (*9*).

At high temperatures under oxygen-free conditions, copper(I) is the preferred oxidation state. Thus, above 725°K, copper(II) chloride decomposes to $(CuCl)_3$ vapor and chlorine (*227*), and CuO yields Cu_2O at ca. 1275° (*318*).

II. Anionic Complexes

A. DIHALOCUPRATE(I) COMPLEXES

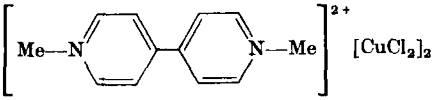
The enhanced solubilities of copper(I) halides or pseudohalides in aqueous solutions of alkali or ammonium halides are due to the formation of anionic complexes (*37*, *121*, *134*, *263*):

$$CuX + MX' \rightleftharpoons M^+[CuXX']^- \qquad (3)$$

In ethanol, containing dissolved HCl, the formation of dichlorocuprate(I) salts is even more favored than in aqueous solution (*187*). This would seem to be generally true for most weakly polar, organic solvents since the cuprate(I) complexes are extracted preferentially into diethyl ether (*91*), tributylphosphate (*321*, *347*), or cyclohexanone (*321*). In the first two solvents the ions have been shown to be linear and centrosymmetric by infrared and Raman spectroscopy (*91*, *347*).

The anions form isolable salts with a variety of cations, e.g., ammonium (*102*, *297*, *304*), nitrogen bases (*70*, *71*, *96*, *97*, *172*, *196*, *297*), alkali metals (*137*, *138*), copper(II) complex cations (*153*, *236*, *266*, *286*), and the triethylsulfonium cation (*97*).

In the salt $[\{N_6P_6(NMe_2)_{12}\}Cu(II)Cl][Cu(I)Cl_2]$ (*236*) the anion is linear, but in



(*228*) the anion has the polymeric beryllium dichloride structure (*288*). Trigonal copper(I) occurs in the dicyanocuprate(I) ion where there are helical Cu–C–N–Cu–C chains with tactic CN groups bound normal to the helices (*92*).

B. TRIHALOCUPRATE(I) COMPLEXES

In most instances further coordination of halide ion takes place and $[CuX_3]^{2-}$ complexes are formed (*23*, *37*, *121*, *134*, *141*, *172*, *186*, *279*, *334*)

$$[CuX_2]^- + X' \rightleftharpoons [CuX_2X']^{2-} \tag{4}$$

Potassium and ammonium trichloro- and tribromocuprate(I) have been prepared (*247*, *350*) and their structures determined by Brink *et al.* (*44*, *45*). The isomorphous anions are made up from CuX_4 tetrahedra sharing corners. Tricyanocuprate(I) salts have also been isolated (*138*, *325*), and the Raman spectrum of the anion in aqueous solution indicates that it is trigonal and contains no coordinated water (*76*). Recently, $[Cu(N_3)_4]^{2-}$ has been reduced electrolytically to $[Cu(N_3)_3]^{2-}$ (*259*).

C. TETRAHALOCUPRATE(I) COMPLEXES

Only the most strongly coordinating anions are capable of forming significant quantities of $[CuX_4]^{3-}$ anions in the equilibrium (*141*, *172*, *203*, *295*)

$$[CuX_3]^{2-} + X' \rightleftharpoons [CuX_3X']^{3-} \tag{5}$$

The most important ion of this stoichiometry is $[Cu(CN)_4]^{3-}$. Its infrared and Raman spectra have been obtained with increasing precision with the passing years (*40*, *66*, *180*, *287*) and together with X-ray crystallography of the potassium salt show it to have a regular tetrahedral grouping about the copper atom (*90*).

D. POLYNUCLEAR ANIONS

The polynuclear anions are usually chlorocuprate(I) complexes, but compound $K[Cu_2(CN)_3]\cdot H_2O$ has been identified in the phase diagram of the CuCN–KCN–H_2O system (*334*). The anion's structure is made up of $[Cu_2(CN)_3]$ sheets with the lattice water clathrated in $(CuCN)_6$ rings (*93*).

The chloro anions are all derived from linked $CuCl_4$ tetrahedral units; for instance in $Cs[Cu_2Cl_3]$ (*349*) there are double chains formed by $CuCl_4$ tetrahedra sharing edges (*43*). In bis-(*N*-benzoylhydrazine)-copper(II) pentachlorotricuprate(I) (*18*), there are cylinders of distorted $CuCl_4$ tetrahedra in which one-fifth of the chloro ligands link four Cu(I) atoms, three-fifths link two copper(I) atoms, and the remaining one-fifth link a copper(I) and copper(II) atom. Several pentacyanotricuprate(I) salts have also been isolated (*138*). There is one free chloride ion in the structure of $[Co(III)(NH_3)_6][Cu_5Cl_{17}]$, and the Cu_5Cl_{16} units consist of four of the ubiquitous $CuCl_4$ tetrahedra, each bound through one corner to a tetrahedrally coordinated, central copper atom (*254*).

E. $[Cu(biX)_n]^{1-2n}$ COMPLEXES

The $[Cu(biX)_n]^{1-2n}$ compounds all occur with sulfur acids. The best understood are the thiosulfato complexes. However, these have been but little investigated compared with their technically important silver analogs. They have usually been prepared by the action of alkali thiosulfates on copper(II) salts, e.g.,

$$4(NH_4)_2S_2O_3 + 2CuCl_2 \longrightarrow 2NH_4[CuS_2O_3] + (NH_4)_2S_4O_6 + 4NH_4Cl \qquad (6)$$

It is also possible to obtain mixed Cu(II)–Cu(I) salts, such as $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2\cdot Y$ ($Y = H_2O, NH_3$), in other reactions due to incomplete reduction (*153*).

The anion most commonly obtained in the preparation of thiosulfato complexes appears to be $[Cu(S_2O_3)_3]^{5-}$ (*41, 100, 300, 320*), and other salts include hydrated sodium, potassium, and ammonium derivatives of $[Cu_2(S_2O_3)_3]^{4-}$ (*320*) and $[Cu(S_2O_3)]^-$ (*300, 320*). Double salts are frequently obtained and examples of these are $[NH_4]_7[Cu(S_2O_3)_4]\cdot 2NH_4X$ ($X = ClO_3, NO_3$), $K_7[Cu(S_2O_3)_4]\cdot 2KNO_3$, and $Na_3[Cu(S_2O_3)_2]\cdot 2NaNO_3$ (*320*). Mixed complexes $Na_2[CuX(S_2O_3)]$ (X = I, NCS) have also been reported (*141*).

Many similar sulfito complexes are known (*300*), e.g., $NH_4[CuSO_3]$, $[NH_4]_4[Cu_2(SO_3)_3]\cdot 3H_2O$, and $[NH_4]_5[Cu(SO_3)_3]\cdot H_2O$, but in the sodium and potassium series double-salt formation is even more prevalent than with the thiosulfatocuprate(I) salts of these cations, e.g., $K[CuSO_3]\cdot 3KHSO_3$.

Treatment of aqueous solutions of copper(II) salts with ammonium polysulfide gives rise to $NH_4[CuS_4]$ (*163*), from which other $[CuS_4]^-$ salts can be obtained (*35, 163, 283*). Two thiocarbonato complexes, $M[CuCS_3]$ ($M = K, NH_4$), are also known (*162*).

III. $[CuXL]_n$ Complexes

In virtually all the $(CuXL)_n$ complexes, the anionic ligand is halide or pseudohalide. It is superficially attractive to regard them as linear copper(I) complexes—neutral analogs of $[Cu(NH_3)_2]^+$ and $[CuCl_2]^-$. However, in the majority of cases where molecular weight or X-ray structural determinations have been made the complexes have been shown to be tetrameric. Severe deviations from orthogonality make the new formulation as "inorganic cubane" molecules (*268*) less apt than the original description of a copper-cornered tetrahedron with a halide bound to each face (Fig. 3). In the structure of $[CuIAsEt_3]_4$ (*234*) the copper atoms are only 4 pm further apart than in copper itself, and because of this, one review considers copper(I) to be seven-coordinate in these complexes (*253*). It is worthy of note that the silver(I) analogs are also tetramers but the similar gold(I) complexes are linear monomeric molecules (*235*).

The majority of the complexes listed in Table I have been prepared

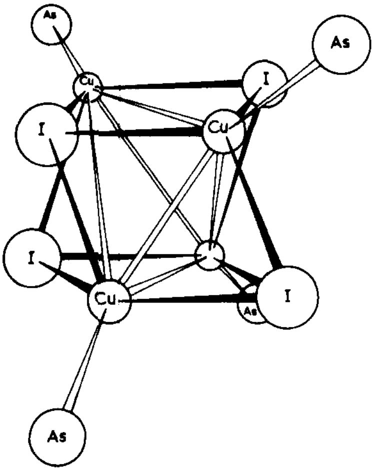


FIG. 3. Structure of $[CuIAsEt_3]_4$. [Redrawn by permission from *J. Chem. Soc., London*, p. 1503 (1936). The ethyl groups have been omitted for clarity.]

TABLE I

TETRAMERIC CuXL COMPLEXES

Ligand	Halide	References
RNH_2 (R = C_8H_{17}, $C_{10}H_{21}$, $C_{18}H_{37}$)	Cl, Br, I	(*354*)
$PHPh_2$	Cl, Br, I	(*1*)
PR_3 (R = Et, Pr^n, Bu^n, C_5H_{11})	I	R = Bu^n (*234*) (*182*)
PEt_3	Cl	(*176*)
PEt_2Ph	I	(*62*)
PPh_3	Cl, Br, I	(*56, 85, 176*)
$PEt_2(p\text{-}C_6H_4\cdot CF_3)$	I	(*62*)
$P(NEt_2)_2Ph$	I	(*114*)
$P(NMe_2)F_2$	Cl	(*74*)
2-Phenylisophosphindoline	Cl, Br, I	(*75*)
AsR_3 (R = Me, Et, Pr^n, Bu^n)	I	(*234*)
$AsEt_3$	Br	(*234*)
$AsMePh_2$	Cl, Br, I	(*267*)
$AsPh_3$	Cl	(*222*)
$AsPh_3$	Br, I	(*178*)

by direct interaction of the ligand and copper(I) halide in an appropriate solvent. Recently, it has been found more convenient to prepare some of the complexes in homogeneous solution from copper(II) halides if the ligand is a tertiary phosphine or arsine (*75*, *176*, *178*).

If $[CuClPPh_3]_4$ is reacted with $NaBH(OMe)_3$ in deoxygenated *N*,*N*-dimethylformamide (DMF), red, hexameric $[CuHPPh_3]_6$ is obtained (*69*). In this complex the copper atoms are located at the apices of an irregular octahedron with triphenylphosphine bound to each and pointing away from the center of the octahedron. The mean Cu–Cu distance is 260 pm (the same as in $[CuIAsEt_3]_4$), so there is some metal–metal bonding (*31*). The presence of the hydrido ligands was not detected by X-ray crystallography nor by NMR or infrared spectroscopy, but the complex reacted with $PhCO_2D$ to give a mixture of H_2 and HD but no D_2.

The above reaction is an example of anion substitution but, more importantly, the tetramers may be cleaved by heterocyclic nitrogen ligands (*176*, *234*),

$$[CuI(PBu^n_3)]_4 + 4\text{bipy} \longrightarrow 4CuI(\text{bipy})(PBu^n_3) \qquad (7)$$

$$[CuBrPPh_3]_4 + 4\text{py} \longrightarrow 2[CuBr(PPh_3)\text{py}]_2 \qquad (8)$$

or by excess ligand (*62*),

$$[CuI\{PEt_2(p\text{-}CF_3\cdot C_6H_4)\}]_4 + 8PEt_2(p\text{-}CF_3\cdot C_6H_4) \rightleftharpoons 4CuI\{PEt_2(p\text{-}CF_3\cdot C_6H_4)_3\}_3 \qquad (9)$$

Several complexes have been found to be dimeric. Infrared spectroscopy shows that the CuNCS(L) complexes (L = py, 2- or 4-picoline, 3,5-lutidine, or quinoline) contain bridging thiocyanato groups (*332*). The mass spectra of CuX{P(cyclohexyl)$_3$} complexes (X = Cl, Br, I) show no peaks of higher mass than those corresponding to dimeric molecules, and the far-infrared spectrum of the chloro complex indicates that they are dimeric with halo bridges (*248*). Triphenylphosphine reacts with copper(I) trifluoroacetate in dichloromethane to give $[Cu(O_2C\cdot CF_3)(PPh_3)]_2$ which is dimeric in chloroform but partially dissociated in dichlorobenzene (*107*).

Polymeric complexes are formed when copper(I) cyanide reacts with ammonia or alkyl and aryl isocyanides. The ammine complex consists of Cu–C–N–Cu–C helices linked by metal–metal bonds to form sheets. The NH_3 ligands bond normal to the copper atoms and interlock with NH_3 protrusions of other sheets (*94*). Complex CuCN(Bu^{n}NC) is polymeric (*272*), and the ethyl, propyl, and 2-butyl isocyanide complexes are also known (*139*).

The reaction of CuCN with MeI surprisingly gives polymeric CuI·MeNC [which can be prepared more obviously from CuI and MeNC (*169*)]; this unusual exchange reaction (*149*) has been confirmed by the determination of the structure of the polymer (*118*). The structure is shown in Fig. 4. Other halocopper(I) isocyanide complexes have been prepared by reaction (10).

$$\mathrm{CuX + RNC \xrightarrow{MeCN} CuX\cdot RNC} \qquad (10)$$

Compound CuClPhNC is also known. By contrast, similar acetonitrile complexes are easily air oxidized, but they can be prepared by reducing CuX_2 (X = Cl, Br) with copper in MeCN (*250*); several alkyl or aryl nitriles complex with CuCl (*290*).

Two complexes are known definitely to be monomeric—the triphenylphosphine sulfide complexes, CuX(Ph_3PS) (X = Cl, Br). They were prepared by reacting the ligand with copper(I) halide in chloroform, and molecular weight determinations in this solvent show them to be monomeric (*95*).

There remains a variety of unstable, insoluble, or incompletely characterized complexes whose true formulas remain open to speculation. Many unstable 1:1 complexes between copper(I) halides and ammonia (*51*) or the lower aliphatic amines (*71*, *281*, *356*) have been studied manometrically, but the compounds formed have high dissociation pressures, and attempts to isolate them have been unsuccessful owing to loss of ligand or to oxidation. Complexes with higher amines (*348*) or with pyridine (*354*) and its oligomers (*178*, *229*, *230*) are, in

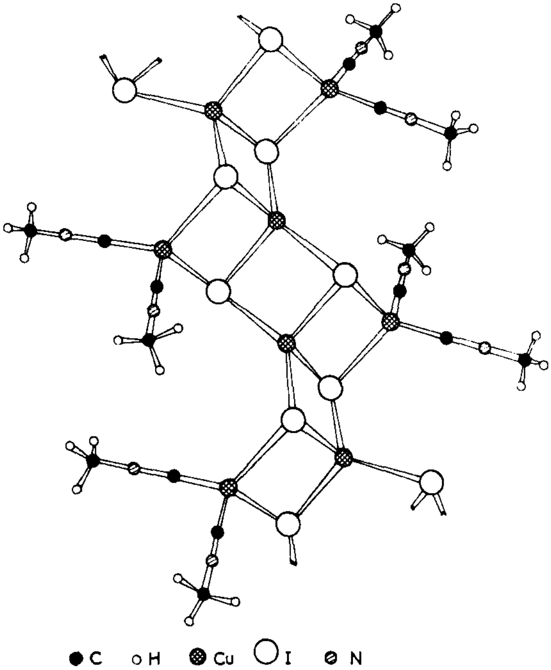


FIG. 4. Structure of [CuI·MeNC]$_\infty$. [Redrawn by permission from *J. Chem. Soc., London*, p. 2303 (1960).]

general, more stable, but the solubility of compounds of the latter class is low.

Similarly, phosphine complexes (*165*, *296*, *309*) easily lose the ligand. No molecular weights are available for the few phosphite complexes isolated (*16*, *17*, *99*) or for the complex CuCl{$P(CH_2SiMe_3)_3$}. Early work on dimethylphenylarsine complexes (*50*) has been corrected (*267*), but the complexes of diphenylmethylarsine (*50*) merit reinvestigation.

Compound CuCl(Et_2NH) can be obtained from the bis(amine) complex, but the molecular weight has not been determined. It is even more unfortunate that no attempts have been made to determine the molecular weights of certain complexes containing sulfur ligands since these could be either monomeric (like $CuClPh_3PS$) or polymeric containing sulfur bridges. Compound CuCl{$SC(NH_2)_2$} has been prepared from copper(II) chloride (*292*) and so have both the bis- and tris(thiourea)copper(I) complexes. Since thiourea is a good bridging ligand, this complex is probably polymeric, as are CuX{$SC(NH_2)(OEt)$} [X = Br

(*299*), NCS (*101*), Cl, I (*101*, *299*)]. Thioacetamide has been shown to be S-bonded (*327*) in CuCl(thioacetamide) (*171*) since the C–S stretch frequency decreases upon coordination.

IV. $Cu_2X_2L_3$ Complexes

Recent X-ray crystallographic investigations of $Cu_2Cl_2(PPh_3)_3$ (*5*) (Fig. 5) and its benzene adduct (*217*) have shown one copper atom in the molecule to be three-coordinate and the other four-coordinate. The following complexes of this type have been isolated from reactions of the ligands with copper(I) halides: $Cu_2Cl_2\{P(p\text{-}CH_3 \cdot C_6H_4)_3\}_3$ (*252*), $Cu_2Cl_2(PHPh_2)_3$ (*1*); $Cu_2X_2(PPh_3)_3$ (X = Cl, Br, I) (*85*); and $Cu_2X_2(NH_3)_3$ (X = Cl, Br, I) (*225*). More recently, other complexes, $Cu_2Cl_2(AsPh_3)_3$ and $Cu_2X_2(SbPh_3)_3$ (X = Cl, Br, I), have been obtained by interaction of the ligands and copper(II) halides in ethanol or with $K[CuI_2]$ in aqueous acetone (*178*). Complex $Cu_2Cl_2\{P(2\text{-pyridyl})Ph_2\}_3$ has been obtained by heating $CuCl_2\{P(2\text{-pyridyl})Ph_2\}_3 \cdot H_2O$ *in vacuo* at 413° (*14*).

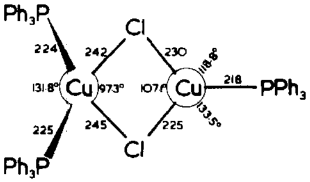


FIG. 5. Structure of $Cu_2Cl_2(PPh_3)_3$ (bond lengths in picometers). [Redrawn by permission from *J. Chem. Soc., Dalton Trans.*, p. 171 (1972).]

The conditions under which the complexes can be isolated are quite critical owing to the lability of the neutral ligands. Nuclear magnetic resonance studies have shown $PHPh_2$ to exchange rapidly at room temperature (*1*), and $P(p\text{-}CH_3 \cdot C_6H_4)_3$ is significantly labile above 193° (*252*). The lability of the ligands contributes toward the destruction of the complexes, since the free ligand produced cleaves the halo bridges, whereas loss of ligand followed by dimerization yields $[CuXL]_4$ species. Thus,

$$8Cu_2X_2L_3 \rightleftharpoons 3[CuXL]_4 + 4CuXL_3 \tag{11}$$

In general, the complexes are not readily accessible but, paradoxically, are often obtained by metathesis from other copper(I) complexes (*56*, *84*, *98*).

V. $CuXL_2$ Complexes

A. COMPLEXES CONTAINING A BIDENTATE ANION

The complexes in this class are generally well-characterized because the denticity of the polyatomic anion is often apparent from its infrared spectrum, and the molecular weights of these compounds in solution approximate their formula weights. Additionally, several complexes of this type have had their structures determined by X-ray crystallography.

Bis(triphenylphosphine)nitratocopper(I) (Fig. 6) has been investigated by all the preceding techniques. It can be prepared from $Cu(NO_3)_2 \cdot 3H_2O$ and PPh_3 in alkanolic solution (*86*) or by recrystallization of $CuNO_3(PPh_3)_3$ from methanol (*177*). The A_1 and B_2 vibrations of the nitrato group in the infrared spectrum of the complex show a separation of ca. 200 cm^{-1} characteristic of bidentate coordination; its molecular weight in chloroform has been reported as 639 (formula wt., 649) (*177*). Its crystal structure has also been determined (*243*, *244*).

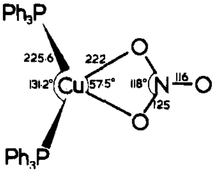


FIG. 6. Structure of $CuNO_3(PPh_3)_2$ (bond lengths in picometers). [Redrawn by permission from *Inorg. Chem.* **8**, 2750 (1969).]

Similar complexes containing two molecules of tri-(*m*-tolyl)- or tri-(cyclohexyl)phosphine have been prepared, and the structure of $CuNO_3\{P(C_6H_{11})_3\}_2$ determined (*10*). The importance of steric crowding between the tertiary phosphine groups of the latter complex is shown by the large P–Cu–P angle and the long Cu–P bonds (Table II).

A related complex whose structure is also known is $CuBH_4(PPh_3)_2$ (*219*, *220*). It has been prepared by reacting $NaBH_4$ with $[CuClPPh_3]_4$ in ethanolic chloroform (*56*) or with an unspecified triphenylphosphinecopper(I) sulfate complex in ethanol (*98*). Its molecular weight in $CHCl_3$ has been found to be 612 (formula wt., 603). The B–H vibrations in its infrared spectrum and those of the corresponding tetradeuteroborato complex (*222*) indicate that the tetrahydridoborato group is bidentate.

Analogous complexes containing tri-(*p*-tolyl)-, tri-(*o*-tolyl)-, and tri-(*p*-anisyl)phosphines are known (*222*).

TABLE II

P–Cu–P ANGLES AND MEAN Cu–P BOND LENGTHS IN $CuX(PR_3)_2$ COMPLEXES

Complex	P–Cu–P	Cu–P (pm)	Reference
$CuNO_3(PPh_3)_2$	131°	225.6	(*244*)
$CuNO_3\{P(C_6H_{11})_3\}_2$	140°	229	(*10*)
$CuBH_4(PPh_3)_2$	123°	227.6	(*220*)
$CuB_3H_8(PPh_3)_2$	120°	228.1	(*221*)
$Cu(CF_3COCHCOCH_3)(PPh_3)_2$	127°	225	(*22*)
$[CuN_3(PPh_3)_2]_2$	122°	226.6	(*359*)

Oligomers of BH_4^- form similar copper(I) complexes, except that in $CuB_3H_8(PPh_3)_2$ (Fig. 7) the hydrogen atoms attached to copper are bonded to different boron atoms (*221*). White $CuB_3H_8L_2$ complexes, where L = PPh_3 (*323*), $AsPh_3$ (*222*), or $PMePh_2$ (*221*), have been precipitated by addition of water to mixtures of CsB_3H_8 (in acetone) and a suitable halocopper(I) complex (in ethanol). The infrared spectra of these complexes show two bands between 2500 and 2200 cm^{-1} due to terminal B–H vibrations; other bands below the latter frequency were assigned to bridging hydrogen atom vibrations. The triphenylarsine and -phosphine complexes have molecular weights in benzene solution close to their formula weights.

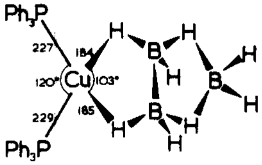


FIG. 7. Structure of $CuB_3H_8(PPh_3)_2$ (bond lengths in picometers). [Redrawn by permission from *Inorg. Chem.* 8, 2755 (1969).]

Bis(triphenylphosphine)copper(I) complexes containing octahydropentaborato or nonahydrohexaborato groups have been synthesized from $CuCl(PPh_3)_3$ and KB_xH_y in dichloromethane–tetrahydrofuran mixtures at 195° (*42*). The latter complex is less stable to aerial oxidation than the former. Terminal B–H vibrations were observed in their infrared spectra, but no vibrations due to bridging hydrogen atoms were reported. Compound $CuB_{10}H_{13}(PPh_3)_2 \cdot CH_2Cl_2$ has been synthesized from $CuCl(PPh_3)_3$ and $NaB_{10}H_{13}$ in dichloromethane (*192*).

Studies using ^1H and ^{11}B NMR have proved of little value in investigating anion structure of the hydridoborato complexes, owing either to nonrigidity of the coordinated anion or to exchange between free and coordinated anion (*27*).

Compound $CuBH_4(PPh_3)_2$ can readily be converted into other copper(I) complexes, thus it reacts with ethanolic perchloric or tetrafluoroboric acids to give salts of the cation $[(Ph_3P)_2CuH_2BH_2Cu(PPh_3)_2]^+$ further, if the perchlorate is reacted with $NaBPh_4$ in methanol, the tetraphenylborate salt can be isolated (*57*). The structure of the cation was inferred from its infrared spectrum, which shows no terminal B–H vibrations. The $CuX(PPh_3)_2$ (X = acac, PhCOCHCOPh, NO_3) complexes are obtained by reacting $CuBH_4(PPh_3)_2$ with acetylacetone, dibenzoylmethane, or nitric acid (*56*), whereas passing HCl gas into a benzene solution of the complex yields $Cu_2Cl_2(PPh_3)_3$ (*98*).

Six bis(triphenylphosphine)(β-diketonato)copper(I) complexes are known. They may be prepared by one or more of reactions (12)–(14).

$$[CuCl(PPh_3)]_4 + Tl^-(\beta\text{-diketonate}) \xrightarrow{C_6H_6} Cu(\beta\text{-diketonato})(PPh_3)_2 \tag{12}$$

(β-diketonate = acac, PhCOCHCOMe, $CF_3COCHCOMe$, $CF_3COCHCOCF_3$) (*129*)

$$Cu(\beta\text{-diketonate})_2 + 3PPh_3 \xrightarrow{EtOH} Cu(\beta\text{-diketonato})(PPh_3)_2 \tag{13}$$

(β-diketonate = $CF_3COCHCOMe$, $CF_3COCHCOCF_3$, or thienyltrifluoroacetylacetonate) (*10*)

$$CuBH_4(PPh_3)_2 + \beta\text{-diketone} \xrightarrow{CHCl_3} Cu(\beta\text{-diketonato})(PPh_3)_2 \tag{14}$$

(β-diketone = $CH_3COCH_2COCH_3$, dibenzoylmethane) (*56*)

Reaction (12) is probably the most useful, since, despite the apparent simplicity of reaction (13), neither $Cu(acac)_2$ nor $Cu(Bu^tCOCHCOBu^t)_2$ (*175*) is reduced under these conditions. The apparent molecular weights of the complexes in chloroform solution are slightly less than their formula weights. This is most probably due to the loss of a triphenylphosphine ligand. Studies using ^1H NMR show the β-diketonato groups to be symmetrically bonded (*129*), and C–O vibrations coupled with C=C were observed in their infrared spectra in the expected region of 1700 to 1500 cm^{-1} (*10, 129*). The structure of $Cu(CF_3COCHCOCH_3)(PPh_3)_2$ has been determined by X-ray crystallography (*22*). A related, monomeric, bis(triphenylarsine) complex may be obtained by fusing the ligand and $Cu(CF_3COCHCOCF_3)_2$ at 343° (*357*).

Certain copper(II) carboxylates can be reduced by triphenylphosphine in alkanolic solution to $Cu(carboxylato)(PPh_3)_2$ complexes, where carboxylate = formate, acetate, benzoate, *o*- or *m*-toluate, *p*-nitrobenzoate, phenylacetate, $\frac{1}{2}$-maleate, $\frac{1}{2}$-fumarate, $\frac{1}{2}$-monochloromaleate, or $\frac{1}{2}$-succinate (*146*). The acetato and benzoato complexes have been obtained less conveniently from the unstable copper(I) salts (*294*). When it was possible to determine the molecular weights of these complexes in chloroform—the dibasic acid complexes were insoluble—the found values agreed closely with the formula weights. Their infrared spectra show them to contain bidentate carboxylato groups (*146*). Thus, it would appear that the dibasic carboxylato groups bridge two $Cu(PPh_3)_2$ units. Generally, complexes of this stoichiometry are formed only from the copper(II) salts of weak acids, but it has proved possible to prepare $CuO_2C \cdot CF_3(PPh_3)_2$ directly from $CuO_2C \cdot CF_3$ and triphenylphosphine (*107*).

Bis(triphenylphosphine)copper(I)(*N*,*N*-dialkyldithioarbamato) complexes have also been prepared. The *N*,*N*-dimethyl and *N*,*N*-diethyl complexes have been obtained by reducing their copper(II) salts with PPh_3 in chloroform, but the *N*,*N*-dipropyl and *N*,*N*-dibutyl derivatives are best prepared by fusing tetrakis-[*N*,*N*-dialkyldithiocarbamatocopper(I)] with the ligand. Complex $Cu(S_2CNEt_2)(PPh_3)_2$ has an apparent molecular weight in solution some 40% lower than the formula weight, but opinions vary as to whether this is due to ionization (*198*) or to loss of a PPh_3 ligand (*46*).

B. Dimeric Complexes

Only a few complexes have definitely been established as dimeric. The best characterized is $[CuN_3(PPh_3)_2]_2$ (Fig. 8), whose structure has been determined by X-ray crystallography (*359*, *360*). The complex was prepared by reacting copper(I) chloride, triphenylphosphine, and sodium azide in chloroform. It was long thought to be monomeric because the reaction,

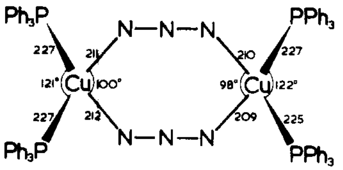


FIG. 8. Structure of $[CuN_3(PPh_3)_2]_2$ (bond lengths in picometers). [Redrawn by permission from *Inorg. Chem.* **10**, 1289 (1971).]

$$[CuN_3(PPh_3)_2]_2 \rightleftharpoons Cu_2(N_3)_2(PPh_3)_3 + PPh_3 \tag{15}$$

gives rise to misleading molecular weight data from solution studies (*294*, *358*). Reactions of this type make it possible that several "monomeric" complexes would prove to be dimeric after more searching investigation. It is believed that the similar complexes $[CuNCS(PPh_2Me)_2]_2$ (*127*) and $[CuXL_2]_2$ ($X = N_3$, NCS; $L = MeOPPh_2$, $EtOPPh_2$) (*361*) are also dimeric.

The bis(triphenylphosphine)azido complex undergoes some interesting addition reactions, with CF_3CN to give a bis(trifluoromethyltetrazole) derivative, and with CS_2 to give a bis(thiotriazole) complex. The latter may be photolyzed in chloroform to $[CuNCS(PPh_3)_2]_2$ (*361*).

A dimeric structure has been proposed for $[Cu(BH_3CN)(PPh_3)_2]_2$ on the basis of its infrared spectrum and a preliminary X-ray crystallographic study. These are consistent with Cu–H–B–C–N–Cu bridges, but no molecular weight in solution was determined to support this view. The complex was prepared by precipitating it from a chloroform solution of $[CuCl(PPh_3)]_4$ and $NaBH_3CN$ by ethanol (*224*).

The molecular weights of $CuX(2\text{-phenylisophosphindoline})_2$ complexes ($X = Cl$, Br, I) and $CuX(PHPh_2)_2$ ($X = Br$, I) in chloroform or benzene led to the conclusion that they are dimeric in solution. The chloro- and bromo- 2-phenylisophosphindoline complexes were prepared by reacting the ligand with CuX_2 ($X = Cl$, Br) in aqueous acetone, and the remainder by interaction of the ligands and copper(I) halides (*1*, *218*). Similarly, the molecular weight determinations made on the amine complexes $[CuCl(NHEt_2)_2]_2$ (*70*), $[CuBr(RNH_2)_2]_2$ [$R = C_8H_{17}$, $C_{10}H_{21}$, $C_{18}H_{37}$ (*354*), and $C_{12}H_{25}$ (*49*)] implied that they are also dimeric. The conductivities of solutions of the bis(dodecylamine) complex in benzene increase with time which is probably due to the rearrangement,

$$[CuXL_2]_2 \rightleftharpoons [CuL_4][CuX_2] \tag{16}$$

This reaction is also believed to take place in nitrobenzene solutions of $[CuX(AsMePh_2)_2]_2$ complexes ($X = Cl$, Br) (*267*).

Complex $CuCl\{SC(NH_2)(OEt)\}_2$ can be prepared by reacting the ligand with either copper(I) or copper(II) chloride in ethanol, or with $CuCl\{SC(NH_2)(OEt)\}$ (*101*). Paradoxically, the complex was found to be dimeric in boiling benzene but monomeric in freezing acetic acid (*299*).

C. MONOMERIC COMPLEXES

Nine complexes of this stoichiometry have been established as monomers containing three-coordinate copper(I). Of these the best characterized is the complex between 2-(dimethylarsino)allylbenzene and copper(I) iodide. This complex is monomeric in chloroform and only slightly associated in concentrated acetone solutions. Further, its mull infrared spectra showed no positional change for the weakly infrared active C=C vibration found at 1640 cm^{-1} in the spectrum of the free ligand; additionally, the ^1H NMR spectrum of the ligand is little changed on complexation (*28*).

Fusion of triphenylphosphine or arsine with CuCN results in the formation of $CuCN(ZPh_3)_2$ (Z = P, As). Their infrared spectra indicate that, although weak cyano bridging occurs in their crystals, they are monomeric in 2-aminoethanol solution (*78*). Compound $CuCN(PPh_3)_2$ has an apparent molecular weight of 685 (formula wt. 611) in chloroform solution (*294*).

The bulky ligand tri(cyclohexyl)phosphine reduced copper(II) chloride or bromide in ethanolic solution to $CuX\{P(C_6H_{11})_3\}_2$ (X = Cl, Br) complexes. The far-infrared spectrum of the chloro complex indicated that it contained terminal chloride, and the molecular weights of these complexes in solution are consistent with a monomeric formulation (*248*). Similarly, the molecular weight of $CuCl(SbPh_3)_2$—obtained by fusion of the ligand with CuCl—in benzene shows it to be monomeric (*329*).

Reaction of $CuCl(PPh_3)_3$ with NaOPh or NaSPh gives the bis(triphenylphosphine)copper(I) phenato or thiophenato complex. Their molecular weights in solution are much lower than their formula weights, as is the apparent molecular weight of $CuCl(PPh_3)_2$ (*294*). This would seem to indicate that the three complexes are monomeric in solution.

In the absence of any evidence to the contrary, the following complexes must be considered to be monomeric, but further investigation would probably show several to be dimeric with halogen bridges. Difficulties in determining their degree of polymerization arise because of the limited solubilities of some of the complexes, although molecular weight determinations were seldom undertaken in work carried out before the 1950s.

Insoluble complexes include $CuI(PPhMe_2)_2$, $CuI(p\text{-}Me_2N\cdot C_6H_4\cdot PR_2)_2$ (R = Me, Et), and $CuI(p\text{-}Me_2N\cdot C_6H_4\cdot AsMe_2)_2$ (*61*, *62*); $CuX(AsPhMe_2)_2$ (X = Cl, Br) (*50*), $CuBr(SbPh_3)_2$ (*178*); and bis{tri-(2-thiophenyl)phosphine}chlorocopper(I) (*170*).

Complexes for which no molecular weight data have been reported despite their solubility are the unstable phosphine complexes, $CuX(PH_3)_2$ [X = Cl, Br (*165*), I (*165*, *309*)], which readily lose one phosphine ligand; bis{tri(cyclohexyl)phosphite}bromocopper(I) (*15*); $CuCl(Me_2NPF_2)_2$ (*74*), which is probably P-bonded; and $CuXpy_2$ [X = Br (*341*), I (*340*)]. The corresponding cyano complex (*340*) may possibly be dimeric since copper(I) cyanide is dimeric in pyridine in contrast to copper(I) bromide (*351*); CuCN also combines with two molecules of EtNC in diethyl ether to give $CuCN(EtNC)_2$ (*161*). With the exception of $CuBr(SbPh_3)_2$, which was obtained from $CuBr_2$, all the above complexes have been obtained as a result of reacting the ligand with a copper(I) salt.

D. $[CuL_2]X$ COMPLEXES

The $[CuL_2]X$ salts commonly occur with $L = NH_3$; three have been prepared in liquid ammonia (*257*, *314*):

$$[Cu(NH_3)_4][NO_3]_2 + Cu \longrightarrow 2[Cu(NH_3)_2]NO_3 \qquad (17)$$

$$Cu_2O + NH_4X \longrightarrow 2[Cu(NH_3)_2]X + H_2O \qquad (X = NO_3, ClO_4) \qquad (18)$$

$$CuI + LiIO_3 \longrightarrow [Cu(NH_3)_2]IO_3 + LiI \qquad (19)$$

By contrast, $[Cu(NH_3)_2]_2SO_4$ or its monohydrate are precipitated by ethanol after either hydrazine sulfate (*278*) or electrolytic (*119*) reduction, respectively, of $CuSO_4$ in aqueous ammonia. Copper metal reduces copper(II) chlorate in aqueous ammonia to a colorless solution which presumably contains the unisolated salt $[Cu(NH_3)_2]ClO_3$ (*248a*).

Copper metal also reduces copper(II) perchlorate to [Cu(4-cyanopyridine)$_2$]ClO_4 in butan-2-ol at 353° in the presence of the ligand. The cyano group's infrared absorption at 2240 cm^{-1} is unchanged on complexation, so the ligands are coordinated solely through the ring nitrogen (*117*).

Bis{tri(cyclohexyl)phosphine}copper(I) perchlorate is obtained on refluxing the tertiary phosphine with copper(II) perchlorate in ethanol; smaller tertiary phosphines give $[Cu(PR_3)_4]ClO_4$ complexes; thus, this complex is obtained because of the impossibility of coordinating more than two tri(cyclohexyl)phosphine ligands to one copper atom (*248*).

Compound $[Cu\{SC(NH_2)_2\}_2]Cl$ (*195*) is perhaps best regarded as an ionic complex since the Cu–Cl distance in its crystals is very long (*322*); the cation is polymeric and made up of trigonal CuS_3 units sharing corners. Nuclear quadrupole resonance (NQR) experiments also lead to the conclusion that the halogen in $[Cu\{SC(NH_2)_2\}_2]X$ and $[Cu\{SC(NH)_2C_2H_4\}_2]X$ (X = Cl, Br) complexes is ionic (*135*). The bis-(2-imidazolidinethione) complexes can be prepared by reacting the ligand with CuX (X = Cl, Br, I) in water (*249*).

VI. $CuXL_3$ Complexes

A. COVALENT COMPLEXES

There are a very large number of complexes in this subgroup. The principal complexes isolated are listed in Table III. It has been widely assumed that the ligands form a distorted tetrahedron around the copper atom. Generally speaking, their physical properties are in accordance with this view. They are unionized in solution, but one neutral ligand is often dissociated in solution, e.g., the molecular weight of $CuO_2C \cdot CF_3(PPh_3)_3$ is half its formula weight in chloroform (*146*) or dichlorobenzene (*107*). The structure found for $CuNO_3(PMePh_2)_3$ (*238*) by X-ray crystallography confirms these assumptions. In this compound the large tertiary phosphine groups encroach upon the small monodentate nitrato group. Cursory studies of the structures of $CuCl(PMePh_2)_3$ (*273*) and $CuCl(PPh_3)_3$ (*6*) indicate that they too have a distorted tetrahedral arrangement of ligands.

A variety of methods has been used to prepare these complexes; the following seem to be of the most general application.

From copper(I) salts (*1*),

$$CuX + 3PHPh_2 \xrightarrow{EtOH} CuX(PHPh_2)_3 \tag{20}$$

from other copper(I) complexes (*133*),

$$[CuCl(PPh_3)]_4 + 8PPh_3 + 4Ph_3GeLi \xrightarrow{(CH_2OMe)_2} 4Cu(GePh_3)(PPh_3)_3 + 4LiCl \tag{21}$$

or from copper(II) salts using the ligand as reducing agent (*176*)

$$2CuCl_2 + 7PPh_3 \xrightarrow[\text{reflux}]{EtOH} 2CuCl(PPh_3)_3 + OPPh_3 \tag{22}$$

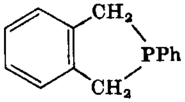
B. IONIC COMPLEXES

With few exceptions, the ionic complexes are derived from sulfur ligands. In $[Cu(SPMe_3)_3]ClO_4$ (*241*) there is a trigonal planar arrangement of ligands around the central copper atom (*111*). There is a whole series of $[CuL_3]X$ complexes where L = Me_3PS, Et_3PS, Pr^i_3PS, Me_2PhPS, Ph_3PS, Ph_3AsS, or Ph_3PSe and X = ClO_4 or BF_4. These have been prepared from the ligand and appropriate copper(II) salt in ethanol, and prior reduction with SO_2 is required for the Ph_3PS, Me_2PhPS, and Ph_3PSe complexes. All the complexes were electrolytes in nitromethane or acetone, and their infrared spectra showed a reduction in the sulfur–pnictide stretch frequency upon coordination.

There also exists a considerable number of ionic tris(thiourea) complexes. Thiourea is capable of reducing copper(II) salts to copper(I) complexes in acid solution to form $[Cu(thiourea)_3]^+$ salts. The following have been isolated: chloride (*194, 195*), nitrate (*194*), oxalate (*194, 195, 298*), monohydrogen arsenate, and phosphate (*298*).

TABLE

ISOLATED $CuXL_3$

	Anionic					
Neutral ligand	F	Cl	Br	I	NO_3	RCO_2
NH_3	—	*(280)*	*(280)*	*(280)*	—	—
$PHPh_2$	—	*(1)*	*(1)*	*(1)*	—	—
PPh_3	*(176)*	*(56)* *(176)*	*(56)* *(176)*	*(56)*	*(177)*	*(107)*[a] *(146)*[b]
	—	—	—	*(75)*	—	—
PMe_2Ph	—	*(218)*	*(218)*	*(218)*	*(10)*	—
$PMePh_2$	—	*(218)*	*(218)*	*(218)*	*(10)*	—
$PEtPh_2$	—	—	—	—	*(10)*	—
$PEt_2(p\text{-}CF_3{\cdot}C_6H_4)$	—	—	—	*(62)*	—	—
$P(C{\equiv}CPh)Ph_2$	—	*(188)*	—	—	—	—
$P(CH_2SiMe_3)_3$	—	*(168)*	—	—	—	—
$AsMePh_2$	—	*(267)*	*(267)*	*(49, 267)*	—	—
$AsPh_3$	—	*(329)*	*(178)*	—	*(177)*	—
$SbPh_3$	—	—	—	—	*(177)*	—
Me_3CNC	—	—	*(272)*	—	—	—

[a] $R = CF_3$.

[b] R = H, CH_3, CF_3, CH_2Cl, Ph, o-tolyl, o-, m-, or $p\text{-}C_6H_4{\cdot}NO_2$, $o\text{-}C_6H_4{\cdot}OH$, ½-succinate.

The structures of the chloride (*193, 269*) and perchlorate have been determined, and both contain copper atoms surrounded tetrahedrally by four sulfur atoms. The perchlorate salt is binuclear (*147*); four of the six thiourea ligands are monodentate and the remaining two bridge the copper atoms. The cation of the chloride is polymeric consisting of CuS_4 tetrahedra sharing corners. This polymeric structure is obviously degraded by water to thiourea(aquo)copper(I) complexes since the conductivities of $[Cu(thiourea)_3]Cl$ solutions increase markedly with increasing dilution (*298*).

Tris-(2-imidazolidinethione)copper(I) acetate and sulfate have similarly been obtained by reducing the appropriate copper(II) salt with the ligand in water. They are presumably ionic since solutions of the latter gave an immediate precipitate of $BaSO_4$ when treated with $BaCl_2$ (*249*). Tris-(*O*-ethylaminothioformate)copper(I) chloride (*101, 299*) and bromide (*299*) have been prepared from the copper(I) salts.

Steric hindrance between the methyl groups of adjacent 2-picoline ligands results in the formation of $[Cu(C_6H_7N)_3]ClO_4$ when $Cu(ClO_4)_2$ is reduced by copper metal in solution of the ligand (*213*). Other 2-substituted pyridines, e.g., 2,5-lutidine, 2-ethyl or 2-(isopropyl)pyridine, give tris(amine) complexes, whereas pyridine or 4-picoline give $[Cu(amine)_4]ClO_4$.

III

COMPLEXES

ligand							
$GePh_3$	$SnCl_3$	BF_4	B_3H_8	B_9H_{14}	$B_{11}H_{14}$	BH_3CN	$B_9H_{12}S$
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
(133)	*(106)*	*(56)*	—	*(192)*	*(192)*	*(223)* *(224)*	*(192)*
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—
—	—	—	—	—	—	*(224)*	—
—	—	—	*(222)*	—	—	*(224)*	—
—	—	—	—	—	—	—	—

VII. [CuL₄]X Complexes

The majority of the $[CuL_4]X$ are either perchlorate or nitrate complexes, but some iodide and tetrafluoroborate salts are known.

The most numerous subgroup is that where L is an alkyl or aryl cyanide. A wide variety of preparative methods have been employed, e.g.,

$$[Ag(MeCN)_4]X + Cu \longrightarrow [Cu(MeCN)_4]X + Ag \quad [X = NO_3\ (\textit{250}),\ ClO_4\ (\textit{29})] \tag{23}$$

$$2Cu_2O + 12RCN + 4Et_2O\cdot BF_3 \longrightarrow 3[Cu(RCN)_4]BF_4 + CuBO_2 + 4Et_2O \quad [R = Me, Et, Ph, C_6H_5CH_2\ (\textit{242})] \tag{24}$$

$$[ArN_2]BF_4 + 4MeCN + Cu \longrightarrow [Cu(MeCN)_4]BF_4 \tag{25}$$

$$[Ph_3C]BF_4 + 4MeCN + Cu \longrightarrow [Cu(MeCN)_4]BF_4\ (\textit{242}) \tag{26}$$

$$Cu_2O + 8MeCN + 2HClO_4(aq) \longrightarrow 2[Cu(MeCN)_4]ClO_4 + H_2O\ (\textit{156, 226}) \tag{27}$$

$$CuX_2 + Cu \xrightarrow{MeCN} 2[Cu(MeCN)_4]X \quad [X = SO_3F\ (\textit{246}),\ NO_3,\ ClO_4,\ BF_4\ (\textit{152})] \tag{28}$$

$$Cu(ClO_4)_2\cdot 6H_2O + Cu + RCN \xrightarrow{\text{butan-2-ol}} [Cu(RCN)_4]ClO_4 \quad [R = Me, Et, Ph, p\text{-}MeO\cdot C_6H_4, p\text{-}NO_2\cdot C_6H_4, \text{1-naphthyl}\ (\textit{200})] \tag{29}$$

Of these, reactions (28) and (29) have undoubtedly the widest application and are the most convenient.

There is much evidence for the ionic nature of these complexes. Many give conducting solutions in solvents such as methyl cyanide, nitromethane, or nitrobenzene. The infrared spectra of the polyatomic anions are all typical of the free anions.

Pyridine, quinoline, or 4-picoline solutions of $Cu(ClO_4)_2$ are reduced by copper metal to $[Cu(amine)_4]ClO_4$ salts. X-Ray crystallographic investigations reveal the tetrakis(pyridine)copper(I) cation is tetrahedral (*212*). Compound $[Cupy_4]ClO_4$ can also be prepared by displacement of MeCN from $[Cu(MeCN)_4]ClO_4$ by pyridine under anaerobic conditions (*199*). The complex $[Cu(p\text{-}CH_3 \cdot C_6H_4 \cdot NC)_4]ClO_4$ is also known (*302*).

Tertiary phosphines (*10, 56, 75, 86*), arsines (*178, 267, 329*), and the phosphite $P(OCH_2)_3CMe$ (*342*) reduce copper(II) salts to $[CuL_4]X$ complexes if X is a poorly coordinating anion. Almost invariably copper(II) perchlorate yields this type of complex, but copper(II) nitrate forms ionic complexes with these ligands only if certain steric conditions are satisfied, e.g., triphenylarsine gives $CuNO_3(AsPh_3)_3$ (*177*), but the smaller tertiary arsine $AsMePh_2$ forms the ionic complex $[Cu(AsMePh_2)_4]NO_3$ (*267*). If triphenylarsine is fused with either CuCl or $CuCl_2$, air-unstable $[Cu(AsPh_3)_4]Cl$ is formed. This salt is a 1:1 electrolyte in nitrobenzene. Complexes $[CuX(AsMePh_2)_2]_2$ (X = Cl, Br, I) are believed to isomerize in nitrobenzene to $[Cu(AsMePh_2)_4][CuX_2]$ salts (*49*).

If copper(II) perchlorate is reacted with tris(dimethylamino)phosphine sulfide in methyl cyanide, complexes $[(Me_2N)_3PS_2P(NMe_2)_3][ClO_4]_2$ and $[Cu\{SP(NMe_2)_3\}_4]ClO_4$ are formed (*313*). This reaction is typical of the reducing action of sulfur ligands. Thus, copper(II) nitrate is reduced to $[Cu(2\text{-imidazolidinethione})_4]NO_3$ by the ligand, and, if this complex is heated with sodium hydroxide, the oxide $[Cu(2\text{-imidazolidinethione})_4]_2O$ is formed. This latter compound is slightly air-sensitive but dissolves in mineral acids to give other copper(I) complexes (*249*). The nitrate salt has been shown to be ionic by polarography (*206*). Thioacetamide reduces copper(II) chloride to $[Cu(thioacetamide)_4]Cl$ (*90*); the infrared spectrum of the cation shows the ligand to be sulfur-bonded (*204*) in accordance with the X-ray crystal study (*333*).

VIII. CuX(biL) Complexes

Although copper is nominally three-coordinate in CuX(biL) complexes, bridging by the anionic ligand has been widely proposed (despite very little evidence for this) to increase the coordination number of copper to its customary four.

Many of the iodo complexes may be prepared from copper(I) iodide by the reaction

$$2CuI + 2biL \xrightarrow[Me_2CO]{KI-H_2O} [CuI(biL)]_2 \qquad (30)$$

[biL = phen, bipy (*176*), 2,2′-pyridylquinoline (*179*), or 8-(dimethylarsino)quinoline (*20*)]

or by displacement of monodentate ligands from other copper(I) complexes, e.g. (*234*),

$$2CuI(Bu^n_3)(bipy) \xrightarrow[Me_2CO]{heat} [CuI(bipy)]_2 + 2PBu^n_3 \qquad (31)$$

or by reduction of a copper(II) salt in the presence of the ligand and iodide ion, e.g. (*328*),

$$CuSO_4 + N_2H_4 \cdot HCl + KI + bipy \longrightarrow [CuI(bipy)]_2 \qquad (32)$$

Other iodo complexes have been isolated containing 1,2-bis(dimethylarsino)benzene (*181*), bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane (*237*), 2,9-dimethyl-1,10-phenanthroline (*145*), 8-methylthioquinoline (*214*), 2-(diphenylphosphino)allylbenzene and 2-(diphenylphosphino)methallylbenzene (*28*), and 2-(dimethylarsino)-*N*,*N*-dimethylaniline (*136*). The structure of the last mentioned complex was investigated by X-ray crystallography and was found, indeed, to be dimeric. Molecular weight determinations have shown bis{bis(diphenylphosphino)methane}di-μ-iododicopper(I) and the corresponding $Ph_2PC_2H_4PPh_2$ complex to be dimeric in dichloromethane (*237*), and the halocopper(I) complexes of 2-(diphenylphosphino)allylbenzene and 2-(diphenylphosphino)methallylbenzene (*28*), and bis(2,9-dimethyl-1,10-phenanthroline)di-μ-acetatodicopper(I) (*146*) to be dimeric in chloroform. One factor that may give rise to misleading molecular weight results is the possibility of ionization isomerism, e.g. (*49*, *181*),

$$[CuI(diars)]_2 \xrightleftharpoons[C_6H_6]{PhNO_2} [Cu(diars)_2][CuI_2] \qquad (33)$$

Ionic complexes of the preceding type are included in Section IX which deals with $[Cu(biL)_2]^+$ complexes.

Only two of the phosphorus atoms in cyclic phosphine ligands $(RP)_4$ (R = Bu^t, C_8H_{17}, cyclohexyl) coordinate to the metal and $(Bu^tP)_4CuCl$ is dimeric in benzene. The other cyclotetraphosphines form similar complexes on reaction with copper(I) halides in carbon tetrachloride (*160*).

The CuCN(biL) complexes (biL = 2,2′-bipyridyl, 1,10-phenanthroline) are monomeric in 2-aminoethanol, but their infrared spectra indicate that they may be di- or polymeric in the solid state; there are no data available to elucidate the structures of the analogous thiocyanato complexes (*78*, *328*).

If the anion is bidentate (but nonbridging), then the complexes are monomeric; this the case for $(Ph_2PC_2H_4PPh_2)CuBH_4$ (*56*) and probably for $(Ph_2PC_2H_4PPh_2)CuNO_3$ (*120*).

The tetrameric complex $(RCu)_4$ (R = 2-benzyldimethylamine) is cleaved by 1,2-bis(diphenylphosphino)ethane (diphos):

$$(RCu)_4 + 8\text{diphos} \xrightarrow[298°]{C_6H_6} 4Ph_2PCu(\text{diphos})\cdot C_6H_6 + 4RH + 4Ph_2PCH{=}CH_2 \qquad (34)$$

It seems likely that this complex is three-coordinate with weakly coordinated benzene occupying the fourth coordination position.

IX. $[Cu(biL)_2]X$ Complexes

The $[Cu(biL)_2]X$ compounds are particularly well-characterized since many are potentially useful in the spectrophotometric determination of copper. The cations containing two molecules of 1,10-phenanthroline or 2,2′-bipyridyl, or their derivatives have molar absorbtivities (ε) in the range 4000–7000 M^{-1} dm^2 for their charge transfer bands in the visible spectrum, and have been extensively investigated (*166*, *173*, *216*, *240*, *251*, *284*, *315–317*). The charge transfer bands in the visible range are lost, however, if partial hydrogenation of the ligand disrupts its extended π-orbital system (*336*).

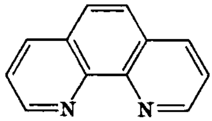
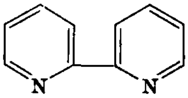
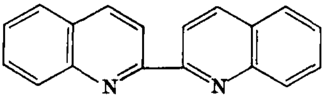
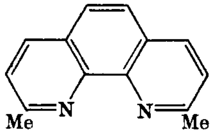
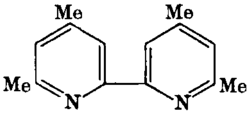
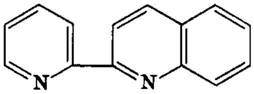
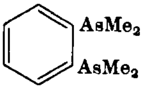
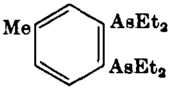
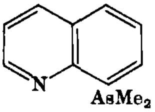
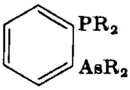
The presence of two bidentate, π-bonding ligands stabilizes copper(I) toward oxidation or disproportionation under analytical conditions. Further, it has been found that the greater the basicity of the nitrogenous ligand, the less readily is the complex oxidized at an electrode (*174*). Spectral and polarographic studies showed that copper(I) was four-coordinate in these complexes, but this has not been confirmed by isolation and analysis of the complexes of the more esoteric ligands in the two series (*8*, *335*).

The complexes may be prepared by (*a*) the action of reducing agents on copper(II) complexes of the ligands (*144*),

$$\begin{gathered} Cu(DMP)_2X_2 + H_3PO_2 \text{ (or } NH_2OH) \longrightarrow [Cu(DMP)_2]X \\ (\text{DMP} = 2,9\text{-dimethyl-}1,10\text{-phenanthroline; } X = ClO_4,\ NO_3,\ \text{or } \tfrac{1}{2}SO_4) \end{gathered} \qquad (35)$$

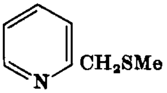
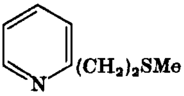
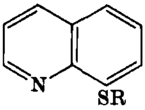
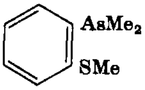
TABLE IV

ISOLATED $[Cu(biL)_2]X$ COMPLEXES

biL	X	References
	I ClO_4 NO_3 Br	(*176, 328*) (*308*) (*177*) (*178*)
	ClO_4, BF_4	(*179*)
	NO_3 ClO_4, BF_4	(*177*) (*179*)
	Phenylalaninate, tyrosinate, tryptophanate ClO_4, NO_3, $\frac{1}{2}SO_4$ Cl, Br, I, I_3	(*208*) (*144*) (*145*)
	ClO_4, NO_3, I, $Br \cdot H_2O$, $Cl \cdot H_2O$, $[CuX_2]$ (X = Cl, Br, I)	(*143*)
	NO_3 BF_4	(*177*) (*179*)
	Br, I, $[CuX_2]$ (X = Cl, Br, I)	(*49, 181*)
	$[CuI_2]$	(*148*)
	ClO_4	(*20*)
	R = Et; Cl, Br, I, $[CuCl_2]$, 4-bromocamphorsulfonate R = Ph; ClO_4	(*73*) (*260*)

(*continued*)

TABLE IV—*continued*

biL	X	References
	ClO_4	(*65*)
	ClO_4	(*64*)
	R = Me; HSO_4, HCO_3, $[CuCl_2]$; R = Me, Ph; ClO_4	(*155*)
	Cl, Br, I, NCS, ClO_4	(*67*)
$Ph_2PC_2H_4PPh_2$	NO_3	(*10*)
	ClO_4	(*120*)
	CF_3CO_2	(*107*)
2-Aminopyridine	I, $[CuX_2]$ (X = Cl, Br, I, NCS)	(*326*)
$Me_2As(CH_2)_3SMe$	ClO_4, $[CuX_2]$ (X = Cl, Br, I)	(*68*)

(*b*) direct interaction of copper(I) halides and ligands (*181*),

$$\mathrm{CuX} + 2\mathrm{diars} \xrightarrow[\mathrm{H_2O}]{\mathrm{KX}} [\mathrm{Cu(diars)_2}]\mathrm{X} \tag{36}$$

(diars = 1,2-bis(dimethylarsino)benzene; X = Br, I)

if a 1:1 ratio of reactants is used, then $[CuX_2]^-$ salts commonly result,

$$2\mathrm{CuI} + 2\mathrm{diars} \xrightarrow[\mathrm{H_2O}]{\mathrm{KI}} [\mathrm{Cu(diars)_2}][\mathrm{CuI_2}] \tag{37}$$

(*c*) using the ligand to reduce a copper(II) salt (*20*),

$$\mathrm{Cu(ClO_4)_2} + 2\mathrm{DMAQ} \xrightarrow{\mathrm{EtOH}} [\mathrm{Cu(DMAQ)_2}]\mathrm{ClO_4} \tag{38}$$

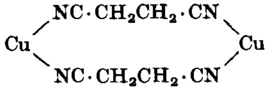
[DMAQ = 8-(dimethylarsino)quinoline]

and (*d*) displacement of monodentate ligands from a copper(I) complex (*177*),

$$\mathrm{CuNO_3(PPh_3)_3} + 2\mathrm{phen} \xrightarrow[353^\circ]{\mathrm{C_6H_6}} [\mathrm{Cu(phen)_2}]\mathrm{NO_3} \tag{39}$$

Isolated complexes of $[Cu(biL)_2]X$ are listed in Table IV. All the complexes are electrolytes in suitable ionizing solvents.

Exceptions to the simple monomeric cation structure are encountered when the bidentate ligand is an α,ω-dinitrile. For example, the complex $[Cu(CNCH_2CH_2CN)_2]NO_3$, first prepared in 1923 (*250*), has recently been shown to have a polynuclear cation made up of



units and free nitrate ions distributed throughout the crystal (*189*); the corresponding complexes containing $CN(CH_2)_3CN$ and $CN(CH_2)_4CN$ ligands have similar structures (*190*). The cation in $[Cu\{(CNCH_2CH_2)_2\}_2]$-ClO_4 is isostructural with that of the nitrate salt (*36*).

X. Organocopper(I) Compounds and Complexes

The widespread use of copper(I) compounds in organic syntheses (*116*) has served to draw attention to the organometallic compounds, which are themselves useful synthetic reagents in organic chemistry (*262*) (Fig. 9).

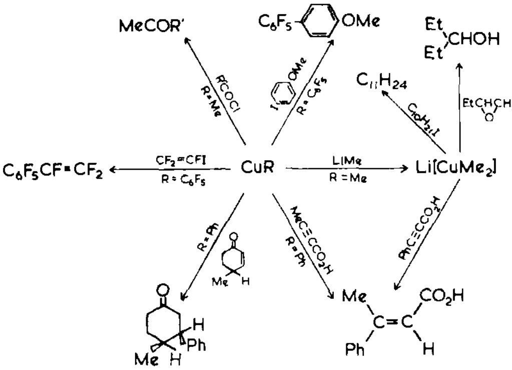


FIG. 9. Some synthetic uses of organocopper compounds. (Data from Ref. *262*)

A. ALKYL AND ARYL COMPOUNDS

The reactive and unstable alkyl and aryl compounds may be prepared at low temperatures from the alkyls and aryls of other metals as follows:

$$\mathrm{CuX + RLi \xrightarrow[273^\circ]{Et_2O} CuR + LiX} \tag{40}$$

[X = I, R = Me (*167*), *cis*- or *trans*-but-2-enyl (*352*);
X = Br, R = Ph (*80*), *o*-tolyl, *p*-tolyl, *o*-anisyl (*55*)]

$$\mathrm{CuX + RMgX' \xrightarrow[273^\circ]{Et_2O} CuR + MgXX'} \tag{41}$$

[X = I, X′ = Br, R = Ph (*150, 293*), *p*-tolyl (*150*); X = X′ = I, R = Ph (*131*);
X = Cl, X′ = Br, R = Et in tetrahydrofuran (THF) at 195° (*345*)]

$$\mathrm{CuCl_2 + LiR \xrightarrow[273^\circ]{EtOH} CuR + LiCl} \tag{42}$$

[R = Me (*130*)]

$$\mathrm{Cu(NO_3)_2 \cdot 3H_2O + PbR_4 \xrightarrow{EtOH} CuR} \tag{43}$$

[R = Me (*25, 26, 82, 83, 132*), Et (*82, 132*), Ph (*132*)]

$$\mathrm{CuCl_2 + ZnR_2 \xrightarrow[273^\circ]{Et_2O} CuR + ZnCl_2 + R\cdot} \tag{44}$$

[R = Me, Et, Pr (*330*)]

$$\mathrm{2Cu + ArN_2BF_4 \xrightarrow[heat]{C_6H_6} CuAr + N_2 + BF_3 + CuF} \tag{45}$$

[Ar = Ph, *o*- or *p*-$\mathrm{C_6H_4NO_2}$, *p*-tolyl (*38*)]

The formation of copper(I) fluoride in reaction (45) seems unlikely, but low yields of aryl copper compounds are obtained owing to pyrolysis during preparation.

None of these methods appears to be of general applicability; a disadvantage of reaction (40)—at least in the case of methylcopper—is that the precipitated alkyl dissolves in excess reagent to give $\mathrm{Li[CuR_2]}$. Preparation from Grignard reagents requires careful choice of halides if optimum yields are to be obtained, and the preparation of ethylcopper is feasible only at low temperatures (*345*).

The decomposition of alkyl and aryl copper compounds has been the subject of much debate. Initially free radical mechanisms were advanced, such theories being supported by the reduced yields of hydrocarbons in the presence of benzoquinone or other free-radical scavengers (*24, 150*). However, under all conditions very poor yields of dimeric alkanes are obtained. These would be the likely products of a free-radical decomposition,

$$\mathrm{2CuR \longrightarrow 2Cu + 2R\cdot \longrightarrow 2Cu + R_2} \tag{46}$$

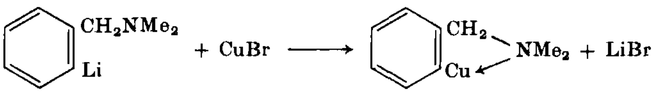
Instead, RH and R − H alkene are formed in approximately equal quantities (*345*), and the following scheme, in which copper(I) hydride participates, has been suggested to explain these products (*352*):

$$\mathrm{CuBu^n(PBu^n_3)} \longrightarrow \mathrm{CuH(PBu^n_3)} + \mathrm{CH_3CH_2CH{=}CH_2} \qquad (47)$$

$$\mathrm{CuH(PBu^n_3)} + \mathrm{CuBu^n(PBu^n_3)} \longrightarrow 2\mathrm{Cu} + 2\mathrm{PBu^n_3} + \mathrm{CH_3(CH_2)_2CH_3} \qquad (48)$$

Biaryls are, however, the main decomposition products of ArCu compounds even though free-radical reactions are not believed to be involved.

Thermally stable arylcopper(I) derivatives result if there is a good donor atom in an aryl side chain, since chelation can occur, e.g.,



(49)

Various aryl-substituted analogs of 2-cupriobenzyldimethylamine can also be obtained by reaction (49) (*338*). The 4-methyl compound has been found to be tetrameric (*140*).

B. FLUOROALKYL AND -ARYL COMPOUNDS

The electron-withdrawing power of fluorine reduces the electron density at the copper–carbon bond and renders it less reactive. Therefore these complexes are more stable than their analogs containing hydrogen.

They can be prepared from Grignard reagents (*53*),

$$\mathrm{R_fMgX} + \mathrm{CuX} \xrightarrow{\mathrm{Et_2O}} \mathrm{R_fCu} + \mathrm{MgX_2} \qquad (50)$$

$$(\mathrm{R_f} = \mathrm{C_6F_5};\ m\text{- or } p\text{-}\mathrm{CF_3C_6H_4};\ m\text{- or } p\text{-}\mathrm{C_6H_4F})$$

or by exchange reactions,

$$m\text{-}\mathrm{CF_3\cdot C_6H_4Cu} + t\text{-}\mathrm{C_4F_9Br} \xrightarrow[273^\circ]{\mathrm{Et_2O\text{–}dioxan}} t\text{-}\mathrm{C_4F_9Cu} + m\text{-}\mathrm{CF_3\cdot C_6H_4Br} \qquad (51)$$

The fluoroalkyls are obtained as 1:1 and 2:1 dioxan adducts after the magnesium halides have been precipitated by this reagent. Their enhanced thermal stability allows them to be freed from dioxan by heating them *in vacuo* for 5 hr at 403°. At higher temperatures they pyrolyze to biaryls, but the *m*-trifluoromethylphenylene compound decomposes in stages (*54*)

$$[m\text{-}\mathrm{CF_3C_6H_4Cu}]_8 \longrightarrow (m\text{-}\mathrm{CF_3C_6H_4})_6\mathrm{Cu_8} + (\mathrm{CF_3C_6H_4})_2 \qquad (52)$$

$$(m\text{-}\mathrm{CF_3C_6H_4})_6\mathrm{Cu_8} \longrightarrow (m\text{-}\mathrm{CF_3C_6H_4})_4\mathrm{Cu_8} + (\mathrm{CF_3C_6H_4})_2 \qquad (53)$$

The intermediate compounds are mixed Cu(I)–Cu(0) complexes. Perfluorophenylcopper decomposes directly to fluorocarbon and copper

$$[C_6F_5Cu]_4 \longrightarrow 4Cu + 2(C_6F_5)_2 \qquad (54)$$

The polymericity of these compounds has been determined by osmometry (*54*), cryoscopy (*52*, *54*), and mass spectrometry (*52*). They are hydrolyzed or oxidized by air to biaryls. Despite being oxidized to biaryls by dibenzoyl peroxide, they do not give rise to free radicals in these decompositions.

C. Complex Copper(I) Alkyls and Aryls

Complexing the unstable organocopper compounds with π-bonding ligands fails to confer much additional stability, but several complexes are sufficiently stable to be isolated. It seems best to prepare them from an existing copper(I) complex, e.g. (*167*),

$$[CuI(PBu^n_3)]_4 + 4LiMe \xrightarrow{273^\circ} 4CuMe(PBu^n_3) + 4LiI \qquad (55)$$

rather than to react an organocopper compound with ligand, e.g. (*330*),

$$CuMe + bipy \xrightarrow{195^\circ} CuMe(bipy) \qquad (56)$$

Other complexes that have been isolated include $CuAr(py)_3$ [Ar = Ph, p-$NO_2 \cdot C_6H_4$ (*38*)], CuMeDMSO (*330*), $CuMe(PPh_3)_3$ (*84*), and $(CuPh)_n(PPh_3)$ [n = 2, 3 (*81*)]. Compound Cu(2-benzyldimethylamine)(diphos) has been prepared by cleaving tetrakis-(2-cupriobenzyldimethylamine) with $Ph_2PC_2H_4PPh_2$ (*339*).

D. Olefin Complexes

Olefinic complexes of copper have been reviewed in Volume 12 of this series (*289*). Since the appearance of this review, [Cu(cycloocta-1,5-diene)$_2$]BF_4 has been prepared by electrolysis of $Cu(BF_4)_2$ in methanolic diolefin at copper electrodes (*231*). Complexes (cycloocta-1,5-diene)$CuO_2C \cdot CF_3$, (cyclooctatetrene)$(CuO_2C \cdot CF_3)_2$, and (cycloocta-1,5-diene)$(CuO_2C \cdot CF_3)_2$ have been obtained as white or pale yellow solids by reacting $CuO_2C \cdot CF_3$ with the olefins in pentane or benzene, respectively (*107*). The structure of Cu_2Cl_2(*trans*-cyclooctene)$_3$ (Fig. 10) has been determined (*124*) and is reminiscent of the structure of $Cu_2Cl_2(PPh_3)_3$ (Fig. 5).

When copper(I) oxide is dissolved in a benzene solution of trifluoromethane sulfonic acid the complex $Cu(CF_3SO_3) \cdot \frac{1}{2}C_6H_6$ results (*319*).

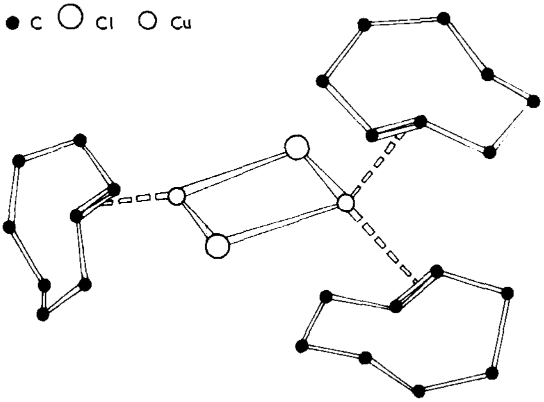


FIG. 10. Structure of Cu_2Cl_2(*trans*-cyclooctene)$_3$. [Redrawn by permission from *Chem. Commun.* p. 1054 (1969).]

This reacts with cycloocta-1,5-diene or *endo*-dicyclopentadiene to give $[Cu(diolefin)_2]O_3S \cdot CF_3$ complexes, and with cyclooctatetrene, cyclododeca-1,5,9-triene, cycloocta-1,3-diene, or norbornylene to give $Cu(olefin)O_3S \cdot CF_3$ complexes; cyclohepta-1,3,5-triene can replace benzene in the parent complex yielding $Cu(CF_3SO_3) \cdot \frac{1}{2}$(triolefin).

Substituted olefins also complex with CuCl. The halide dissolves in allyl alcohol owing to complex formation (*183*, *184*). Other unsaturated alcohols give complexes of the type (alkenol)CuCl and $[(alkenol)Cu]^+$ when added to solutions of CuCl in aqueous HCl (*185*). Similar complexes are formed with various unsaturated carboxylic acids, and the stability of the complexes is influenced by the stereochemistry about the double bond (*13*). Maleic acid, however, forms the anionic complex $[CuCl(O_2C \cdot CH{=}CH.CO_2H)]^-$ in addition to the neutral and cationic complexes (*11*, *12*).

E. CYCLOPENTADIENYL COMPLEXES

The cyclopentadienyl complex $Cu(C_5H_5)PEt_3$ was formerly believed to contain a σ-bonded cyclopentadienyl group (*355*). This erroneous conclusion was reached because of its reactivity toward acids, but it was at variance with the behavior of π-bonded complexes such as ferrocene. Careful reappraisal of its infrared spectrum (*87*, *122*) led to the view that the cyclopentadienyl group was π-bonded; this was confirmed by X-ray crystallography (*103*). The structure of $Cu(\pi\text{-}C_5H_5)(PPh_3)$ (Fig. 11) has been determined to a high degree of precision (*89*).

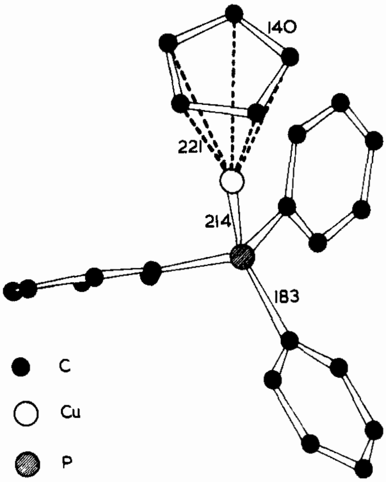


Fig. 11. Structure of Cu(π-C_5H_5)(PPh_3) (bond lengths in picometers). [Redrawn by permission from *J. Amer. Chem. Soc.* **92**, 2353 (1970).]

The most convenient route to the complexes is from an iodocopper(I) complex (*88*),

$$[CuIL]_n + nTl(C_5H_5) \xrightarrow{\text{pentane}} nCu(C_5H_5)L + nTlI \qquad [L = PEt_3,\ PBu^n_3,\ PPh_3,\ P(OMe)_3,\ CH_3NC] \tag{57}$$

However, cyclopentadienyl and indenyl *t*-butyl isocyanide complexes have been obtained by the original method, that is, by heating Cu_2O with hydrocarbon and ligand. Although Cu(π-C_5H_5)(Bu^tNC) is undoubtedly isostructural with the tertiary phosphine complexes, the indenyl complex, Cu(indenyl)$(Bu^tNC)_3$, is almost certainly σ-bonded on account of its infrared and NMR spectra to say nothing of its stoichiometry (*303*).

An unstable carbonyl complex (*88*) has also been prepared,

$$CuCl + CO + Tl(C_5H_5) \xrightarrow[273^\circ,\,10\text{ days}]{\text{pentane}} Cu(\pi\text{-}C_5H_5)(CO) + TlCl \tag{58}$$

F. Carbonyl Complexes

Although copper(I) compounds have been widely used as adsorbents for CO in classic methods of gas analysis (*324*), the stability of the complexes is low, and the 1:1 complexes of CO and copper(I) halides have high dissociation pressures (*30*, *233*, *346*). Apart from the cyclopentadienyl complex already mentioned, the only really stable complexes are those with copper(I) trifluoroacetate (*310*). These may be prepared either in trifluoroacetic acid,

$$Cu_2O + CO + CF_3CO_2H \longrightarrow CuO_2C\cdot CF_3(CO)\cdot CF_3CO_2H \qquad (59)$$

or in aqueous solution

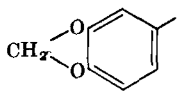
$$Cu_2O + CO + (CF_3CO)_2O + H_2O \longrightarrow CuO_2C\cdot CF_3(CO) \qquad (60)$$

Trifluoroacetic acid may be removed from the adduct *in vacuo*, but it requires prolonged pumping to remove carbon monoxide. The C–O stretch in the infrared spectrum of $CuO_2C\cdot CF_3(CO)$ occurs at 2155 cm^{-1} a value similar to that of 2093 cm^{-1} for the cyclopentadienyl complex (*88*).

G. ACETYLIDES AND ACETYLENE COMPLEXES

Acetylene reacts with copper(I) halides in ammoniacal solution to give the dangerously explosive copper(I) acetylide (*301*); a monohydrate has also been prepared (*306*). The compound can also be prepared in liquid ammonia (*256*).

Monosubstituted acetylenes give polymeric monoacetylides:

$[CuC{\equiv}CR]_n$ [R = Me (*34*), p-MeO·C_6H_4,

(*232*)]

The methylacetylide is probably a tetramer such as the gold(I) compound, and there may be interaction between the metal atoms and triple bonds in addition to the acetylide linkage.

If the monosubstituted acetylides are prepared in liquid ammonia, alkynylocuprate(I) complexes can be formed if there is excess of alkali acetylide present (*225*):

$$CuI + MC{\equiv}CR \longrightarrow CuC{\equiv}CR \xrightarrow{MC\equiv CR} M[Cu(C{\equiv}CR)_2] \xrightarrow{MC\equiv CR} M_2[Cu(C{\equiv}CR)_3] \qquad (61)$$

(M = Na, K; R = H, Me, Ph)

Several of these complexes are precipitated as ammoniates, and they also undergo metathetical reactions:

$$2Na[Cu(C{\equiv}CPh)_2] + [Ni(NH_3)_6][SCN]_2 \xrightarrow{NH_3} [Ni(NH_3)_6][Cu(C{\equiv}CPh)_2]_2 + 2NaNCS \qquad (62)$$

The polymeric acetylides are cleaved by tertiary phosphines or aryl isocyanides, e.g.,

$$[\mathrm{CuC{\equiv}CBu^t}]_n + n\mathrm{PMe_3} \xrightarrow{\mathrm{C_6H_6}} n/3[\mathrm{Cu(C{\equiv}CBu^t)(PMe_3)}]_3 \qquad (63)$$

This yellow-green complex is trimeric in benzene, but dimeric in nitrobenzene (*72*). By analogous reactions, many other tertiary phosphine complexes of monoalkylacetylides have been obtained. Among these is $[\mathrm{Cu(C{\equiv}CPh)PMe_3}]_4$ (Fig. 12), in which two copper atoms are each bound to two trimethylphosphine ligands and the tetramer is held together by metal–metal bonds and interactions with the acetylene ligands (*79*).

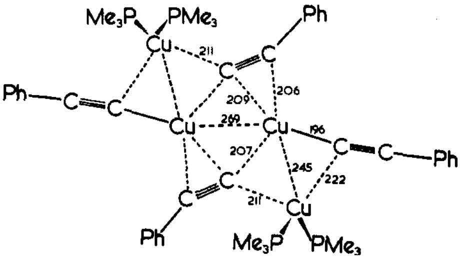
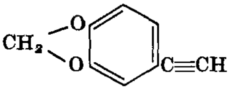


FIG. 12. Structure of $[\mathrm{Cu(C{\equiv}CPh)PMe_3}]_4$ (bond lengths in picometers). [Redrawn by permission from *Acta Crystallogr.* **21**, 957 (1966).]

Complexes $\mathrm{Cu(C{\equiv}C{\cdot}C{\equiv}CPh)(PR_3)}_n$ have also been prepared and are claimed to be more stable to aerial decomposition than the monoacetylide complexes (*72*).

Weak ammoniates of $[\mathrm{Cu(C{\equiv}CPh)}]_3$ are formed when the complex is dissolved in liquid ammonia (*34*). A stronger monomeric complex is formed when the phenylacetylide is reacted with *p*-tolyl isocyanide in pyridine–diethyl ether at 263° K (*191*).

At low temperatures in acid or ethanolic solution, CuCl adds acetylene to give $\mathrm{CuCl{\cdot}C_2H_2}$ (*63*), and $\mathrm{(CuCl)_3{\cdot}C_2H_2}$ (*164*), respectively. These observations are supported by a study of the slow equilibrium between the reactants (*271*). Addition compounds are formed between CuCl and phenylacetylene or (*232*),



These are difficult to free from alkyne and, in ammoniacal solution, are converted to the corresponding acetylides.

The structure of CuCl(hepta-1,6-diyne) consists of Cl–Cu–Cl chains cross-linked by the diyne. Compound CuCl(but-2-yne) is tetrameric, and has a puckered Cu_4Cl_4 ring with the copper atoms on the perpendiular bisectors of the triple bonds. Unlike the C=C bond in Zeise's salt, the C≡C bond in the alkyne complex is coplanar with the copper and two adjacent chlorine atoms (*58*).

XI. Miscellaneous Compounds

A. COMPLEXES CONTAINING NEUTRAL BRIDGING LIGANDS

Various pyrazines (*210*, *211*) and quinoxalines (*32*) react with copper(I) halides to give complexes of the general formula $(CuX)_2(biN)$. The infrared spectrum of $(CuCN)_2$quinoxaline shows the cyano groups to be terminal, and it seems most likely that the complexes have the structure XCu(biN)CuX. Complexes of similar formula have been obtained by reducing $CuCl_2$ with hypophosphorous acid or KI in the presence of azo-2-pyridine (*19*). However, it is believed that these contain trigonal copper and have the structure shown in Fig. 13.

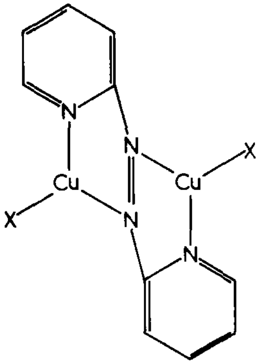


FIG. 13. Probable structure of $[CuX(azo\text{-}2\text{-}pyridine)]_2$ complexes.

The linear ditertiary phosphine $Ph_2PC{\equiv}CPPh_2$ (DPPA) forms six complexes of the formula $(CuX)_2(DPPA)_3$ [X = Cl, Br, I, NCS, NO_3 (*60*), BH_4 (*59*, *60*)], which are believed to have the structure shown in Fig. 14. It has been assumed in the past that the $(CuX)_2(diphos)_3$ complexes [X = Cl, Br, I (*237*), NO_3 (*10*), N_3 (*128*)] had a similar structure. However, recent X-ray structural determinations on the azido (*128*) (Fig. 15) and chloro (*4*) complexes show them to contain only one bridging diphos ligand, and the other diphos complexes are almost certainly isostructural. The azido complex can be reacted with trifluoromethyl cyanide in chloroform to give a bis[2-{5(trifluoromethyl)-tetrazolato}] complex wherein the two copper atoms are linked by a diphos ligand (*126*).

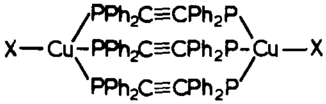


FIG. 14. Probable structure of the $(CuX)_2(Ph_2PC{\equiv}CPPh_2)_3$ complexes.

There are several other complexes containing the ligands $Ph_2PC_2H_4PPh_2$ or $(Ph_2P)_2CH_2$ that may contain neutral bridging ligands. They are best isolated from reactions of copper(I) halides under specified conditions and include $Cu_4X_4(biL)_2$ ($X = Cl, Br, I, biL = (Ph_2P)_2CH_2$; $X = Cl, Br, biL = Ph_2PC_2H_4PPh_2$). The molecular weights of the $Cu_4Cl_4(diphos)_2$ complex in both dichloroethane and chloroform are in accordance with this formula, but the solutions are unstable as their conductivity increases with time (*237*). Similar complexes containing one more molecule of bidentate ligand, i.e., $Cu_4X_4(biL)_3$, may be isolated from benzene solutions. Eight tricopper(I) complexes have also been prepared. The $[CuX(diphos)]_3$ ($X = Cl, Br$) complexes are trimeric in dilute chloroform solution but have higher apparent molecular weights in more concentrated solutions. This is also the case

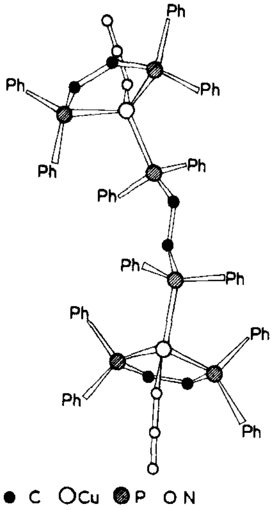


FIG. 15. Structure of $Cu_2(N_3)_2(diphos)_3$. [Redrawn by permission from *Inorg. Chem.* **10**, 2776 (1972).]

with the $Cu_3X_3(biL)_2$ (X = Cl, Br, I, biL = $(Ph_2P)_2CH_2$, $Ph_2PC_2H_4PPh_2$) complexes. The diphos complexes appear to be coordinatively unsaturated since they readily retain chlorinated solvent in their crystals.

Polymeric complexes are formed when copper(I) chloride reacts with dialkylhydrazines (*105*) or with 3,5,5-trimethylpyrazolidine. In $Cu_2Cl_2(MeN{=}NMe)$ the structure consists of parallel Cl–Cu–Cl chains cross-linked by weak Cu–Cl bonds and strong Cu–N σ bonds (*47*). Structures of CuI(PhN=NH) and $Cu_4Cl_4(PhN{=}NH)$ may be similar (*282, 290*). Diazoaminobenzene copper(I) (*110, 245*) can be prepared from copper and the ligand; it is dimeric with each copper linearly coordinated to 1,1′*N* or 3,3′*N* atoms (*48*). The cation in $[Cu(PhN_2Ph)]ClO_4$ may have a related structure (*265*).

B. COMPLEXES OF TRIDENTATE LIGANDS

6,4′,6″-Triphenyl-2,2′,2″-tripyridyl gives colored, complex, copper(I) ions suitable for spectrophotometric analysis (*307*). Complexes CuBr(triars) [triars = bis-(2-dimethylarsinophenyl)methylarsine] (*142*), $CuI[MeAs\{(CH_2)_3AsMe_2\}_2]$ (*21*), and $CuCl\{Me(CS)CH_2(CS)CH_2(CS)Me\}$ (*123*) have also been prepared. These complexes are monomeric and analogs of the $CuXL_3$ complexes. It is possible that tri-(2-pyrryl)-phosphine is tridentate (via two nitrogen atoms and the phosphorus atom) in its chloro- and bromocopper complexes obtained from the copper(II) salts.

1,3,5-Trithian yields polymeric complexes when reacted with CuCl in ethanol. Complexes $(CuCl)_3(C_3H_6S_3)$ and $(CuCl)_3(C_3H_6S_3)_2$ may be isolated, depending on the conditions used. The structure of the latter complex contains chains of copper atoms alternately bridged by two chloro and two trithian ligands. The chains are cross-linked by bonding between copper atoms and the third sulfur atom of trithian (*108*).

C. COMPLEXES CONTAINING DITHIO LIGANDS

Complexes with dithio ligands have been isolated containing the following ligands: $S_2P(OPr^i)_2$ (*104*), S_2CNRR' [R = R′ = Me, Et, Pr^n, Bu^n, C_5H_{11}, Pr^i, Bu^i, *iso*-C_5H_{11}, cyclohexylene, cyclopentylene; R = Et, R′ = Pr^n; R = Me, R′ = Ph (*2, 3*)], and S_2PR_2 (R = Et, Pr^n) (*201, 202*).

The molecular weights of the *N,N*-dialkyldithiocarbamato complexes indicate that they are tetramers in solution. This has been confirmed by X-ray crystallography of the diethyl complex (*158*) which has

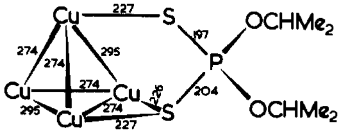


FIG. 16. Partial structure of tetrakis[*O,O*-di(isopropyl)phosphorodithioatocopper(I)] (bond lengths in picometers). [Redrawn by permission from *Inorg. Chem.* **11**, 612 (1972).]

a similar structure to that of tetrakis[*O,O*-di(isopropyl)phosphorodithioatocopper(I)] (*209*) (Fig. 16). By contrast, *N,N*-diethyldiselenocarbamatocopper(I) is monomeric (*337*). However, *N,N*-dipropylmonothicarbamatocopper(I) is hexameric and contains a central octahedron of copper atoms (*159*). Higher polymerization occurs in the anion of $[PhMe_3N]_4[Cu_8\{S_2C_2(CN)_2\}_6]$ (*115*) which contains a cube of copper atoms embedded in a distorted icosahedron of sulfur atoms (*239*).

D. POLYNUCLEAR COMPLEXES CONTAINING OTHER SULFUR LIGANDS

The ability of the sulfur atom in thiourea and related ligands to bridge copper(I) atoms results in a large number of complex structures. Unfortunately, many were first isolated before the advent of modern techniques of structural investigation.

One compound, $[Cu_4\{SC(NH_2)_2\}_9][NO_3]_4$ (*344*), has had its structure determined by X-ray crystallography, which revealed that there were five different types of Cu–S bonds in the polymeric structure. Other thiourea salts known include $[Cu_2\{SC(NH_2)_2\}_5]X_2$ ($X = NO_3$, $\frac{1}{2}SO_4$) (*298*), and the nitrate and cyanate of the similar cation $[Cu_2(\text{2-imidazolidinethione})_5H_2O]^{2+}$ (*249*).

Aquothiourea complexes are produced by hydrolysis of thiourea-copper(I) salts, e.g., $[Cu\{SC(NH_2)_2\}_2H_2O]X$ ($X = NO_3$, HSO_4, ClO_4, $\frac{1}{2}C_2O_4$) (*195*).

The phenylthiocarbamide complexes $[Cu_2(PhCSNH_2)_6]SO_4$ and $[Cu_2(PhCSNH_2)_3]X_2$ ($X = Cl$, $\frac{1}{2}SO_4$) (*305*) are also known.

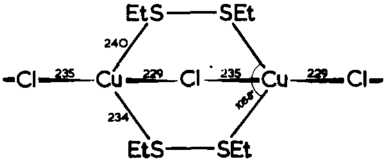


FIG. 17. Structure of $[CuCl(Et_2S_2)]_\infty$ (bond lengths in picometers). [Redrawn by permission from *Acta Chem. Scand.* **21**, 1000 (1967).]

An interesting bridged structure is found in $CuClEt_2S_2$ (Fig. 17) which contains both chloro and disulfide bridges; the complex was prepared by reacting CuCl with diethyl disulfide (*39*).

E. Complexes Containing Two Different Neutral Ligands

These complexes with two different neutral ligands may be obtained by displacement or addition reactions (*176*):

$$[CuX(PR_3)]_4 + 4phen \longrightarrow 4CuX(PR_3)(phen) \qquad (64)$$

$$CuX(PPh_3)_3 + phen \longrightarrow CuX(PPh_3)(phen) \qquad (65)$$

If the anion is poorly coordinating, ionic complexes result (*56*), e.g., $[Cu(PPh_3)_2(phen)]ClO_4$.

The behavior of the nitrato group in $CuNO_3(PPh_3)_3$ is intermediate (*177*): only large bidentate ligands form $CuNO_3(PPh_3)(biN)$ complexes in boiling benzene, whereas at room temperature $[Cu(PPh_3)_2(biN)]NO_3$ complexes are formed. With $CuNO_3(ZPh_3)_3$ (Z = As, Sb) only the first type of complex is formed, owing to the weakness of Cu–As and Cu–Sb bonds.

Tertiary arsines, phosphines, and stibines can also be displaced from their $CuX(ZPh_3)_3$ or $Cu_2X_2(Z'Ph_3)_3$ (Z = As, P; Z' = As, P, Sb; X = halogen) complexes by pyridine and related amines to give $CuX(ZPh_3)(amine)$ complexes. The structures of these are uncertain since their dissociation or decomposition in solution makes molecular weight data unreliable (*176*, *178*).

F. Other Complexes

The following unusual complexes have been isolated: a red polymeric complex of formula $[CuClpy(C_6H_4O_2)]_\infty$ reputed to contain bridging *p*-benzoquinone molecules (*151*); the salt $[Cu(HCN)]F$, obtained by dissolving CuCN in liquid HF (*109*); and $(CuCN)_3 \cdot MeI$ from a sealed tube reaction of the components (*149*). Similarly, $(CuCl)_2 \cdot PCl_3$ results from dissolving CuCl in PCl_3 (*99*). A structural study of the first complex would be helpful and reinvestigation of the remainder beneficial.

There are several well-defined mixed Cu(I)–Cu(II) complexes containing cyano or thiocyanato anions. These are $Cu(II)Cu(I)_2(NH_3)_4(CN)_4$, its 1,2-diaminoethane analog $Cu(II)Cu(I)_2(en)_2(CN)_4$ (*77*), and $Cu(II)Cu(I)(NH_3)_3(NCS)_3$ (*125*). The last complex is polymeric and contains tetrahedrally coordinated copper(I) atoms which are S-bound to two thiocyanato ligands and N-bound to two further thiocyanato ligands. The distorted octahedral coordination of the copper(II) atoms is made up of three ammine ligands, one N-bonded thiocyanato group, and two long bonds to the S atoms of other thiocyanato groups. All the NCS groups bridge two copper atoms.

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