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Polynuclear complexes of copper(I) halides: coordination chemistry and catalytic transformations of alkynes

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Abstract. Characteristic features of the coordination chemistry of Cu(I) and mechanisms of catalytic conversions of alkynes in the CuCl – MCl – H_2O – HC≡CR system (MCl is alkali metal or ammonium chloride or amine hydrochloride; R = H, CH_2OH, $CH=CH_2$, *etc.*) are analysed based on studies of the compositions and structures of copper(I) chloride (bromide) complexes, alkyne π-complexes and ethynyl organometallic polynuclear compounds formed in this system in solutions and in the crystalline state. The role of polynuclear complexes in various reactions of alkynes is discussed. The bibliography includes 149 references.

I. Introduction

Copper(I) complexes occupy a significant place in the chemistry of coordination compounds and in the development and evolution of homogeneous metal-complex catalysis. Copper(I) salts in quinoline were the first catalysts used in homogeneous hydrogenation.[1,2] Copper(I) chloride was among the first commercial homogeneous metal-complex catalysts (dimerisation of acetylene).[3,4] Acetylenic complexes of copper(I) were prepared for the first time by Chavastelon as early as 1898 in studies of the reactions of CuCl with C_2H_2 in aqueous solutions of KCl.[5,6] The compositions $2KCl\cdot 8CuCl\cdot C_2H_2$, $KCl\cdot 4CuCl\cdot C_2H_2$, $KCl\cdot 2CuCl\cdot C_2H_2$ and $2CuCl\cdot C_2H_2$ were assigned to the crystalline adducts isolated.[5–7] However, interest in the reactions of acetylene with CuCl and in catalysis by copper(I) complexes has particularly increased[3,4,8,9] after brilliant studies on catalysis of dimerisation and hydrochlorination of acetylene by copper(I) chloride complexes performed by Nieuwland[3,10] and the development of the commercial synthesis of chloroprene and synthetic rubber neoprene by Carothers (Du Pont de Nemours; see the monograph[3]). Thus, Nieuwland and coworkers[10] (in 1929 – 1931) were the first to perform the catalytic synthesis of linear oligomers of C_2H_2 by the reaction of a concentrated solution of NH_4Cl and CuCl in water (the molar ratio $NH_4Cl : CuCl : H_2O = 2 : 3 : 7$) with acetylene.

$$2HC\equiv CH \xrightarrow[pH\sim 4,\ \sim 80\ ^\circ C]{NH_4Cl,\ CuCl,\ H_2O} H_2C=CHC\equiv CH$$

$$3HC\equiv CH \xrightarrow[\sim 20\ ^\circ C]{NH_4Cl,\ CuCl,\ H_2O} H_2C=CHC\equiv CCH=CH_2$$

Conversions of acetylene in these systems are accompanied by a sharp decrease in pH of the medium (from ~ 4 to 1.1 at 80 °C). Alkali metal chlorides[11] or amine hydrochlorides (hereinafter, MCl)[12] can be used instead of NH_4Cl as a component of the catalytic Nieuwland system. Concentrated solutions of MCl and CuCl proved to be also very efficient catalysts of other catalytic reactions of acetylene (for example, the addition of H_2O, HCl, HCN, RSH and C_5H_6; see Refs 1 and 13), dienes and dichlorobutenes.[14]

The major proposals for the mechanisms of various reactions of alkynes catalysed by copper(I) chloride complexes, including oxidation processes with the participation of the Cu(I) – Cu(II) system, were developed in 1960 – 1990.[13,14] Certain specific features of copper(I) halide complexes are of most interest in their coordination chemistry and catalysis, among which are the pronounced tendency to form polynuclear complexes and, consequently, the possibility of the occurrence of multielectron processes, the formation of polynuclear π-complexes and σ-organometallic compounds with μ_2- and μ_3-bridging groups, the formation of heterovalent polynuclear complexes[15] and the ability to activate alkynes, alkenes and dienes in various addition, substitution and oxidation reactions.

The distinguishing feature of concentrated solutions of MCl and CuCl in water is the formation of a large number of polynuclear $(Cu_mCl_n)^{(n-m)-}$ complexes, which can participate to a variable extent in the same catalytic process and react with acetylene and its derivatives giving rise to intermediate π- and σ-complexes with different compositions and structures and of different nature. The understanding of the mechanism of catalytic reactions depends substantially on the available information on the structures of possible intermediates. Until recently, investigations of these intermediates were restricted to isolation of adducts and determination of their chemical compositions. During the last 15 years, a series of studies has been aimed at synthesising copper-containing complexes both of chloride (inorganic) and π- and σ-organocopper compounds and establishing their crystal structures.[16–19]

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In this review, the data on the coordination chemistry, synthesis and structures of complex compounds of CuCl (CuBr) with acetylene and its derivatives and on catalysis with the participation of copper(I) chloride (bromide) complexes and alkynes are generalised and systematised and the possible mechanisms of oligomerisation of acetylene and other processes catalysed by copper complexes are discussed. In this connection, particular attention will be given to catalytic reactions of acetylene and its derivatives proceeding in highly concentrated aqueous solutions of MCl and CuCl because it is in these homogeneous systems that copper(I) chloride complexes exhibit the highest catalytic activity.[13]

Researchers from the former Soviet Union and the Community of Independent States (primarily, from Russia and Ukraine) have made a significant contribution to these investigations. In the present review, these studies are considered in detail.

II. Complexes of copper(I) halides in solutions and in the crystalline state

Systems of copper(I) chloride with aqueous solutions of alkali metal chlorides, ammonium chloride or amine hydrochlorides are of such great interest that studies of the state of copper in these solutions and mechanisms of their catalytic reactions, which were started late in the 19th century, are being continued. Investigations of the solubility[8] and other physicochemical properties of concentrated solutions of MCl and CuCl in water and isolation of the products obtained in the reaction of acetylene with CuCl, which incorporate one, two, three or even six CuCl molecules per C_2H_2 molecule,[4,7,11,20] provided evidence that these solutions contained polynuclear complexes with composition $(Cu_mCl_n)^{(n-m)-}$.

1. Physicochemical properties of concentrated $MCl-CuCl-H_2O$ solutions

The abundant data on the solubility of CuCl in aqueous solutions of MCl have been reported in a monograph.[4] The $NH_4Cl-CuCl-H_2O$ system has been studied extensively.[21,22] The solubility of CuCl increases sharply as the concentration of NH_4Cl increases and the mole fraction of water decreases (Figs 1 and 2). The [CuCl] : [NH_4Cl] ratio is noticeably larger than unity at 80 and 100 °C, which is indicative of the formation of polynuclear copper(I) chloride complexes. This is also evident from calculations of the Bjerrum formation function $\tilde{n}$ (or the Sillén function Z) based on the results of the potentiometric determination of the equilibrium concentration of the ligand ($[Cl]^-$):

$$\tilde{n} = \frac{[Cl^-]_\Sigma - [Cl^-]}{[CuCl]_\Sigma}.$$

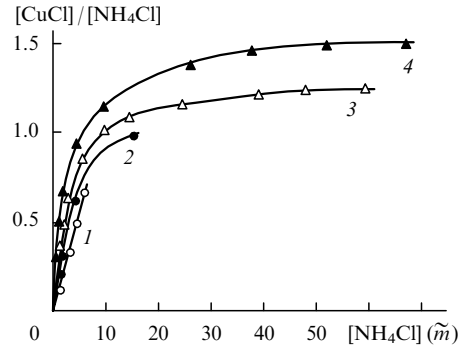


Figure 1. Dependence of the [CuCl]/[NH_4Cl] molar ratio on the molal concentration of NH_4Cl at different temperatures.[21] T (°C): (*1*) 25; (*2*) 50; (*3*) 80; (*4*) 100.

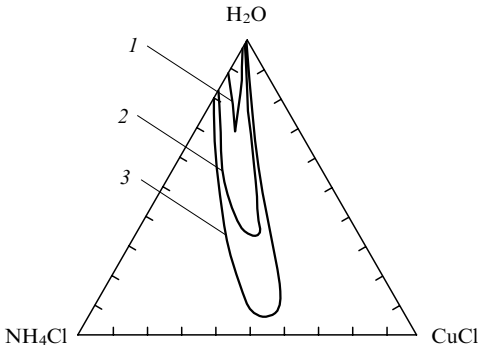


Figure 2. Triangular phase diagram of the solubility of CuCl (mole fractions).[21] T (°C): (*1*) 25; (*2*) 80; (*3*) 100.

At the overall concentration of NH_4Cl and NH_4NO_3 of 10 $\tilde{m}$ ($\tilde{m}$ is the molal concentration), the $\tilde{n}$ value changes from 2.80 to 1.73 as the concentration of CuCl changes from 0.5 to 10 $\tilde{m}$ and the concentration of NH_4Cl changes from 1.5 to 10 $\tilde{m}$ (80 °C). The dependence of $\tilde{n}$ on [CuCl] also indicates the existence of polynuclear complexes.[22]

Dissolution of CuCl in solutions of NH_4Cl is a slightly endothermic process (ΔH^0 changes from 16.7 to 4.18 kJ mol^{-1} as the concentration of NH_4Cl changes from 1.5 to 15 $\tilde{m}$) and is accompanied by an increase in the entropy (ΔS^0_{298} changes from 36 to 45 J mol^{-1} K^{-1}).[21,23] Dissolution of CuCl is accompanied by dehydration of chloride ions resulting in an increase in p_{H_2O} and the activity of water (a_{H_2O}).[23] In the range of CuCl concentrations from 0 to 10 $\tilde{m}$ ([NH_4Cl] = 8.84 $\tilde{m}$), the a_{H_2O} value increases from ~ 0.74 to 0.83 (55 °C) and 0.88 (85 °C).

$$m\,CuCl_{solid} + p\,Cl(H_2O)_q^- \rightleftharpoons [Cu_mCl_{m+p}(H_2O)_{pq-x}]^{p-} + x\,H_2O.$$

Studies of concentrated solutions of copper(I) chloride in NH_4Cl by electronic spectroscopy[24] (λ_{max} were 200, 235 and 273–400 nm) demonstrated that these solutions contain two groups of complexes because the optical density of the solution increases in the region of 250–290 nm and decreases in the region of 340–370 nm as the concentration of NH_4Cl increases. The absorption band in the region of 340–370 nm is the sum of absorption bands of different polynuclear complexes.

A comparison of the absorption spectra of chloride and bromide complexes in solutions in KX (5 $\tilde{m}$, X = Cl or Br) in the regions of 273 and 300–330 nm at the CuX concentrations of 0.01 and 0.4 $\tilde{m}$ demonstrated[22] that the shifts of the absorption maxima to the long-wavelength region are no larger than 5–8 nm on going from Cl^- to Br^-. It was assumed[24,25] that the longer-wavelength bands ($\lambda \simeq 320$ nm, $\varepsilon_{Br^-} \simeq 150$) belong to the forbidden transitions $3d^{10} \rightarrow 3d^9 4s^1$ and the bands at 200 and 273 nm belong to the transitions $3d^{10} \rightarrow 3d^9 4p^1$.

2. Complexation equilibria in the $MCl-CuCl-H_2O$ and $NH_4Cl-CuCl-H_2O$ catalytic systems

The equilibria of the formation of copper(I) chloride complexes in rather dilute solutions have been studied in detail.[26] The concentration stability constants ($\bar{\beta}_{m,n}$) for the complexes $(Cu_mCl_n)^{(n-m)-}$ in the $NaClO_4-NaCl-HCl-CuCl$ system with an ionic strength of the solution I = 5 mol litre^{-1} and [HCl] = 0.1 mol litre^{-1} (25 °C) were determined by two methods. The potentiometric method was used for [NaCl] = 0.2–0.88 mol litre^{-1} and [CuCl] $\leqslant$ 0.012 mol litre^{-1} and for [NaCl] = 0.2–4.268 mol litre^{-1} and [CuCl] $\leqslant$ 0.047 mol litre^{-1}. The solubility method was used for [NaCl] $\leqslant$ 5.0 mol litre^{-1} and [CuCl] $\leqslant$ 1.16 mol litre^{-1}. In the latter case, polynuclear complexes were revealed and the $\bar{\beta}_{2,4}$ value for $Cu_2Cl_4^{2-}$ was evaluated (Table 1). The constant pK_s = 6.73 was also determined by Andrews and Keefer.[32]

Table 1. Stability constants ($\bar{\beta}_{m,n}$) for selected $(Cu_mCl_n)^{(n-m)-}$ complexes.

Temperature /°C	Ionic strength of the solution /mol litre^{-1}	$\log\bar{\beta}_{1,2}$	$\log\bar{\beta}_{1,3}$	$\log\bar{\beta}_{1,4}$	$\log\bar{\beta}_{2,4}$	pK_s	Ref.
25	0	5.31				6.50	27, 28
20	0	5.30	5.70				29
25	5.0	6.00	5.99	<4.7	13±0.2	7.38	26
25	6.5 [a]	6.04	5.98	5.6	12.2	6.73	30
25	14.0 [a]	6.30	6.08	5.7	12.8		31

Note: K_s is the solubility product for $CuCl_{solid}$. [a] The equilibrium constant $\beta_{m,n} = \beta^*_{m,n}/\gamma_{m,n}$; the constant sum of the concentrations ($\widetilde{m}$) of $NH_4Cl + NH_4NO_3$.

With the aim of establishing the compositions of copper(I) chloride complexes in solutions concentrated with respect to CuCl and NH_4Cl, which were used in catalytic reactions of alkynes,[3,4,8] the equilibria in the $NH_4Cl-CuCl-H_2O$ system were examined at 25, 50 and 80 °C at the concentrations of CuCl varying from 0.03 to 10 $\widetilde{m}$ (at 80 °C) and at different constant concentrations of the supporting electrolyte, *viz.*, $NH_4Cl + NH_4NO_3$ (6.5, 10 and 14 $\widetilde{m}$).[30,31,33] The activities of the Cu^+ (a_{Cu^+}) and Cl^- (a_{Cl^-}) ions used in the cited studies were calculated based on the potentials of copper and silver-chloride electrodes measured in chains with transference (with respect to a standard hydrogen electrode). For the standard conditions (p_{H_2} = 1 atm, $a_{H^+} = 1$, $a_{Cu^0} = 1$, $a_{AgCl_{(sol)}} = 1$, $a_{Ag^0} = 1$), these activities are directly proportional to the thermodynamic activities of individual Cu^+ and Cl^- ions and are taken as equal to these values at $E_D = 0$ (E_D is the diffusion potential). Under the conditions of E_D = const,[30,31,33] the proportionality coefficient (which is close to unity) remains constant throughout the concentration ranges of CuCl and NH_4Cl, which made it possible to obtain reliable data on the compositions of the complexes. The activity coefficient of Cl^- (γ_{Cl^-}) was found to remain constant at the constant concentration of NH_4^+ ions throughout the concentration ranges of CuCl and NH_4Cl. It was assumed that $\gamma_{(Cu_mCl_n)^{(n-m)-}}$ also remains constant under these conditions. The compositions of polynuclear complexes were determined and the stability constants were estimated using the Sillén–Hedström method.[34,35] When using the a_{Cu^+} and a_{Cl^-} values, the stability constants $\beta_{m,n}$ differ from the thermodynamic constants $\beta^*_{m,n}$ by the activity coefficient $\gamma_{m,n}$.

$$\beta_{m,n} = \frac{\beta^*_{m,n}}{\gamma_{m,n}}.$$

The $\beta_{m,n}$ values for 19 $(Cu_mCl_n)^{(n-m)-}$ complexes are given in Table 2. It should be taken into account that the $\beta_{m,n}$ constants for complexes with large m (4 or 5) and n (7, 8 or 9) values calculated by this method can exhibit an error of up to one order of magnitude. Hence, it can only be said with assurance that single-, double- and triple-charged anions containing from one to four copper atoms exist in solution. The discrepancy between the experimental and calculated concentrations of CuCl at all temperatures is no higher than 10%.[22] It can be seen from Table 2 that the multiply-charged complexes ($n-m = 4$) and complexes with $m = 5$ disappear as the temperature increases, the compositions of the complexes being virtually independent of the increase in $[NH_4^+]$. The possibility of the determination of a large number of complexes and their compositions by the Sillén–Hedström method follows primarily from the independent determination of the a_{Cu^+} and a_{Cl^-} values. Calculations of the activity (and concentration) of Cl^- ions by the Hedström equation with the use of the a_{Cu^+}, $[CuCl]_\Sigma$ and $[Cl^-]_\Sigma$ values demonstrated that the calculated and experimental a_{Cl^-} values coincide only up to the CuCl concentrations of 0.5 $\widetilde{m}$. At higher concentrations, the discrepancy increases due to the low accuracy of the graphical method of solution of the Hedström equation.[35]

Table 2. Stability constants ($\beta_{m,n}$) for the reaction $mCu^+ + nCl^- \rightleftharpoons (Cu_mCl_n)^{(n-m)-}$ at different temperatures and molal concentrations ($\widetilde{m}$) of NH_4^+ (see Ref. 31).

Complex anion	25 °C		50 °C	80 °C
	$[NH_4^+] = 6.5$	$[NH_4^+] = 14.0$	$[NH_4^+] = 10.0$	$[NH_4^+] = 10.0$
$CuCl_2^-$	1.1×10^6	2.0×10^6	7.0×10^5	4.8×10^5
$CuCl_3^{2-}$	9.6×10^5	1.2×10^6	2.8×10^5	1.0×10^5
$CuCl_4^{3-}$	4.0×10^5	5.0×10^5	7.3×10^4	2.0×10^4
$Cu_2Cl_3^-$	2.0×10^{12}	7.5×10^{12}	1.6×10^{12}	1.3×10^{11}
$Cu_2Cl_4^{2-}$	1.5×10^{12}	6.4×10^{12}	7.0×10^{11}	5.0×10^{10}
$Cu_2Cl_5^{3-}$	1.0×10^{12}	5.5×10^{12}	4.0×10^{11}	2.8×10^{10}
$Cu_2Cl_6^{4-}$	4.3×10^{11}	1.5×10^{12}	2.0×10^{11}	1.0×10^{10}
$Cu_3Cl_4^-$	3.6×10^{18}	1.7×10^{19}	1.5×10^{18}	3.0×10^{16}
$Cu_3Cl_5^{2-}$	4.0×10^{18}	2.3×10^{19}	1.1×10^{18}	3.0×10^{16}
$Cu_3Cl_6^{3-}$	2.8×10^{18}	1.7×10^{19}	5.0×10^{17}	7.0×10^{15}
$Cu_3Cl_7^{4-}$	1.8×10^{18}	1.5×10^{19}	3.0×10^{17}	–
$Cu_4Cl_5^-$	2.0×10^{25}	2.4×10^{26}	3.0×10^{24}	6.0×10^{21}
$Cu_4Cl_6^{2-}$	2.0×10^{25}	1.2×10^{26}	1.8×10^{24}	5.0×10^{21}
$Cu_4Cl_7^{3-}$	5.0×10^{24}	8.0×10^{25}	1.0×10^{24}	–
$Cu_4Cl_8^{4-}$	5.0×10^{24}	–	–	–
$Cu_5Cl_6^-$	1.0×10^{32}	8.0×10^{32}	–	–
$Cu_5Cl_7^{2-}$	5.0×10^{31}	8.0×10^{32}		
$Cu_5Cl_8^{3-}$	3.0×10^{31}	–		
$Cu_5Cl_9^{4-}$	2.0×10^{31}			

Analysis of the distribution of the complexes (Fig. 3) demonstrated that polynuclear complexes appear in noticeable amounts starting with a CuCl concentration of 3–4 $\widetilde{m}$. The total concentration of the $(Cu_mCl_n)^{(n-m)-}$ complexes with m = 2, 3 and 4 reaches ~ 30% of the sum of the concentrations of all complexes. Based on the $\beta_{m,n}$ values (Table 2) determined at I = 6.5 and with the a_{Cu^+} and a_{Cl^-} values, which were measured [26] for the maximum concentrations of NaCl and CuCl, it can be demonstrated that the mole fraction of complexes with $m \geqslant 2$ is smaller than

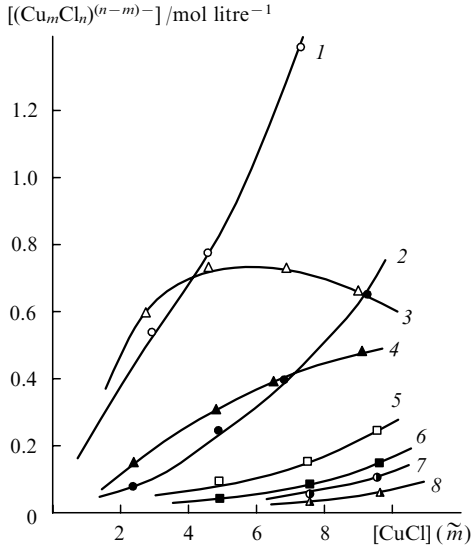


Figure 3. Distribution of the $(Cu_mCl_n)^{(n-m)-}$ complexes in the $CuCl-NH_4Cl-H_2O$ system depending on the concentration of CuCl (80 °C, $[NH_4^+] = 10\ \widetilde{m}$).
(*1*) $CuCl_2^-$; (*2*) $Cu_2Cl_3^-$; (*3*) $CuCl_3^{2-}$; (*4*) $Cu_2Cl_4^{2-}$; (*5*) $Cu_3Cl_5^{2-}$; (*6*) $Cu_3Cl_4^-$; (*7*) $Cu_4Cl_6^{2-}$; (*8*) $Cu_4Cl_5^-$.

Table 3. Enthalpy of the reaction $m\,Cu^+ + n\,Cl^- \rightleftharpoons (Cu_mCl_n)^{(n-m)-}$.

$(Cu_mCl_n)^{(n-m)-}$	ΔH°_{298} /kJ mol^{-1}	$(Cu_mCl_n)^{(n-m)-}$	ΔH°_{298} /kJ mol^{-1}
$CuCl_2^-$	-17.1 ± 2	$Cu_2Cl_6^{4-}$	-70.6 ± 4
$CuCl_3^{2-}$	-36.3 ± 2	$Cu_3Cl_4^-$	-89.5 ± 6
$CuCl_4^{3-}$	-48.5 ± 2	$Cu_3Cl_5^{2-}$	-93.6 ± 6
$Cu_2Cl_3^-$	-55.6 ± 4	$Cu_3Cl_6^{3-}$	-111.5 ± 6
$Cu_2Cl_4^{2-}$	-66.9 ± 4	$Cu_4Cl_5^-$	-139.6 ± 10
$Cu_2Cl_5^{3-}$	-73.6 ± 4	$Cu_4Cl_6^{2-}$	-147.1 ± 10

Note. $[NH_4^+] = 10\ \tilde{m}$.

5%. Because of this, these complexes were not determined experimentally.[26] Interestingly, the different approaches gave close values of the stability constants $\bar{\beta}_{m,n}$ and $\beta_{m,n}$ for $CuCl_2^-$ and $CuCl_3^{2-}$ (see Table 1).

Since the activity coefficients of different chlorides (KCl, NaCl and NH_4Cl) in aqueous solutions are virtually independent of the temperature, it was assumed that $d\gamma_{m,n}/dT \simeq 0$. This assumption was used for the estimation of the ΔH values of the reactions[33] (Table 3)

$$m\,Cu^+ + n\,Cl^- \rightleftharpoons (Cu_mCl_n)^{(n-m)-}.$$

The $\beta_{m,n}$ values change in parallel with the temperature (the dependence of $\log\beta_{m,n}$ on $1/T$ is linear).[33] The $\beta_{m,n}$ values at 25 °C and at $[NH_4^+] = 10\ \tilde{m}$ were determined by the linear interpolation of the values given in Table 2. The addition of each successive CuCl molecule to the $(Cu_mCl_n)^{(n-m)-}$ complex causes a decrease in the ΔH value, on the average, by 30–42 kJ mol^{-1}. According to the estimates obtained, the formation of polynuclear complexes from smaller complexes is also accompanied by a decrease in the enthalpy (Table 4). However, the equilibria are noticeably shifted to the right at rather low temperatures (below 50–60 °C) due to a large decrease in the entropy. An increase in the $\beta_{m,n}$ values as the concentration of the cations increases may be associated both with the decrease in $\gamma_{m,n}$ and with the formation of outer-sphere complexes with the NH_4^+ ion. The effect of the anionic complexes with $n-m \geqslant 2$ on the ionic strength of the solution was assessed[13] with the use of the Moiseev–Flid equation,[36,37] which describes the dependence of the acidity function of HCl ($-H_0$) on the ionic strength of the solution (I).

$$-H_0 = \log c_{H_3O^+} + LI - \log a_{H_2O},$$

where L is a constant dependent on the nature of the salt and the solvent ($L = 0.051\ \tilde{m}^{-1} \equiv 0.063$ mol^{-1} litre at 40–80 °C and $[HCl] = 0.18-0.8\ \tilde{m}$).

The measurements demonstrated[38] that the H_0 value remained unchanged over a wide range of CuCl concentrations at $[HCl] = 0.16\ \tilde{m}$ (80 °C) (Fig. 4).[13] Taking into account the change in the a_{H_2O} value, the ionic strength increases by no more than 0.5 for $[NH_4Cl] = 12\ \tilde{m}$ on going from the $NH_4Cl-HCl-H_2O$ system to the $NH_4Cl-CuCl-HCl-H_2O$ system. Hence it follows that multiply-charged anions have virtually no effect on the ionic strength due to their low concentrations (calculated from the data in Table 2) as well as due to their interactions with NH_4^+ ions. Therefore, the $\beta_{m,n}$ value (taking into account the coordination of water) should be represented by the following equation:[31]

$$\beta_{m,n} = \sum_p \sum_q \frac{\beta^*_{m,n}}{\gamma_{m,n,p,q}} a^p_{NH_4^+} a^q_{H_2O}.$$

Table 4. Thermodynamic parameters for the association reactions.

Reactions	ΔH°_{298} /kJ mol^{-1}	ΔS°_{298} /J mol^{-1} K^{-1}
$CuCl_2^- + CuCl_2^- \rightleftharpoons Cu_2Cl_4^{2-}$	-31.8	-100.3
$CuCl_2^- + Cu_2Cl_3^- \rightleftharpoons Cu_3Cl_5^{2-}$	-20.9	-62.7
$CuCl_2^- + Cu_3Cl_4^- \rightleftharpoons Cu_4Cl_6^{2-}$	-40.5	-121.2
$Cu_2Cl_3^- + Cu_2Cl_3^- \rightleftharpoons Cu_4Cl_6^{2-}$	-35.9	-112.8

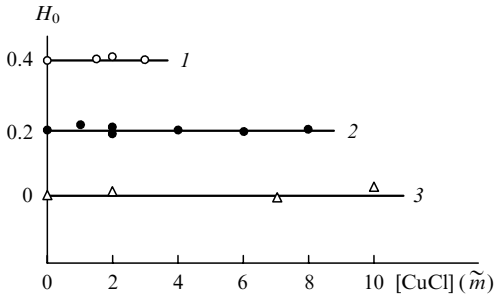


Figure 4. Effect of the concentration of CuCl on the acidity function H_0 at 80 °C and at different concentrations of NH_4Cl ($[HCl] = 0.16\ \tilde{m}$).[13] $[NH_4Cl]$: (*1*) 5 $\tilde{m}$; (*2*) 9 $\tilde{m}$; (*3*) 12 $\tilde{m}$.

The presence of various polynuclear complexes and their participation in catalytic reactions were confirmed in subsequent studies of ethynyl complexes of copper in solution, research on the synthesis and isolation of crystalline complexes and investigations on the kinetics of the reactions catalysed by copper(I) complexes.

3. Crystal chemistry of $(Cu_mX_n)^{(n-m)-}$ anionic complexes

Analysis of the available information on the compositions and crystal structures of complexes isolated from copper halide systems is necessary for an understanding of the mechanisms of catalytic processes and reasons for high catalytic activities of concentrated solutions containing polynuclear copper complexes. In this section, we analyse the structures of the $(Cu_mX_n)^{(n-m)-}$ anions and consider the effect of the outer-sphere M^+ cation on the structures of the complexes.

All types of $(Cu_mX_n)^{(n-m)-}$ anions found in the structures of copper(I) halide complexes can be divided into four groups, *viz*., island, chain (including ribbon), layered and framework structures. The structural classification of the $(Cu_mX_n)^{(n-m)-}$ anions is given in Table 5.

Crystal-chemical analysis of the complexes demonstrated that the copper atoms in the $(Cu_mX_n)^{(n-m)-}$ anionic fragments (X = Cl or Br) are most often located in a tetrahedral environment (the coordination number is 4) formed by the Cl or Br atoms. The vertices of the tetrahedra are generally located at different distances from the central atom. The X–Cu bond lengths depend on the coordination number of the X atom, *i.e*., on the degree of association of the Cu(I) coordination polyhedra. On the whole, the X atoms characterised by larger coordination numbers are located at larger distances from the central atom (see Table 5).

Planar-trigonal coordination (the coordination number is 3) about the Cu atoms was also found in copper(I) halide complexes. The angular or linear environments (the coordination number is 2) occur more rarely. Among the structurally characterised copper(I) halide complexes, no isolated tetrahedral CuX_4^{3-} anions were found. Apparently, discrete CuX_3^{2-} anions containing the metal atom in a planar-trigonal environment also do not exist.

In the $(Cu_mX_n)^{(n-m)-}$ anions containing two or more Cu atoms, the coordination polyhedra can be linked to each other in different fashions, *viz*., through vertices, edges or faces. The coordination polyhedra are more often linked in a combined mode simultaneously through vertices and edges, which in some cases gives rise to $(Cu_mX_n)^{(n-m)-}$ anions with zeolite-like structures. The numerous cavities of the latter structures can be occupied by small molecules ($HC\equiv CH$, H_2O, $CuC\equiv CH$, *etc*.) and even complexes [for example, the Cu(II) complexes in com-

Table 5. Structural characteristics of the $(Cu_mX_n)^{(n-m)-}$ anions in copper(I) halide complexes.

Compound	Anion	Structural type	Coordination number of Cu	Interatomic distances /Å					Ref.
				Cl – Cu [a]	μ_2-Cl – Cu	μ_3-Cl – Cu	μ_4-Cl – Cu	Cu···Cu	
(PyH)$CuCl_2$ (**1**)	CuX_2^-	chain	4, 3	2.269(4), 2.269(4)	2.353(4), 2.433(4)			2.803(5)	39
$KCuBr_2 \cdot 1/2\,H_2O$ (**2a**) [b]	CuX_2^-	layered	4		2.44(1), 2.545(8)			2.891(8)	40
$NH_4CuBr_2 \cdot 1/2\,H_2O$ (**2b**) [b]	CuX_2^-	"	4		2.44(1), 2.545(8)			2.891(8)	18
K_2CuCl_3 (**3a**)	CuX_3^{2-}	chain	4	2.34(2), 2.35(2)	2.44(2), 2.48(2)			4.08(1)	41
K_2CuBr_3 (**3b**) [b]	CuX_3^{2-}	"	4	2.34(2), 2.35(2)	2.44(2), 2.48(2)			4.08(1)	41
$(NH_4)_2CuBr_3$ (**3c**) [b]	CuX_3^{2-}	"	4	2.34(2), 2.35(2)	2.44(2), 2.48(2)			4.08(1)	42, 43
$(NH_4)_2CuCl_3$ (**4**)	CuX_3^{2-}	"	4	2.34(2), 2.35(2)	2.44(2), 2.48(2)			4.08(1)	43
$CsCu_2Cl_3$ (**5**)	$Cu_2X_3^-$	chain (II)	4		2.37(1), 2.37(1)		2.45(1), 2.45(1)	2.81(1)	44
(ImH)Cu_2Cl_3 (**6**) [c]	$Cu_2X_3^-$	chain (I)	4, 3		2.283(4), 2.366(4)	2.375(3), 2.513(4)		2.748(3)	45
$Cs_3Cu_2Cl_5$ (**7**)	$Cu_2X_5^{3-}$	chain	4	2.262(5), 2.262(5)			2.34(1), 2.881(8)	2.911(8)	46
$(Me_4N)_3Cu_2Br_5$ (**8**) [b]	$Cu_2X_5^{3-}$	island	3	2.38(1), 2.38(1)	2.40(1), 2.40(1)			–	47
$(NH_4)_2Cu_3Cl_5 \cdot 1/3\,H_2O \cdot 1/15\,CuCl$ (**9a**)	$Cu_3X_5^{2-}$	framework	4, 3 + 1		2.25(1), 2.30(1)	2.30(1), 2.71(1)	2.40(1), 2.68(1)	2.98(1)	48
$(NH_4)_2Cu_3Cl_5 \cdot 4/9\,H_2O \cdot 1/9\,C_2H_2$ (**9b**) [d]	$Cu_3X_5^{2-}$	"	4, 3 + 1		2.25(1), 2.30(1)	2.30(1), 2.71(1)	2.40(1), 2.68(1)	2.98(1)	49
$(NH_4)_2Cu_3Cl_5 \cdot 4/9\,H_2O \cdot 4/9\,C_2H_2$ (**9c**) [d]	$Cu_3X_5^{2-}$	"	4, 3 + 1		2.25(1), 2.30(1)	2.30(1), 2.71(1)	2.40(1), 2.68(1)	2.98(1)	49
$Rb_9Cu_{13}Cl_{22} \cdot (H_3O^+Cl^-)$ (**9d**)	$Cu_3X_5^{2-}$	"	4, 3 + 1		2.25(1), 2.30(1)	2.30(1), 2.71(1)	2.40(1), 2.68(1)	2.98(1)	48
$NH_4Cu_4Cl_3(I,Cl)_2$ (**10**)	$Cu_4X_5^-$	chain	4	2.29(2), 2.39(2)			2.60(2), 2.74(2)	2.48(2)	50
$(C_6H_5NH_3)_3Cu_4Cl_7$ (**11**)	$Cu_4X_7^{3-}$	"	4, 3	2.549(7), 2.549(7)	2.240(8), 2.41(1)	2.56(1), 2.631(8)		2.801(9)	51
$(PyH)_2Cu_5Cl_7 \cdot 1/5\,H_2O$ (**12**)	$Cu_5X_7^{2-}$	framework	4, 3	2.31(2), 2.31(2)	2.24(2), 2.64(2)	2.48(2), 2.63(2)		2.74(2)	18
$Rb_4Cu_5Cl_9$ (**13**)	$Cu_5X_9^{4-}$	chain (ribbon)	4		2.196(5), 2.578(5)	2.299(6), 2.652(5)		3.092(4)	52
$(MeEt_3N)_3Cu_6Br_9$ (**14**) [b]	$Cu_6X_9^{3-}$	island	4, 2		2.386(3), 2.528(2)		2.697(3), 2.697(3)	2.650(3)	53
$Rb_{11}Cu_{15}Cl_{16}Br_6(Cu^{II}Cl_6) \cdot CuC{\equiv}CH$ (**15a**)	$Cu_{15}X_{24}^{9-}$	layered	4, 2		2.287(7), 2.340(7)	2.305(7), 2.63(1)		3.006(6)	54
$Rb_{11}Cu_{15}Cl_{16}Br_6(Cu^{II}Cl_6)$ (**15b**)	$Cu_{15}X_{24}^{9-}$	"	4, 2		2.287(7), 2.340(7)	2.305(7), 2.63(1)		3.006(6)	54
$\{Rb_{11}[Cu_2(H_2O)_2]\}Cu_{15}Cl_{24}(Cu^{II}Cl_6)$ (**16**)	$Cu_{15}X_{24}^{9-}$	"	4, 2		2.287(7), 2.340(7)	2.305(7), 2.63(1)		3.006(6)	55

Notes. For the Cu – Cl bonds, the first and second figures correspond to the minimum and maximum values, respectively; for the Cu – Cu bonds, the shortest distances are given. The complexes **2a** and **2b**, the complexes **3a** – **c** and **4**, the complexes **9a** – **d** and the complexes **15a**,**b** and **16** are isostructural. [a] The distances from the Cu atom to the nonbridging Cl atom; [b] the Cu – Br bond lengths are given; [c] ImH is the imidazolium cation; [d] acetylene is adsorbed and does not occupy particular crystallographic positions.

pounds **15a**,**b** and **16**; see Table 5] to form 'guest–host' systems. The fact that the coordination polyhedra about the Cu atoms are linked *via* edges (faces) results in short Cu ··· Cu contacts typical of cluster compounds (see Table 5).

Let us consider the types of the $(Cu_mX_n)^{(n-m)-}$ anions found in the structures of copper(I) halide complexes in detail. Two types of mononuclear anions, *viz*., CuX_2^- and CuX_3^{2-}, are known. The CuX_2^- anion serves as an independent unit of the $(CuX_2^-)_n$ polymeric anions, which exist as chains or layers in complexes **1** and **2a**,**b**, respectively (see Table 5). In both case, the coordination polyhedra about the Cu atoms are linked to each other both through vertices and edges.

In isostructural compounds **3a** (or **3b**,**c**) and **4**, the $(CuX_3^{2-})_n$ chain fragments of identical structure are formed based on the CuX_3^{2-} anion. In these compounds, the coordination tetrahedra about the Cu(I) atoms are linked only through vertices.

The binuclear $Cu_2X_3^-$ anion can produce two types of $(Cu_2Cl_3^-)_n$ chain fragments. Fragments of the first type are observed in complex **6** and are formed by the Cu(I) coordination tetrahedra and triangles linked to each other simultaneously through vertices and edges. The second type (complex **5**) is formed by the Cu(I) coordination tetrahedra linked to each other exclusively through edges.

For yet another binuclear $Cu_2X_5^{3-}$ anion, both the island and chain modes of arrangement of the anionic fragments are observed. Complex **8** contains the $Cu_2Br_5^{3-}$ anion of the island type. In this complex, two coordination triangles about the Cu(I) atoms are linked *via* a shared vertex. In complex **7**, the $(Cu_2Cl_5^{3-})_n$ chain anion consists only of the Cu(I) coordination tetrahedra, which are linked to each other both through vertices and edges.

The trinuclear $Cu_3X_5^{2-}$ anion was found in isotypic compounds **9a**–**c** with the zeolite-like framework structures formed by the Cu(I) coordination polyhedra linked to each other both through vertices and edges. The $(Cu_3Cl_5^{2-})_n$ framework anion was also found in complex **9d** whose composition can be represented as $Rb_2Cu_{3-x}Cl_{5-x}\cdot(2/9H_3O^+Cl^-)$ ($x = 0.1$) by analogy with the compounds **9a**–**c**. Crystals of these four compounds were isolated from the catalytic MCl–CuCl–H_2O system (M = NH_4^+ or Rb^+) in the presence of which oligomerisation of C_2H_2 was performed. The compounds **9a**–**d** can be considered as stable stoichiometric points in the region of a phase with the variable composition $M_2Cu_3Cl_5\cdot x\cdot(yC_2H_2)$, where $x = 3/9H_2O\cdot$ $\cdot 1/15CuCl$ and $(2/9H_3O^+Cl^-)$ at $y = 0$ for M = NH_4^+ and Rb^+, respectively, and $x = 4/9H_2O$ at $y = 1/9$ or 4/9 for M = NH_4^+.

The tetranuclear $Cu_4X_5^-$ anion forms an unusual [from the viewpoint of the mode in which the coordination polyhedra about the Cu(I) atoms are linked] $(Cu_4X_5^-)_n$ chain fragment. In complex **10**, these fragments exist as the Cu(I) coordination tetrahedra linked to each other *via* edges and faces.

The tetranuclear $Cu_4X_7^{3-}$ anion is observed in complex **11**. These anions form $(Cu_4Cl_7^{3-})_n$ chains in which the coordination tetrahedra and triangles about Cu(I) are linked to each other through vertices and edges.

In the structurally characterised copper(I) halide complexes, two types of pentanuclear anions, *viz*., $Cu_5X_7^{2-}$ and $Cu_5X_9^{4-}$, were found. In complex **12**, the $(Cu_5Cl_7^{2-})_n$ anions are built of the coordination tetrahedra and triangles about the Cu(I) atoms, which are successively linked to each other through vertices and edges to form a zeolite-like framework structure.

The $Cu_5X_9^{4-}$ anions in complex **13** are linked in a ribbon-like $(Cu_5X_9^{4-})_n$ fragment in which the Cu(I) coordination polyhedra are linked to each other both through vertices and edges.

The island $Cu_6Br_9^{3-}$ fragment is an example of a hexanuclear anion. In complex **14**, this anion consists of four Cu(I) coordination tetrahedra linked to each other exclusively through edges. Two opposite vertices of this fragment are additionally coordinated by two Cu atoms with the coordination number 2.

Finally, the polynuclear $Cu_{15}X_{24}^{9-}$ anion was found in the zeolite-like structure **16**. The anions form a $[Cu_{15}Cl_{24}(Cu^{II}Cl_6)]_n$ layer in which the coordination polyhedra about Cu(I) are linked to each other through vertices and edges. The 'guest–host'-type structures of **15a**,**b** contain the structurally similar $[Cu_{15}Cl_{16}Br_6(Cu^{II}Cl_6)]_n$ anionic layers in which some crystallographic positions are partially occupied by Cl atoms.

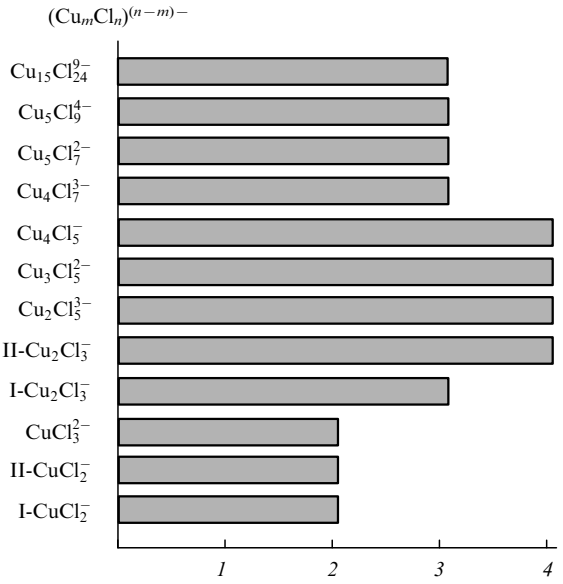


Figure 5. Relationship between the degree of association of the coordination polyhedra about the metal atoms and the number of nuclei (m) for the $(Cu_mCl_n)^{(n-m)-}$ anion; (*1*) terminal Cl; (*2*), (*3*) and (*4*) μ_2-, μ_3- and μ_4-Cl, respectively.

For a range of the above-described structural fragments in copper(I) chloride complexes, a marked trend is observed toward their complication as the number of nuclei in the $(Cu_mCl_n)^{(n-m)-}$ anions increases. The relationship between the number of nuclei in the $(Cu_mCl_n)^{(n-m)-}$ fragment (m) and the character of the bridging Cl atom (μ_n, where $n = 2$, 3 or 4) can be represented by a diagram (Fig. 5). It can be readily seen from Fig. 5 that an increase in m is accompanied by an increase in the ability of the chlorine atoms to act as bridging ligands. Thus, the very low degree of association of the Cu(I) coordination polyhedra is characteristic of the anionic fragments at $m = 1$, whereas complex structural forms of anions appear at $m = 2$, 3 or 4. For $m \geqslant 4$, though the ability of the bridging chlorine atoms to undergo association is somewhat lower, the structural fragments are, on the whole, complex.

This regularity agrees well with the results of studies of the equilibria in the CuCl–MCl system.[13, 30, 31, 33] Thus among the $(Cu_mCl_n)^{(n-m)-}$ complexes ($m = 1-5$ and $n = 2-7$), which are present in concentrated solutions of NH_4Cl and CuCl, the complexes with $m = 2$, 3 and 4 prevail. Therefore, the ability of the Cu(I) coordination polyhedra to form complex $(Cu_mCl_n)^{(n-m)-}$ associates at $m \geqslant 2$, 3 or 4 is, apparently, one of the major reasons for the high catalytic activity of concentrated solutions of MCl and CuCl.

Complex associates in solution are formed from coordination polyhedra of layered, chain, island or framework types upon cleavage of the bridging μ_n-Cl bonds by water molecules or Cl^- anions, which occupy the coordination vacancies in $(Cu_mCl_n)^{(n-m)-}$ complexes in solutions.

Let us consider the effect of the nature of the outer-sphere M^+ cation involved in the MCl–CuCl–H_2O system on the crystal structures of the anionic copper(I) halide complexes.

As mentioned above, dissolution of CuCl and formation of anionic complexes in aqueous solutions of MCl proceed according to the reaction

$$m\mathrm{CuCl}_{\mathrm{solid}} + p\mathrm{Cl}(\mathrm{H_2O})_q^- \rightleftharpoons [\mathrm{Cu}_m\mathrm{Cl}_{m+p}(\mathrm{H_2O})_{pq-x}]^{p-} + x\mathrm{H_2O}.$$

It is known that copper chloride is a salt, which contains covalent polar Cu – Cl bonds and is characterised by a framework sphalerite-like structure.[56] Dissolution of CuCl in aqueous solutions of ionic salts MCl involves destruction of the crystal lattice of CuCl under the action of adsorbed Cl^- anions with the simultaneous cleavage of some Cu – Cl bonds and the appearance of individual $(Cu_mCl_n)^{(n-m)-}$ fragments resulting in the establishment of the equilibria between these fragments. Both processes are accompanied by dehydration of Cl^- ions present in the solution. Apparently, the structures of the anions (as well as the stoichiometry of the equilibria) are determined to a large extent by the nature of the M^+ cations. The crystal structures of the complexes isolated from solutions also depend on the type (the size, symmetry, configuration, charge density and other characteristics) of the outer-sphere cation involved in complexation.

Analysis of the structural data demonstrated that NH_4^+ cations can form crystalline complexes with extremely complex zeolite-like structures, such as the complexes **9a**–**c**, due to the tetrahedral form of the ammonium cations. The latter interact with Cl^- ions through N(H)···Cl hydrogen bonds[57] imparting the directed character to the $M^+ \cdots Cl^-$ ionic bonding, which is responsible for the 'code' of the structure construction of the complex as a whole. The skeleton structures **1**, **6**, **11** and **12** containing planar PyH^+, ImH^+ (Im is imidazole) and $C_6H_5NH_3^+$ cations are also formed through (N)H···Cl hydrogen bonds. The replacement of NH_4Cl by KCl gives rise to the complexes **2a**, **3a** and **3b** in which K^+ cations cannot form directed bonds with Cl^- ions, and, consequently, no complex combinations of the Cu(I) coordination polyhedra are observed.

Apparently, the ability of NH_4^+ cations and protonated amines to generate complex structural forms of $(Cu_mCl_n)^{(n-m)-}$ anions through spatially oriented $M^+ \cdots Cl^-$ interactions giving rise to outer-sphere complexes in solution is one of the reasons for the fact that catalytic activities in systems containing NH_4^+ and amine hydrochlorides are higher than those in the $KCl-CuCl-H_2O$ systems.

III. Organocopper compounds

In the previous section, we considered $M_{(n-m)}Cu_mX_n$ complexes, which were formed in concentrated aqueous solutions of MCl and CuCl and isolated from solutions in the crystalline state. The compositions and structures of these complexes give an idea of the state of the initial catalytic system. In the course of the reaction of the $MCl-CuCl-H_2O$ system with acetylene (for example, under conditions of the oligomerisation according to Nieuwland), acetylene molecules and then products of their conversions (mono- and disubstituted derivatives) form π- and σ-organocopper compounds with $(Cu_mCl_n)^{(n-m)-}$ anions.[4,13]

In the first stage, π-complexes form. Then these complexes are converted into compounds of the mono- and diacetylenide types depending on pH of the medium.[58] In the initially weakly acidic medium, organometallic compounds exist predominantly as acetylenide (ethynyl) derivatives, which can be reversibly converted into π-complexes as pH decreases. The latter complexes are the major products of the reactions of alkynes with Cu(I) in acidic solutions. In this section, we will consider π- and σ-organocopper complexes, which are formed in the course of the reactions of acetylenic compounds with concentrated aqueous solutions of MCl and CuCl. Analysis of the structural features of polynuclear ethynyl complexes of copper(I) is required for an understanding of their role in catalytic processes (provided that the structures of the major fragments of the crystalline compounds are retained in solution). Selected structural characteristics of the compounds under consideration are given in Tables 6–9. For simplicity, the types (modes) of coordination of the C≡C group (η^1 or η^2) are denoted by σ or π, respectively (or σ,π-mode if both modes of coordination occur).

Examination of the data given in Tables 6–9 allows one to judge the efficiency of π-interactions in copper(I) π-complexes, to estimate the degree of activation of the triple bond and the alkyne molecule by the metal ion, to follow the possible pathways of conversions of π-complexes into acetylenide (ethynyl) complexes

Table 6. Mode of coordination of the C≡C group and the geometric characteristics of the π-coordinated Cu(I) units in the structures of π-complexes of copper(I) halides with acetylene and its monosubstituted derivatives.

Complex	Mode of coordination of the C≡C group	Cu – C* distance /Å	Sum of LCuL angles in the base of the polyhedron /deg	Cu – X_{ax} bond length /Å	Difference in Cu – C distances /Å	C≡C bond length /Å	Ref.
$Cu_2Cl_2(HC\equiv CH)$ (**17**)	μ-η^2,η^2	2.01(8)	356.1	2.75(3)	0.00(8)	1.18(14)	20
		1.76(8)	359.4	3.08(4)	0.00(8)		
		2.12(7)	356.5	3.07(4)	0.11(7)	1.26(13)	
		1.99(9)	350.5	2.67(3)	0.07(9)		
		2.16(9)	348.9	2.99(5)	0.00(9)	0.94(24) [a]	
		2.29(9)	351.5	2.74(4)	0.00(9)		
$Cu_3Cl_3(HC\equiv CH)$ (**18**)	μ-η^2,η^2	2.01(3)	352.8	2.663(6)	0.08(3)	1.12(4) [a]	20
		2.01(3)	352.8	2.663(6)	0.08(3)		
		1.97(2)	349.4	2.596(7)	0.02(2)	1.32(5)	
		1.97(2)	349.4	2.596(7)	0.02(2)		
$Cu_6Cl_6(HC\equiv CH)$ (**19**) [b]	μ-η^2,η^2	–	–	–	–	–	17
$KCu_3Cl_4(HC\equiv CH)$ (**20**)	μ-η^2,η^2	1.940(4)	359.2	3.177(2)	0.011(4)	1.26(1)	20
		1.940(4)	359.2	3.177(2)	0.011(4)		
		1.947(4)	359.5	3.462(2)	0.004(4)	1.28(1)	
		1.947(4)	359.5	3.462(2)	0.004(4)		
$NH_4Cu_3Cl_4(HC\equiv CH)$ (**21a**)	μ-η^2,η^2	1.94(1)	359.3	3.664(5)	0.00(1)	1.32(2)	59
		1.94(1)	359.4	3.583(5)	0.00(1)		
		1.93(1)	359.0	3.256(5)	0.03(1)	1.25(1)	
		1.93(1)	359.0	3.256(5)	0.03(1)		
$RbCu_3Cl_4(HC\equiv CH)$ (**21b**)	μ-η^2,η^2	2.03(3)	359.5	3.674(9)	0.00(3)	1.33(3)	60
		1.93(3)	359.9	3.596(9)	0.00(3)		
		1.89(2)	358.5	3.307(9)	0.04(2)	1.27(3)	
		1.89(2)	358.5	3.307(9)	0.04(2)		

Table 6 (continued).

Complex	Mode of coordination of the C≡C group	Cu−C* distance /Å	Sum of LCuL angles in the base of the polyhedron /deg	Cu−X_{ax} bond length /Å	Difference in Cu−C distances /Å	C≡C bond length /Å	Ref.
$KCu_8Cl_9(HC\equiv CH)_4 \cdot 1/2\, HCu_2Cl_3 \cdot H_2O$ (**22**)	μ-η²,η²	1.948(4)	356.7	2.832(2)	0.000(4)	1.23(1)	20
		1.948(4)	356.7	2.832(2)	0.000(4)		
$NH_4Cu_8Cl_9(HC\equiv CH)_4 \cdot 2/5\, \{[Cu(H_2O)_2] \cdot [CuCl_2] \cdot \cdot H_2O\}$ (**23**)	μ-η²,η²	1.957(5)	356.9	2.846(4)	0.000(5)	1.233(9)	61
		1.957(5)	356.9	2.846(4)	0.000(5)		
$CuCl(HC\equiv CPh)$ (**24**)	η²	1.941(4)	358.8	3.037(1)	0.067(4)	1.213(5)	62
$CuCl(HC\equiv CCH_2Cl)$ (**25**)	η²	1.912(4)	358.6	3.102(1)	0.000(4)	1.204(5)	62
$CuCl(HC\equiv CCH_2OH)$ (**26**)	η²	1.92(1)	358.7	3.078(4)	0.012(9)	1.20(1)	62
$Cu_2Cl_2(HC\equiv C(CH_2)_4C\equiv CH)$ (**27**)	η²;η²	1.946(6)	359.7	3.134(2)	0.024(6)	1.196(9)	63
$Cu_2Cl_2(HC\equiv CCH_2OH)$ (**28**)	μ-η²,η²	1.94(1)	357.5	2.467(9) [c]	0.00(1)	1.26(2)	64
		1.98(1)	354.7	2.725(5)	0.02(1)		
		1.95(1)	358.7	3.303(6)	0.03(1)	1.24(2)	
		1.99(1)	349.1	2.604(5)	0.04(1)		
		1.91(1)	359.8	3.730(6)	0.01(1)	1.25(2)	
		2.10(1)	341.3	2.416(6)	0.08(1)		
$(C_6H_5NH_3)Cu_2Cl_3(HC\equiv CCH_2OH)$ (**29**)	μ-η²,η²	1.93(1)	359.8	3.058(7)	0.006(9)	1.27(1)	65
		1.964(9)	354.8	2.830(7)	0.027(9)		

Note. Hereinafter, Cu−C* is the distance from the copper atom to the midpoint of the multiple bond. [a] The positions of the C atoms in the acetylene fragment were not refined because of the low stability of the complexes; [b] the first stage of X-ray diffraction analysis; [c] X_{ax} is the O atom of the alcoholic group.

Table 7. Mode of coordination of the C≡C group and the geometric characteristics of the π-coordinated Cu(I) units in the structures of π-complexes of copper(I) halides with alkenynes.

Complex	Mode of coordination of the C≡C group	Cu−C* distance /Å	Sum of LCuL angles in the base of the polyhedron /deg	Cu−X_{ax} bond length /Å	Difference in Cu−C distances /Å	C≡C bond length /Å	Ref.
$Cu_7Cl_7(HC\equiv CCH=CH_2)_3$ (**30**)	μ-η²,η²	1.98(1)	354.2	2.643(6)	0.03(1)	1.26(2)	66
		1.96(2)	353.8	2.647(6)	0.02(2)		
$CuCl(CH_2=CHCH_2C\equiv CCH_2OH)$ (**31**)	η²	1.92(2)	359.5	3.516(7)	0.10(2)	1.14(3) [a]	67
$Cu_2Cl_2(CH_2=CHCH_2C\equiv CPh)$ (**32**)	η²	1.953(7) [b]	357.1	2.930(2)	0.063(7)	1.35(1)	68
		1.937(7)	359.1	2.924(2)	0.010(7)	1.23(1)	
$Cu_2Br_2(CH_2=CHCH_2C\equiv CPh)$ (**33**)	η²	1.85(12) [b]	357.5	2.63(3)	0.03(12)	1.3(1)	69
		1.94(9)	358.4	3.04(3)	0.03(9)	1.2(1)	
$Cu_2Cl_2(CH_2=CHC\equiv CCH=CH_2)$ (**34**)	η²	1.961(4) [b]	355.5	2.705(1)	0.050(4)	1.361(6)	70
$Cu_3Cl_3(CH_2=CHC\equiv CCH=CH_2)$ (**35**)	η²	1.951(7) [b]	359.8	3.147(2)	0.034(6)	1.34(1)	70
		1.962(7) [b]	357.2	2.881(2)	0.008(6)	1.36(1)	
		1.910(6)	359.9	3.380(2)	0.002(5)	1.225(8)	
$Cu_3Cl_3(CH_2=CHCH_2C\equiv CCH_2CH=CH_2)$ (**36**)	η²	1.97(1) [b]	350.5	2.627(3)	0.07(1)	1.35(2)	71
		1.86(1)	360.0	3.742(3)	0.00(1)	1.18(2)	
$Cu_3Br_3(CH_2=CHCH_2C\equiv CCH_2CH=CH_2)$ (**37a**) (modification A)	η²	2.00(4) [b]	358.2	3.028(7)	0.12(4)	1.45(5)	71
		1.99(4) [b]	353.1	2.895(6)	0.24(3)	1.36(5)	
		2.05(4)	359.5	3.450(6)	0.07(3)	1.21(5)	
$Cu_3Br_3(CH_2=CHCH_2C\equiv CCH_2CH=CH_2)$ (**37b**) (modification B)	η²	1.99(3) [b]	359.6	3.36(3)	0.00(3)	1.37(4)	72
		1.98(3) [b]	358.6	3.05(2)	0.10(3)	1.36(4)	
		1.92(3)	359.9	3.33(3)	0.03(2)	1.18(3)	

[a] The positions of the corresponding C atoms were not refined because of the disorder of the C≡C groups in the crystal; [b] the Cu(I) atom is coordinated by the C≡C bond.

and to analyse the characteristic structural features of polynuclear ethynyl compounds.

1. Complexes of CuX with acetylene and its derivatives

The triple bond consists (in addition to the σ-bond) of two mutually orthogonal π-bonds, which are potentially able to interact with Cu(I). In the structures of copper(I) chloride complexes, acetylene always acts as a bridging π-ligand and is coordinated simultaneously by two metal atoms (Fig. 6). In this respect, the acetylene ligand is isolobal to the bridging μ^2-Cl ligand. Some monosubstituted acetylene derivatives in π-complexes with CuCl behave analogously (for example, **28**–**30**; see Tables 6 and 7). However, the C≡C bond in π-complexes of a series of alkynes and alkenynes, for example, of disubstituted acetylene derivatives (like the alkene bond), is coordinated exclusively by one copper atom [compounds **24**–**27**, **38**–**42** and **31**–**37**

Table 8. Mode of coordination of the C≡C group and the geometric characteristics of the π-coordinated Cu(I) units in the structures of π-complexes of copper(I) halides with disubstituted acetylenes.

Complex	Mode of coordination of the C≡C group	Cu–C* distance /Å	Sum of LCuL angles in the base of the polyhedron /deg	Cu–X_{ax} bond length /Å	Difference in Cu–C distances /Å	C≡C bond length /Å	Ref.
$CuCl(Me_3SiC{\equiv}CSiMe_3)$ (**38**)	η^2	1.923(3)	360.0	–	0.003(3)	1.227(5)	73
$CuCl(HOCH_2C{\equiv}CCH_2OH)$ (**39a**)	η^2	1.928(3)	359.3	3.183(1)	0.024(3)	1.219(4)	40
$CuBr(HOCH_2C{\equiv}CCH_2OH)$ (**39b**) [a]	η^2	–	–	–	–	–	40
$KCuBr_2(HOCH_2C{\equiv}CCH_2OH)$ (**40a**)	η^2	1.923(7)	359.9	–	0.000(7)	1.24(1)	40
$KCuCl_2(HOCH_2C{\equiv}CCH_2OH)$ (**40b**) [a]	η^2	–	–	–	–	–	40
$Cu_2Cl_2(Bu^tC{\equiv}CSC{\equiv}CBu^t)$ (**41**)	η^2; η^2	1.886(4)	360.0	3.550(3)	0.029(4)	1.232(4)	74
		1.916(4)	359.8	3.501(3)	0.36(4)	1.071(5) [b]	
$[Cu_2Cl_2(Bu^tC{\equiv}CSC{\equiv}CBu^t)]_n$ (**42**)	η^2; η^2	1.88(2)	359.4	–	0.04(2)	1.25(2)	74
		1.87(2)	358.8	3.01(1)	0.12(2)	1.13(2) [b]	
		1.91(2)	359.3	3.34(1)	0.02(2)	1.24(2)	
		1.88(2)	359.3	–	0.09(2)	1.23(2)	

[a] The first stage of X-ray diffraction analysis. [b] The positions of the corresponding C atoms were not refined because of the disorder of the C≡C groups in the crystal.

Table 9. Mode of coordination of the C≡C group and the geometric characteristics of the π-coordinated Cu(I) units in the structures of σ,π-complexes of copper(I) halides.

Complex	Mode of coordination of the C≡C group	Cu–C* distance /Å	Sum of LCuL angles in the base of the polyhedron /deg	Cu–X_{ax} bond length /Å	Difference in Cu–C distances /Å	C≡C bond length /Å	Ref.
$(ImH)_4Cu_9Cl_{11}(C{\equiv}CH)_2$ (**43**)	μ-η^1,η^1				–	1.21(2)	45
$(PyH)_4Cu_9Cl_{12}(C{\equiv}CH)$ (**44**)	μ-η^1,η^1				–	1.19(7)	39
$(NH_4)_8Cu_{29}Cl_{29}(C{\equiv}C)_4\cdot 7H_2O$ (**45**)	μ_3-η^1,η^1,η^1,	2.18(3)	159.1 [a]		0.34(3)	–	75
	μ-η^2,η^2,	2.01(2)	358.4	2.980(9)	0.01(2)	1.27(5) [b]	
	μ_3-η^1,η^1,η^1	2.01(2)	358.4	2.980(9)	0.01(2)	–	
	μ-η^1,η^1,	2.06(2)	359.1	2.79(1)	0.06(2)	1.23(5)	
	μ_3-η^2,η^2,η^2,	2.06(2)	359.1	2.79(1)	0.06(2)	–	
	μ_3-η^1,η^1,η^1			–	–	–	
$(ImH)Cu_4Cl_4(C{\equiv}CCH_2OH)\cdot H_2O$ (**46**)	μ-η^1,η^1, μ-η^2,η^2	2.01(1)	353.9	2.773(5)	0.01(1)	1.29(2)	45
		2.01(1)	353.9	2.730(5)	0.01(1)		
$NH_4Cu_4Cl_4(C{\equiv}CCH_2OH)\cdot H_2O$ (**47**) [c]	μ-η^1,η^1, μ-η^2,η^2	–	–	–	–	–	18
$(NH_4)_2Cu_4Cl_5(C{\equiv}CCH_2OH)\cdot H_2O$ (**48**)	μ-η^1,η^1, μ-η^2,η^2	1.986(8)	355.9	2.850(3)	0.028(8)	1.29(1)	76
		2.005(8)	358.0	2.979(3)	0.028(8)		
$(C_6H_5NH_3)_2Cu_4Cl_5(C{\equiv}CCH_2OH)$ (**49**)	μ-η^1,η^1, μ-η^2,η^2	2.00(2)	354.8	2.937(9)	0.04(2)	1.25(4)	77
		2.01(2)	357.5	2.944(0)	0.03(3)		
$Cs_2Cu_5Cl_6(C{\equiv}CCH_2OH)$ (**50**)	μ-η^1,η^1, μ-η^2,η^2	1.94(3)	359.1	3.061(7)	0.08(2)	1.22(3)	78
		1.98(2)	358.8	3.23(1)	0.03(2)		
$Rb_3Cu_7Cl_9(C{\equiv}CCH_2OH)\cdot H_2O$ (**51**)	μ_3-η^1,η^1,η^1, μ-η^2,η^2	2.09(2)	358.9	3.558(7)	0.00(2)	1.23(3)	52
		1.97(2)	359.9	3.489(6)	0.02(2)		
$(PyH)_2Cu_8Cl_8(C{\equiv}CCH_2OH)_2\cdot H_2O$ (**52**)	μ_3-η^1,η^1,η^1, μ-η^2,η^2	1.974(5)	356.6	2.973(3)	0.024(5)	1.258(6)	39
	μ-η^1,η^1, μ-η^2,η^2	1.994(5)	355.9	2.754(3)	0.009(5)		
		1.989(5)	352.8	2.728(3)	0.127(5)	1.267(6)	
		2.020(5)	358.8	2.931(3)	0.009(5)		
$(C_6H_5NH_3)_3Cu_8Cl_{10}(C{\equiv}CCH_2OH)\cdot 2H_2O$ (**53**)	μ-η^1,η^1, μ-η^2,η^2	1.97(1)	360.0	3.392(9)	0.04(1)	1.25(2)	51
		1.98(1)	355.8	2.858(9)	0.02(1)		
$HO(CH_2)_2NH_3Cu_9Cl_8(C{\equiv}CCH_2OH)_2\cdot(H_2O)_2$ (**54**)	μ_3-η^1,η^1,η^1, μ-η^2,η^2	1.988(6)	356.1	2.778(3)	0.012(7)	1.259(8)	79
		1.965(6)	358.7	2.979(3)	0.069(6)		
$Cu_{25}Cl_{17}(C{\equiv}CCH{=}CH_2)_8\cdot 14H_2O$ (**55**)	μ-η^1,η^1,	1.93(4)	357.7	–	0.03(3)	1.21(5)	66
	μ-η^2,η^2	2.00(3)	357.2	–	0.03(3)		

[a] The coordination number of Cu is 2; [b] the η^2-mode of coordination of the C≡C group to three Cu(I) atoms; [c] the first stage of X-ray diffraction analysis.

(Fig. 7)]. Moreover, the C≡C bond of the alkenyne ligand (*i.e.*, the more sterically hindered bond) successfully competes with the peripheral vinyl groups even in conjugated systems (complex **35**). In the case of the CuCl complex with allylpropargyl alcohol (**31**), the C=C bond of the allyl group, unlike the C≡C bond, is not coordinated to the copper atom. Therefore, the ability of the C≡C bond to be involved in the π-interaction with copper(I) is higher than that of the C=C bond.

According to the Dewar–Chatt–Duncanson concept,[13,80,81] the formation of acetylene complexes with Cu(I) compounds ($3d^{10}4s^04p^0$) is accompanied by interactions between the frontier molecular orbitals (MO) of acetylene and the metal complex [for

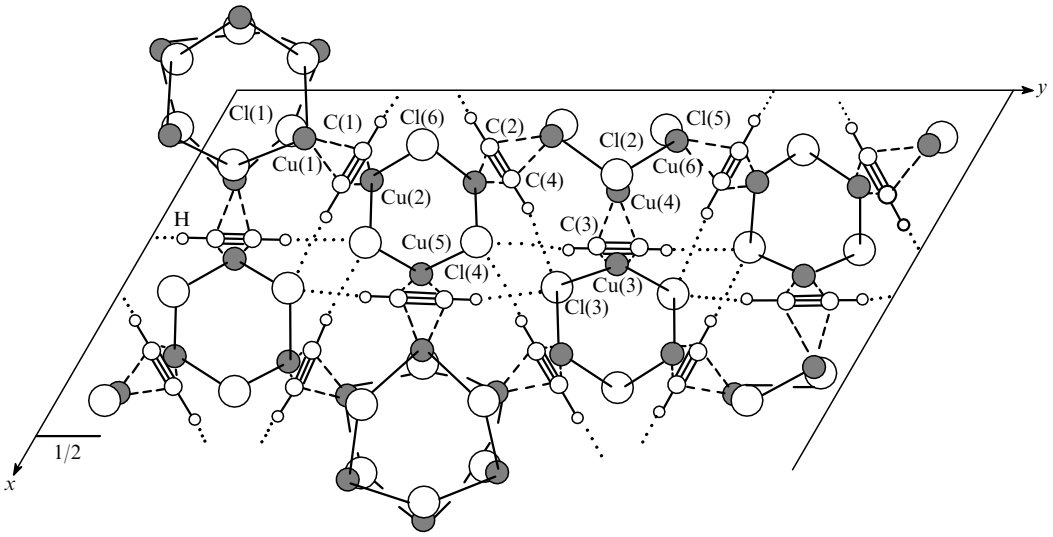


Figure 6. Projection of the structure of $Cu_2Cl_2(HC\equiv CH)$ (**17**) onto the *xy* plane.

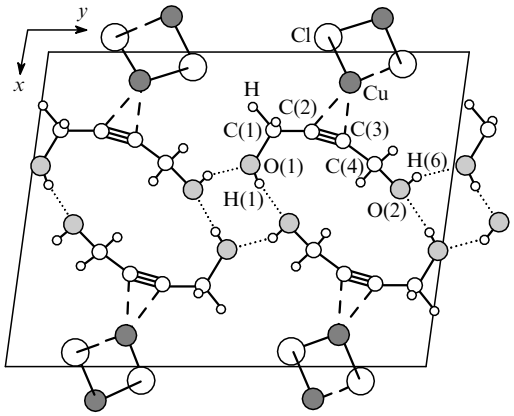


Figure 7. Projection of the structure of $CuC_2(HOCH_2C\equiv CH_2OH)$ (**39a**) onto the *xy* plane.

example, $(Cu_mCl_n)^{(n-m)-}$] giving rise to two three-centre MOs. One of them is formed by the overlap of the unoccupied sp^3-hybridised orbital of Cu(I) with the bonding π-MO of acetylene (the donor-acceptor component of the M ← L bond, where M is metal and L is alkyne), whereas the second MO is formed due to overlapping of one of the symmetry-suitable occupied *d* orbitals of the metal atom and the antibonding π*-MO of acetylene (the dative component of the M → L bond). Both three-centre bonds contribute to the increase in the strength of the Cu − π-ligand bond; however, they have different effects on the properties of the π-ligand. For example, the occupation of the antibonding π*-MO of acetylene with the electrons of the metal atom (the dative component) in Cu(I) π-complexes leads to a change in the C≡C−R angle (*cis* distortion) and elongation of the C≡C bond. In turn, donation of electrons from π-MO of acetylene to one of the sp^3-hybridised orbitals of Cu(I) (the donor-acceptor component) results in a decrease in the electron density on the C≡C bond due to which the carbon atoms acquire positive charges (δ+) and this π-coordinated acetylene group acts as a soft electrophile. The transfer of the electron density from the ligand to Cu(I) leads also to a decrease in the distance from the Cu(I) atom to the midpoint of the C≡C bond.

In essence, the above-considered model of the bond in the metal (M) π-complex with alkyne is synergistic because an increase in the M ← L component leads to an increase in the back M → L transfer.[82] However, these components make different contributions to π-interactions. Calculations of the energies of the Cu(I) − acetylene bond [or the Cu(I) − ethylene bond] demonstrated[83] that the contribution of the donor-acceptor electron transfer to the bond energy is approximately three times larger than that of the dative interaction. Hence, the specificity of activation of the acetylene bond on the metal centre in Cu(I) − π-complexes is primarily determined by interactions of the M ← L type. High-level quantum-chemical calculations[84,85] of the $Cu(C_2H_2)^+$ complex (taking into account the low-lying excited states) demonstrated that the $Cu^+ - C_2H_2$ bond is predominantly ionic in character and the Coulomb Cu(I) ion − π-ligand interaction makes the major contribution (the C≡C bond length is 1.242 Å, the C≡CH angle is 168.7°). This is consistent with the conclusion[83] that the electron transfer to the metal atom prevails. The ionic character of the bonds was also revealed in bisalkyne complexes $Cl_2X(C\equiv CH)_2\cdot CuMe$ (X = C, Si or Ti).[86] In these complexes, CuMe even donates electrons to the π-ligand.

The Cu(I) − (C≡C) [or Cu(I) − (C=C)] bonding in copper(I) chloride π-complexes leads to deformation of the tetrahedral environment about the metal atom characteristic of Cu(I) σ-compounds toward the trigonal pyramid and even toward the planar triangle.[87,88] Deformation of coordination polyhedra is associated with the appearance of a deficiency of electron density in the $d_{x^2-y^2}$ orbital† due to its interaction with antibonding MOs of the multiple carbon − carbon bond. In contrast, the d_{z^2} orbital, which is directed toward the axial ligand (for example, Cl_{ax}), possesses residual electron density. Hence, the interaction of Cu(I) with the multiple carbon − carbon bond is accompanied both by shortening of the bonds between the copper atom and the ligands located in the base of the pyramid and by elongation of the Cu − L_{ax} bond, *i.e.*, the Cu(I) atom moves toward the base of the polyhedron. The more efficient the dative component of the π-bond, the more substantial the deformation, the distance from the Cu atom to the midpoint of the multiple carbon − carbon bond (Cu − C*) being also shorter due to the synergism of the Cu(I) ← L and Cu(I) → L components. Knowing the parameters of the coordination unit, such as the Cu − C* distance, the Cu − X_{ax} bond length (X_{ax} is the axial Cl or Br atom), the sum of the LCuL angles ($\sum_{LCuL}$) in the base of the polyhedron, which characterises the deviation of the metal atom from the equatorial plane,‡ and

† The $d_{x^2-y^2}$ and d_{z^2} orbitals in the initial tetrahedral ligand field after the removal of degeneracy are characterised by lower energies than the remaining three orbitals of d_ε symmetry.[89]

‡ The sums of the LCuL angles equal to 329.5° and 360° correspond to two limiting cases, *viz.*, to the ideal tetrahedron and planar triangle.

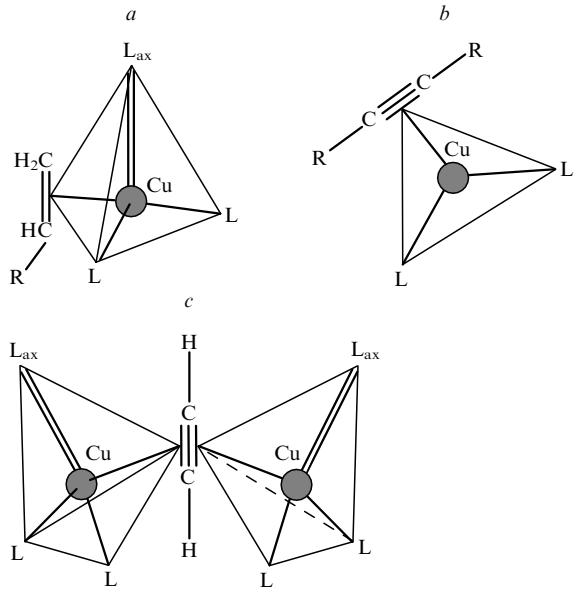


Figure 8. Modes of coordination in the π-complexes of CuCl and CuBr; (*a*) the trigonal pyramid typical of the Cu(I) atom π-coordinated by the C=C bond; (*b*) the planar-trigonal environment of Cu(I) in π-complexes with disubstituted acetylene derivatives; (*c*) the bridging π-coordination of the C≡C bond to the Cu atoms in π-complexes of C_2H_2 and its monosubstituted derivatives.

the length of the π-coordinated multiple carbon–carbon bond, one can assess the state of the C≡C (or C=C) group π-activated on the metal centre and the efficiency of the Cu(I)–(C≡C) [Cu(I)–(C=C)] interaction. The above-mentioned parameters for a series of molecular and anionic copper(I) chloride π-complexes are given in Tables 6–8.

To reveal the differences in the behaviour of the C≡C and C=C bonds with respect to Cu(I), let us consider the data on the alkenyne π-complexes of CuCl and CuBr (Table 7). In the structures of alkenyne complexes **30**–**37**, the coordination environment about the Cu(I) atom, which is π-coordinated to the C=C bond, is most often a tetrahedron slightly deformed toward the trigonal pyramid (Fig. 8 *a*). The complexes **34** and **35** contain conjugated alkenyne ligands. However, the Cu(I) coordination polyhedron in the complex **34** is more similar to the tetrahedron than that in the complex **35**. In the structure of **35**, the C=C groups interact more efficiently with Cu(I) due to the involvement of the C≡C bond in π-coordination of the metal atom. The distances from the copper atom to the midpoint of the C=C (Cu–C*) bond in the complexes **30**–**37** are in the range of 1.951(7)–2.00(4) Å, which indicates that the efficiency of the π-bonding is smaller than that of Cu–(C≡C). In particular, the Cu–C*(C=C) distances in the complex **35** are 1.951(7) and 1.962(7) Å, whereas the Cu–C*(C≡C) contact is substantially shorter [1.910(6) Å]. More substantial differences are observed in the structure of **36** in which the multiple bonds of the ligand are isolated [the Cu–C*(C=C) and Cu–C*(C≡C) bonds are 1.97(1) and 1.86(1) Å, respectively]. In this complex, the metal atom coordinated by the C≡C bond is in a planar-trigonal environment (Fig. 8 *b*), whereas the Cu atoms coordinated by the C=C bond are in a trigonal-pyramidal environment. In the copper(I) bromide complexes **33** and **37a**,**b**, the corresponding geometric parameters of the coordination π-units differ only slightly from each other due to steric hindrances caused by the bulkier bromine atoms. In the complex **32**, the geometric characteristics of the Cu(I) polyhedra formed with the participation of the C≡C or C=C groups are also only slightly different, which suggests that the π-interactions of these bonds with the metal atom are virtually identical in efficiency. To put it differenlty, the efficiency of π-coordination of the C≡C bond decreases due to the presence of the phenyl substituent giving rise to steric hindrances. On the whole, the Cu(I) atoms in alkenyne π-complexes tend to interact predominantly with the C≡C bond.

The affinity of alkyne ligands for Cu(I) is particularly pronounced both in molecular and anionic copper(I) halide π-complexes (**24**–**27** and **38**–**42**; Tables 6 and 8). If the C≡C group of the alkyne is coordinated only to one Cu atom, the environment of the latter is exclusively planar-trigonal (Fig. 8 *b*). In this case, very short Cu–C*(C≡C) distances [1.886(4)–1.92(1) Å] are observed, which is indicative of efficient interactions (compounds **25**, **26** and **38**–**42**). In the compounds **24** and **27**, the Cu–C*(C≡C) distances are 1.941(4) and 1.946(6) Å, respectively. Efficient π-interactions in the complexes **24** and **27** are hindered by the phenyl group at the C≡C bond and the bridging character of the octadiyne molecule, respectively.

The propargyl alcohol molecules in the molecular (**28**) and anionic (**29**) π-complexes and the vinylacetylene molecule in the compound **30** whose terminal C≡C group acts as a bridging π-ligand simultaneously coordinated to two metal atoms (Fig. 8 *c*), exhibit peculiar behaviour with respect to Cu(I). One of two copper atoms of the Cu(I)–(C≡C)–Cu(I) unit is always located somewhat closer to the midpoint of the triple bond. If the coordination polyhedra of Cu(I) in the the complexes **28**–**30** are arranged in order of increasing Cu–L_{ax} distances, it can be readily seen that the deformation of the Cu coordination polyhedra from the virtually regular tetrahedron [Cu–L_{ax}, 2.416(2) Å] to the trigonal pyramid [Cu–L_{ax}, 2.605(5)–3.058(7) Å] and then to planar-trigonal coordination [Cu–L_{ax}, 3.738(6) Å] is accompanied by a corresponding shortening of the Cu–C*(C≡C) distance, which indicates an increase in the efficiency of π-bonding in the series under consideration.

The triple bond in the π-complexes of acetylene (**17**–**23**; Table 6), as in the above-considered complexes **28**–**30**, is coordinated simultaneously to two metal atoms (Fig. 8 *c*). This coordination is retained both in molecular and anionic compounds. In the structures of the compounds **17**–**23**, the Cu–C* distances are noticeably longer than those in alkyne and alkenyne π-complexes and are similar to the Cu(I)–(C=C) distances. The average Cu–C* distance in the molecular π-complexes of acetylene **17** (see Fig. 6) and **18** [1.97(2)–2.29(9) Å] are noticeably larger that those in the anionic compounds **20**–**23** [1.89(2)–1.957(5) Å]. The latter compounds are characterised by virtually planar-trigonal environments about the metal atom.

Therefore, the C≡C group is more prone to interaction with Cu(I) than the C=C group even if the former occupies a position inside the ligand, which is less favourable for coordination to the metal atom. To account for this fact, let us use the data on the electron-donating and electron-withdrawing properties of the ethylene and acetylene molecules and the C_2H_2 molecule π-coordinated to Cu(I).

It is known that acetylene in the ground state exhibits the weaker electron-donating properties (two HOMOs have lower energies) and the weaker electron-withdrawing properties (two LUMOs have higher energies) compared to ethylene.[13,90] However, in the case of *cis*-distortion of the alkyne molecule in the coordination sphere about the metal atom, the degeneracy of the MOs is removed. As a result, the energies and geometric parameters of the frontier MOs of the alkyne change and it becomes both a better electron-acceptor and electron-donor than alkene. Therefore, the more efficient Cu(I)–(C≡C) π-interaction results from the presence of two π-MOs in the alkyne molecule, which are split into MOs with different energies ($\pi_{\|}$ and $\pi_{\perp}$), as well as from the stronger *cis*-distortion of the molecule compared to that of alkenes.

Due to the presence of two MOs in the alkyne, it can interact with Cu(I) and other metals as a bridging ligand and can coordinate two Cu(I) atoms. In this case, as mentioned above, the Cu–C* distances in the Cu(I)–(C≡C) π-units are noticeably shorter than those in the Cu(I)–(C≡C)–Cu(I) π-units, which indicates that the efficiency of the π-interaction in the first case is

higher. This fact is in agreement with the general regularities of coordination chemistry according to which the bond between a bridging μ-L ligand and the metal atom is always weaker than that with the participation of the terminal ligand. This also takes place in the cases of μ-Cl, μ-Me, μ-CO and μ-C_2H_2. In particular, this fact can be explained as follows: if each π-MO of alkyne acts independently (as alkene), two π-MOs, which are weaker π-donors than the highest $\pi_{\|}$-MO of acetylene in the nonbridging π-complex, are involved in bonding. It is also possible that $\pi_{\|}$-MO as well as $\pi^*_{\|}$-MO and $\pi^*_{\perp}$-MO are involved in the formation of the coordination bond in the Cu(I)−(C≡C) units.[91] However, this question calls for special investigation.

The efficiency of the interaction between Cu(I) and the multiple carbon–carbon bond affects not only the distance from Cu(I) to the midpoint of the Cu−C* bond, which is determined by the contribution of the donor-acceptor component, but also the length of the coordinated bond determined predominantly by the dative component. The data in Tables 6–8 demonstrate that the smaller the difference in the Cu−C distances (δ), the longer the C≡C or C=C bond. Thus, two crystallographically independent C_2H_2 ligands in the crystal of the compound **21a** (Fig. 9) differ in the C≡C bond length [1.25(1) and 1.32(2) Å]. This is indicative of the higher and lower efficiency of the correspodning dative components of the Cu(I)−(C≡C) π-interactions. In the second case [the coordination unit with the participation of the C(1)≡C(1′) bond], the asymmetry of the Cu−C bonds is absent, whereas the less elongated C(2)≡C(2)′ bond is located somewhat asymmetrically with respect to the Cu atom [δ = 0.03(1) Å], which decreases the efficiency of the dative Cu(I)−C(2)≡C(2)′ interaction. This tendency was revealed for a rather large number of examples. However, the C≡C bond in the Cu(I)−(C≡C) π-unit of the compound **36** is not elongated [1.18(2) Å] in spite of the total symmetry of the Cu−C distances (δ = 0 Å), although the Cu−C* distance [1.86(1) Å] is indicative of a substantial charge transfer M ← L increasing the degree of ionicity of the bond.

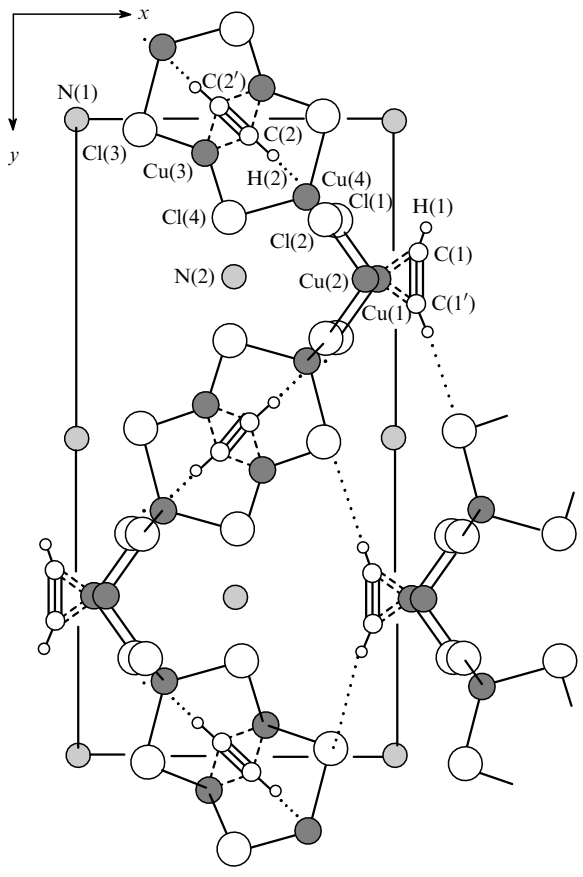


Figure 9. Projection of the structure of $NH_4Cu_3Cl_4(HC{\equiv}CH)$ (**21a**) onto the *xy* plane.

In most of the structurally studied Cu(I) π-complexes, the terminal carbon atom of the terminal C=C bond is generally located somewhat closer to the Cu atom, whereas the coordinated inner C≡C bond in alkyne and alkenyne ligands is most often symmetrical with respect to the Cu atom. Apparently, the inner C≡C bond is more stable to the shift with respect to the Cu−C* axis than the C=C bond due to the presence of two π-MOs in the former case. However, the C≡C group in CuCl π-complexes with terminal alkynes is characterised by a high tendency to form the asymmetrical Cu(I)−(C≡C) π-unit primarily due to the formation of ≡C−H···Cl hydrogen bonds with the participation of the terminal H atom.

Acetylene and its monosubstituted derivatives are characterised by high CH-acidity.[90] The dipole moment (μ) of the C−H bond in acetylene is 1.0 D. The positive charge of the dipole is localised on the H atom (the same direction of the dipole of the =C−H bond is observed in alkenes; however, μ for alkenes is approximately 0.6 D). The acidity of the C−H bond in alkynes increases upon the formation of π-complexes with Cu(I) and some other metals. Due to polarisation of the $C^{\delta-}-H^{\delta+}$ bond, π-complexes become strong acids, which can dissociate to form acetylenide compounds depending on pH of the solution. The tendency for dissociation is associated not only with polarisation of the C−H bond, but also with the high stability of coordination products of the resulting $RC{\equiv}C^-$ anions with Cu(I).[4,13] At the same time, polarisation of the C−H bond in π-complexes is favourable for hydrogen bonding with the chloride ion or the coordinated chloride ligand. Thus, acetylene or its monosubstituted derivatives in strongly acidic media form π-complexes with CuCl. In these complexes, ≡C−H···Cl hydrogen bonds exert a stabilising effect on the structures of the compounds.[92,93] The energies of the hydrogen bonds of this type are comparable with that of the π-interaction [$E_{C-H\cdots Cl} \sim 20$ kJ mol^{-1}; $E_{Cu(I)-(C\equiv C)} \sim 50$ kJ mol^{-1}]. In structures of π-complexes with acetylene, the ≡C−H···Cl contacts cause additional polarisation of the Cu−Cl bonds, thus being favourable for strengthening of the π-bonding in the Cu(I)−(C≡C)−Cu(I) unit,[17] which is, in turn, reflected in the geometry of the π-coordinated C≡C bond. Moreover, there is a particular relationship between elongation of the coordinated C≡C bond and the length of the ≡C−H···Cl hydrogen bond. Thus elongation of the triple bond is accompanied by weakening of the corresponding C(H)···Cl contact. An increase in the C≡C bond length due to weakening of the donor-acceptor interaction and strengthening of the dative interaction leads to a decrease in polarisation of the C−H bond and weakening of the hydrogen bond. On the contrary, a smaller elongation of the triple bond due to the stronger donor-acceptor interaction and an increase in polarisation of the C−H bond results in a stronger hydrogen bond and shortening of the H···Cl distance. The electron-withdrawing chlorine atoms, in turn, can substantially affect polarisation of the C−H bonds of the π-coordinated acetylene molecule due to the C(H)···Cl interaction. Thus the stronger the C(H)···Cl hydrogen bond, the higher the degree of polarisation of the $\equiv C^{\delta-}-H^{\delta+}$ bond. In other words, the formation of the C−H···Cl hydrogen bond enhances the donor-acceptor interaction, which, in turn, strengthens the hydrogen bond. The scheme of action of the ≡C−H···Cl hydrogen bonds in the structures of copper(I) chloride π-complexes of C_2H_2 is shown in Fig. 10.

The characteristics of the ≡C H···Cl hydrogen bonds in the structures of CuCl π-complexes with acetylene and its monosubstituted derivatives are graphically represented in Fig. 11. According to the criteria reported in a study,[94] the C−Cl distances indicate the existence of a hydrogen bond. It can be seen from the plot that there is a linear correlation between the elongation of the π-coordinated C≡C bond and the H···Cl distance. However, this is true only for π-complexes (anionic and molecular) in the structures of which the C≡C bond of the ligand molecule acts a

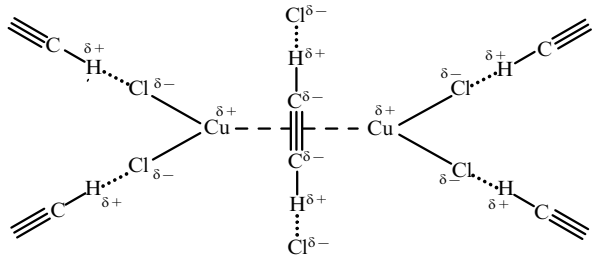


Figure 10. Scheme of $\equiv C\,H\cdots Cl$ hydrogen bonds in the structures of copper(I) chloride π-complexes of acetylene.

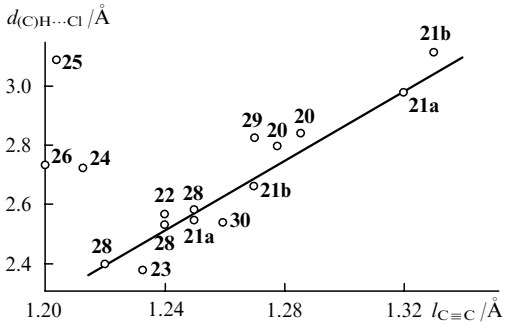


Figure 11. Correlation between the $(C)H\cdots Cl$ distance and the $C\equiv C$ bond lengths in CuCl π-complexes with acetylene and its monosubstituted derivatives (the linear correlation coefficient $r = 0.85$).

bridge to form the $Cu(I)-(C\equiv C)-Cu(I)$ π-unit. The complexes **24**–**26** are exceptional (see Fig. 11) due to the formation of the $Cu(I)-(C\equiv C)$ π-unit in which the π-interaction characteristic of nonbridging π-complexes prevails. Against its background, the polarising effect of the $\equiv C\,H\cdots Cl$ contact is less significant.

Hydrogen bonds play an important role in the structures of the anionic π-complexes **20** and **21a**. In the complex **20**, the lengths of the hydrogen bonds between the hydrogen atoms of two crystallographically independent C_2H_2 molecules and the chlorine atoms are virtually equal [2.85(8) and 2.80(9) Å]. In the structure of **21a**, these bonds are substantially different [2.98(12) and 2.55(12) Å] due to which the π-coordinated triple bond of one C_2H_2 molecule is substantially elongated [1.32(2) Å] compared to the second bond [1.25(1) Å]. In the structure of **20**, the parameters of the π-coordinated triple bond are virtually identical [1.28(1) Å] and correspond to the average value for the two limiting $C\equiv C$ bond lengths in the structure of **21a**. In these isostoichiometric complexes, the differences are observed not only in the geometric parameters of the crystallographically independent π-coordinated units, but also in the symmetry of their unit cells due to the different effect of the $\equiv C-H\cdots Cl$ hydrogen bonds. The structures of the complexes **20** and **21a** contain structurally similar (but not identical) $(Cu_4Cl_4)_n$ chain fragments (Fig. 12). Thus, all units of the chain in the structure of **20** have the symmetry *2* (Fig. 12 *b*), whereas the Cu_4Cl_4 units in the chains of the structure of **21a** are characterised by the symmetry *2* and *m* (Fig. 12 *a*). Apparently, this effect caused by the replacement of the K^+ ions by the NH_4^+ ions results from the $NH_4^+\cdots Cl^-$ interaction. Thus the ammonium cation's adopting the tetrahedral configuration forms $(N)H\cdots Cl$ hydrogen bonds [2.20–2.87(9) Å], which is favourable for the formation of the crystal structure of the complex **21a**, which differs from the crystal structure of the complex **20**. Therefore, the competition of two interactions, *viz*., $M^+\cdots Cl^-$ and $\equiv C-H\cdots Cl$, rather than the $\equiv C-H\cdots Cl$ hydrogen bond affects the geometry of the π-coordinated $C\equiv C$ bond in the C_2H_2 molecule in the anionic complexes. In the anionic CuCl π-complexes with acetylene and its monosubstituted derivatives, the efficiency of the $Cu(I)-(C\equiv C)$ π-interaction depends on the

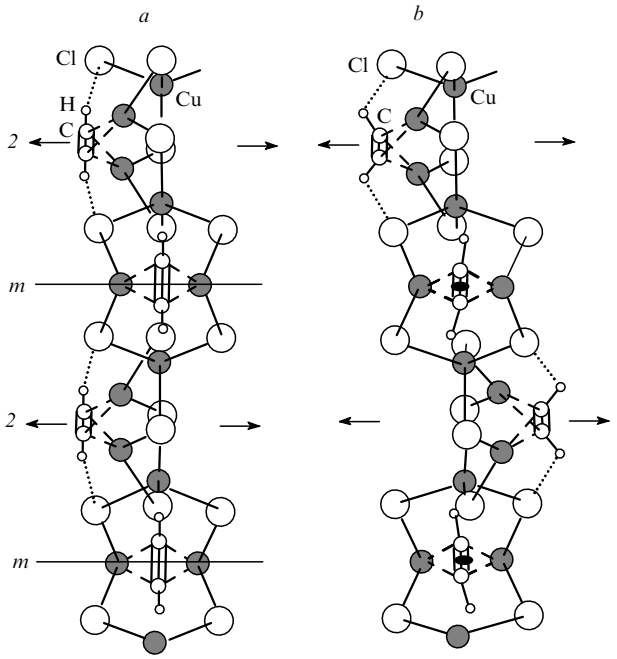
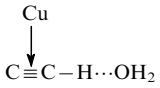


Figure 12. Chain fragments $(Cu_4Cl_4)_n$ in the structures of the complexes $NH_4Cu_3Cl_4(HC\equiv CH)$ **21a** (*a*) and $KCu_3Cl_4(HC\equiv CH)$ **20** (*b*).

efficiency of $\equiv C-H\cdots Cl$ hydrogen bonding whose strength is determined by the type of the outer-sphere M^+ cation (cations of alkali metals, ammonium or protonated amines). In the case of soluble anionic π-complexes, hydrogen bonding can also occur if the bridging or terminal chlorine atoms forming the coordination polyhedra occupy convenient positions. Weak hydrogen bonds between the NH_4^+ ion and the terminal Cl atoms can also exist. The possibility of hydrogen bonding with the participation of water molecules is also beyond question



In this connection, the role of the M^+ cations as a component of the Nieuwland catalyst $(MCl-CuCl-H_2O)$ becomes apparent.

2. Acetylenide (ethynyl) complexes of copper(I)

As mentioned above, the formation of ethynyl compounds (compounds possessing at least one $M-C\equiv$ bond) in protophilic media (or in the presence of bases) is a characteristic feature of the reactions of acetylene and monosubstituted alkynes with Cu(I) complexes. The polarisation of the $\equiv C-H$ bond in Cu(I) π-complexes is substantial and the strength of the resulting $Cu-C\equiv$ bond is so high that the Cu^+ ion reacts with C_2H_2 to form $CuC\equiv CH$ even in strongly acidic media in the $Cu_2SO_4-H_2SO_4$ system (up to $[H_2SO_4] = 20\%-25\%$). This reaction is accompanied by the formation of vinylacetylene in small amounts.[95]

$$Cu(C_2H_2)^+ + H_2O \rightleftharpoons CuC_2H + H_3O^+$$

Studies of the formation of the so-called 'yellow' complexes in the reactions of C_2H_2 with solutions of $(Cu_mCl_n)^{(n-m)-}$ polynuclear anions by spectrophotometric and potentiometric methods demonstrated that the following equilibria occur in solutions at 25–80 °C depending on the acidity of the medium [58]

$$(Cu_m)(C_2H_2) \underset{-H^+}{\rightleftharpoons} (Cu_m)C_2H \overset{(Cu_p)}{\underset{-H^+}{\rightleftharpoons}} (Cu_{m+p})C_2.$$

By increasing the acidity of the medium, one can go from symmetrical acetylenide (Cu_{m+p})(C_2^{2-}) to unsymmetrical (Cu_m)(C_2H^-) and again to the (Cu_m)(C_2H_2) π-complex.

The formation of solid acetylenide complexes containing Cu_2C_2 has been thoroughly studied by Vestin.[96] In particular, the equilibrium constant of the formation of the 'violet' complex **56** ($K = a^2_{HCl}/p_{C_2H_2} = 4$ at 25 °C) was measured

$$C_2H_2 + (x+2)\,CuCl_{solid} \overset{K}{\rightleftharpoons} C_2Cu_2(CuCl)_{x(solid)} + 2HCl$$

56

and the composition of the 'yellow' solid complex **57** was established

$$C_2H_2 + 8CuCl_{solid} + 2K^+ \rightleftharpoons K_2C_2(CuCl)_{8(solid)} + 2H^+.$$

57

It was concluded[96] that the solution of the $CuCl-KCl-H_2O$ system contains the $[C_2(CuCl)_n]^{2-}$ anion. Unsymmetrical ethynyl complexes in solutions[58] {[HCl] = 0.05–0.6 $\tilde{m}$, the acidity of the medium (h_0) is 0.2–5, pH = 1.1–0.0} have predominantly the compositions $[Cu_4Cl_4(C\equiv CH)]^-$ and $[Cu_4Cl_5(C\equiv CH)]^{2-}$.

Recently, ethynyl complexes and acetylenide complexes of copper(I) chloride have been synthesised and their structures have been studied (see Table 9 and references therein). These studies provided convincing evidence that unsymmetrical polynuclear ethynyl complexes $[Cu_mCl_n(C\equiv CR)]^{(n-m+1)-}$ do exist. New structures, which have not been described previously for non-halide complexes, were revealed.[97–116]

In the case of acetylene, the $(ImH)_4Cu_9Cl_{11}(C\equiv CH)_2$ (**43**)[45] and $(PyH)_4Cu_9Cl_{12}(C\equiv CH)$ (**44**)[39] compounds were obtained as insoluble (crystalline) acetylenide complexes. In these complexes, the C≡CH group is bridging and is coordinated to the copper atoms only through one α-carbon atom (the μ-η¹-, η¹-C≡CH- or σ,σ-modes of coordination) (Fig. 13). The C≡C bond lengths in these complexes are 1.21(2) and 1.19(7) Å, respectively, and the Cu–C bond lengths are 1.97(1) and 1.92(3) Å. This type of the ligand is rather often observed in ethynyl complexes of the $Cu_2(C\equiv CR)_2L_4$ (L = PR_3) type.[97] For simplicity, these ethynyl compounds will be called σ-complexes. The complex **43** contains the $Cu_4Cl_5(C_2H)^{2-}$ anion. In the acetylenide complex $(NH_4)_8Cu_{29}Cl_{29}(C\equiv C)_4\cdot 7H_2O$ (**45**), the C_2^{2-} anion, unlike the C_2H^- anion, is coordinated both in the η¹- and η²-modes (σ,π-mode) and serves as a bridge between eight copper atoms (Fig. 14). In the structure of **45**, two crystallographically independent C_2^{2-} species are present. Each of these species acts as a

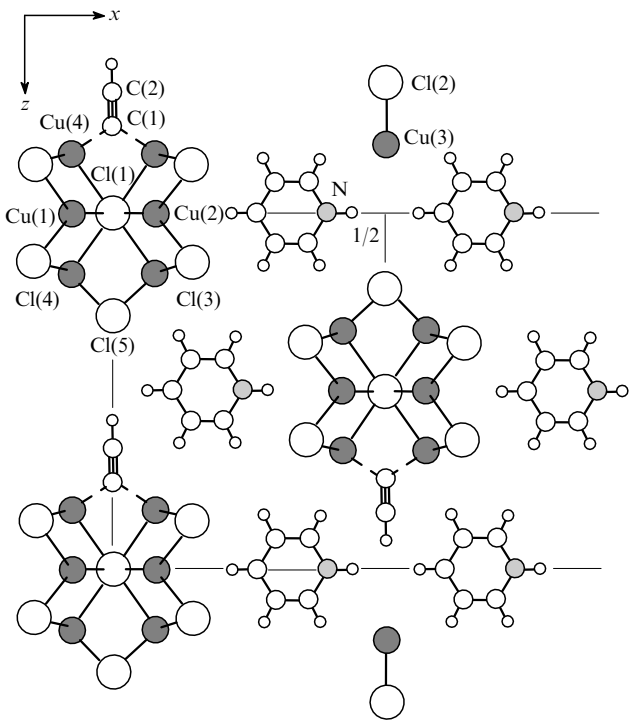


Figure 13. Projection of the structure of $(PyH)_4Cu_9Cl_{12}(C\equiv CH)$ (**44**) onto the *xz* plane (one layer is shown).

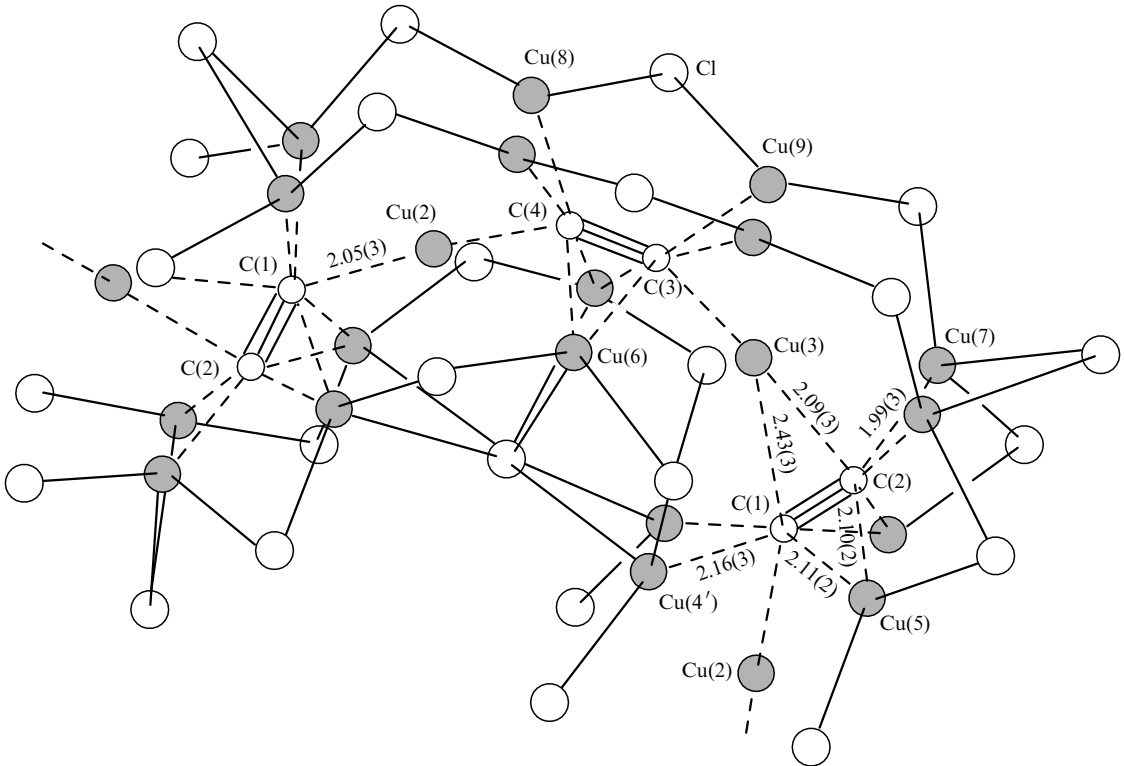


Figure 14. Fragment of the structure of the $(NH_4)_8Cu_{29}Cl_{29}(C\equiv C)_4\cdot 7H_2O$ complex (**45**). The distances from the Cu(3) and Cu(5) atoms to the midpoint of the C(1)–C(2) bond are 2.18(3) and 2.01(2) Å, respectively.

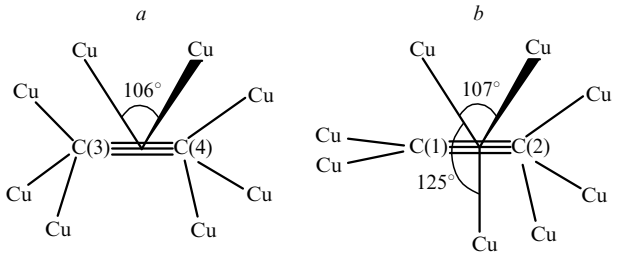
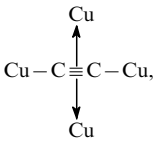


Figure 15. π,σ-Coordination units in the structure of the $(NH_4)_8Cu_{29}Cl_{29}(C\equiv C)_4\cdot 7H_2O$ complex (**45**).

bridging σ,π,σ-ligand, which coordinates simultaneously eight metal atoms. Noteworthy are the modes of coordination of the Cu(I) atoms by two independent C_2^{2-} species. Each of two carbon atoms of the C(3)≡C(4) group forms σ-bonds with three copper atoms (Fig. 15 *a*). Therefore, the C(3)≡C(4) group is coordinated in the μ_3-η^1,η^1,η^1,μ_2-η^2,η^2,μ_3-η^1,η^1,η^1-mode, *i.e.*, this group acts as the σ,π,σ-ligand. The effect of six copper(I) atoms η^1-coordinated to the C_2^{2-} ion and two copper atoms η^2-coordinated to the same ion on the C≡C bond is so high that the geometry of the η^2-unit changes and the Cu−C*−Cu angle reaches 106°. In this case, the C(1)≡C(2) bond can additionally coordinate the third copper atom (Fig. 15 *b*). Apparently, the unusual mode of coordination to the copper(I) atoms is the characteristic feature of the C_2^{2-} anion. Thus the perfectly planar coordination σ,π,π,σ-unit



was found in the structure of the complex $[Cu_4(Ph_2PCH_2PPh_2)_4(C\equiv C)](BF_4)_2\cdot 4Me_2CO$.[117] In this unit, the Cu−C*−Cu angle is 180°. Apparently, the structure of the 'yellow' complex studied by Vestin [96] also contains the fragments (*a*) and (*b*) (see Fig. 15). The σ,π-coordination of several copper atoms by the C_2^{2-} group gives rise to clusters in which the shortest Cu···Cu distance is 2.452(6) Å. Coordination of the ethynyl ligand to three copper(I) atoms (μ_3-η^1,η^1,η^1-C≡C) to form the trinuclear cluster is also very typical of ethynyl complexes.[97] The question about the nature of the η^2-bonds between the C≡C group and three metal atoms deserves special analysis.

Structural motifs found in ethynyl complexes containing RC≡C groups are widely diversified. The efficiency of η^2-coordination of the Cu(I) atom by the RC≡C group depends on the η^1-mode of coordination. The geometric parameters of the π-coordination units in the structures of the CuCl σ,π-complexes with acetylene and its terminal derivatives [which, according to the criteria used in the previous section of this chapter, characterise the efficiency of the Cu(I)−(η^2-C≡CR) bonding] are given in Tables 9 and 10. It can be readily seen that two metal atoms in the coordination π-unit (μ-η^2,η^2-C≡CR) in cluster ethynyl complexes of copper(I) are located at somewhat different distances from the midpoint of the C≡C bond, as in the CuCl π-complexes with $HC\equiv CCH_2OH$ and $HC\equiv CCH=CH_2$ [compounds **28** and **29** (see Table 6) and **30** (see Table 7)]. However, shortening of the Cu−C* distance in σ,π-complexes, which is determined primarily by the donor-acceptor component of the π-interaction, unlike that in CuCl π-complexes with $HC\equiv CCH_2OH$ and $HC\equiv CCH=CH_2$, is not accompanied by an increase in the dative transfer, *i.e.*, it does not cause additional deformation of the trigonal-pyramidal environment about the Cu(I) atom. Moreover, the σ,π-complexes are characterised by the following effect: the smaller elongation of the Cu−X_{ax} distance in the coordination π-unit (μ-η^2,η^2-C≡CR) corresponds to the shorter Cu−C* distance due, apparently, to the synergism of the Cu(I)−(η^1-C≡CR) and Cu(I)−(η^2-C≡CR) interactions. Such mutual strengthening of the η^1- and η^2-bonds is manifested to a greater or lesser extent depending on the number of the σ-coordinated Cu atoms and their arrangement with respect to the C≡C group.

Table 10. The CuC*Cu angles in the π-coordinated Cu(I) units in the structures of π,σ-complexes of CuCl with acetylene and its terminal derivatives.

Complex	CuC*Cu angle /deg	Cluster type	Ref.
45	125(1)	–	75
	125(1)	–	
	107(1)	–	
	106(1)	–	
46	93.5(6)	II	45
48	95(1)	II	76
49	93.6(9)	II	77
50	97(1)	I	78
51	90.4(7)	IV	52
52	96.9(2)	I	39
	89.8(2)	IV	
53	96.9(6)	III	51
54	98.1(3)	IV	79
55	98(2)	III	66

In this connection, it is worthwhile to consider the stereochemistry of the $[Cu_4(C\equiv CR)]$ and $[Cu_5(C\equiv CR)]$ clusters found in the structures of copper(I) chloride σ,π-complexes with terminal derivatives of acetylene. Four major types of cluster were distinguished (see Table 10). The differences in their structures are determined by the difference in the orientation of two mutually perpendicular π-MOs of the ethynyl group of the σ,π-coordinated C≡CR ligand with respect to the plane *P* passing through the C≡C bond (Fig. 16). In the structures of the complexes containing clusters of type I, the plane of one of the π-MOs of the C≡C group (for example, $\pi_\parallel$) coincides with the plane *P*, *i.e.*, the π-coordinated C(2) atom and the C≡C bond together with two σ-bonded Cu(3) and Cu(4) atoms are in a single plane, whereas the normal *mn* to this plane coincides with the axis of another $\pi_\perp$-MO [the Cu(1)−C* axis] (Fig. 16 *a*). Both π-MOs of the C≡C group ($\pi_\parallel$ and $\pi_\perp$) in clusters of the types II–IV, unlike those in clusters of type I, are located at an angle of 45° to the normal *mn* (as well as to the plane *P*). [In the case of clusters of the types III and IV (Fig. 16 *c*,*d*), the plane *P* passes perpendicularly to the normal *mn* to retain the spatial orientation of the π-coordinated copper(I) atoms analogous to that in clusters II (Fig. 16 *b*).] The clusters II, III and IV differ primarily in the orientation of the σ-coordinated Cu atoms. Thus, the σ-coordinated Cu(3) and Cu(4) atoms in clusters of the type II lie in the plane *P* (Fig. 16 *b*). The rotation of these σ-coordinated Cu(3) and Cu(4) atoms about the C≡C axis by 90° in such a way that they form a new plane (*Q*) with the normal *mn* leads to clusters of the type III (Fig. 16 *c*). The replacement of one σ-coordinated Cu(4) atom by two atoms [Cu(4) and Cu(5)] in such a way that these atoms are no longer located in the plane *Q* [the Cu(4) and Cu(5) atoms are located behind and in front of the plane *Q*, respectively; the Cu(4)C(1)Cu(5) angle ≈ 80°] gives rise to a cluster of the type IV (Fig. 16 *d*). In addition to the above-considered four cluster types, combined types of clusters are also observed in the structures of Cu(I) σ,π-complexes. An example is the $[Cu_8]$ cluster in the structure of **52**, which consists of clusters of the types I and IV linked to one another through the bridging Cu atom (Fig. 17). The $[Cu_9]$ cluster in the structure of **54** is composed of two clusters of the type IV (Fig. 18). Clusters of the types I–IV were found for the first time in ethynyl complexes of copper(I) chloride.

In the structures of σ,π-complexes containing clusters of the type I, the coplanar arrangement of the π- and σ-coordinated metal atoms [for example, the π-coordinated Cu(3) atom and the σ-coordinated Cu(1) and Cu(2) atoms in the structure of **50** (Fig. 19)] and the C≡C bond leads to the mutual strengthening

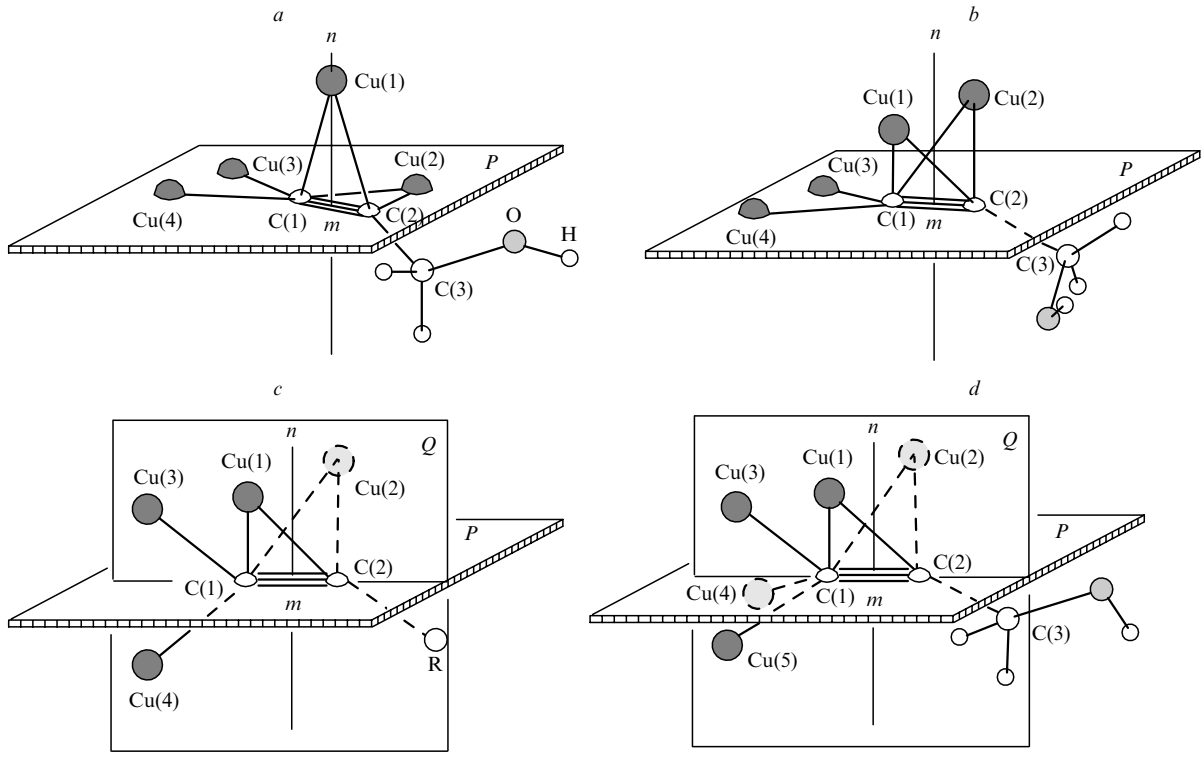


Figure 16. Types of clusters observed in the structures of ethynyl copper chloride complexes: (*a*) type I {the $[Cu_4(C\equiv CCH_2OH)]$ cluster}; (*b*) type II {the $[Cu_4(C\equiv CCH_2OH)]$ cluster}; (*c*) type III {the $[Cu_4(C\equiv CR)]$ cluster, where R = $CH=CH_2$ or CH_2OH}; (*d*) type IV {the $[Cu_5(C\equiv CCH_2OH)]$ cluster}; *mn* is the normal to the plane *P*.

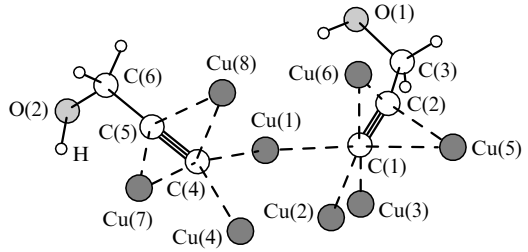


Figure 17. Cluster fragment $[Cu_8(C\equiv CCH_2OH)_2]$ in the structure of $(PyH)_2Cu_8Cl_8(C\equiv CCH_2OH)_2\cdot H_2O$ (**52**).

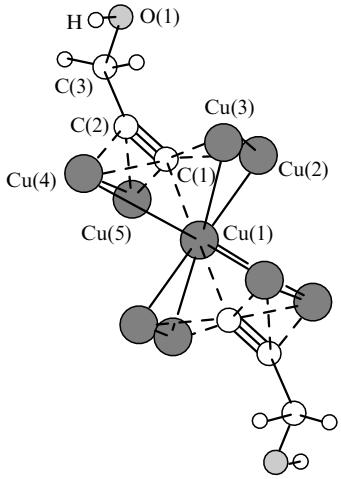


Figure 18. Cluster fragment $[Cu_9(C\equiv CCH_2OH)_2]$ in the $[HO(CH_2)_2NH_3]Cu_9Cl_8(C\equiv CCH_2OH)_2\cdot 2H_2O$ complex (**54**).

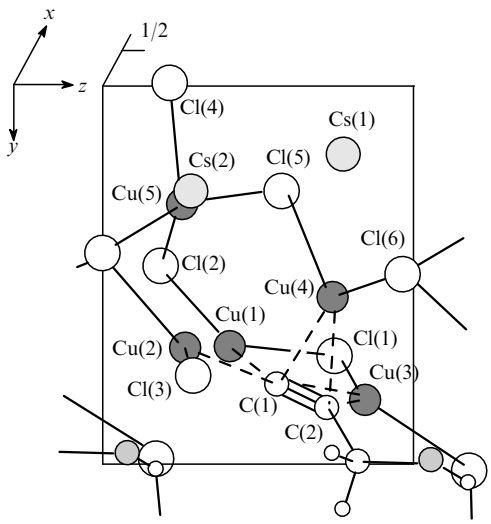


Figure 19. Fragment of the structure of $Cs_2Cu_5Cl_6(C\equiv CCH_2OH)$ (**50**).

of two individual types of interactions, *viz*., the acetylenide and π-interactions. This process becomes so efficient that the coordination polyhedra about the σ- and π-coordinated copper(I) atoms become planar-trigonal (see Tables 9 and 10). Apparently, this synergism occurs due to the angular overlapping simultaneously of three orbitals, *viz*., the occupied $d_{x^2-y^2}$ orbitals of the σ-[Cu(1)] and π-coordinated [Cu(3)] metal atoms, and the antibonding unoccupied MO (for example, $\pi^*_{\|}$) of the acetylene bond. It should be noted that there are spatial prerequisites for this 'three-centre' overlapping in the structure of **50** [the Cu(2)C(1)Cu(1), Cu(1)C(1)Cu(3) and Cu(2)C(1)Cu(4) angles are 81.3(9)°, 84.2(9)° and 89.9(9)°, respectively]. However, mutual strengthening of the Cu(I)–(η^1-C≡CR) and Cu(I)–(η^2-C≡CR) interac-

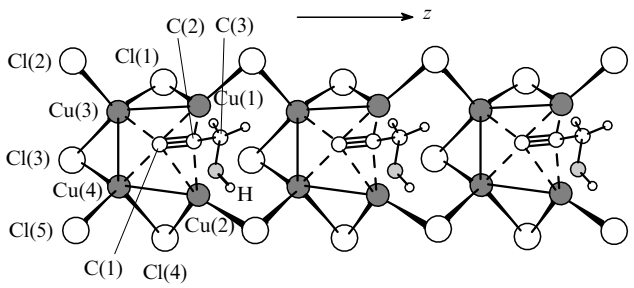


Figure 20. Anion $[Cu_4Cl_5(C\equiv CCH_2OH)^{2-}]_n$ in the structure of the $(NH_4)_2Cu_4Cl_5(C\equiv CCH_2OH)\cdot H_2O$ complex (**48**).

tions does not cause the expected substantial elongation of the C≡C bond in the complex **50** [1.22(3) Å] because the above-described angular dative process causes polarisation of the $C(1)^{\delta-}\equiv C(2)^{\delta+}$ bond. Quite a different situation is observed in the case of formation of the cluster of the type II (see Fig. 16 *b*). In this cluster, strengthening of two types of interactions (σ and π) is less efficient for geometric reasons because two π-MOs of the alkyne are located at an angle of 45° to the normal *mn*. As a result, the coordination polyhedra about the σ-coordinated Cu(I) atoms in the structures of **46**, **48** (Fig. 20) and **49** remain tetrahedral, whereas the π-coordinated Cu(I) atoms are characterised by the trigonal-pyramidal environment. In this case, the C≡C bond is substantially elongated [1.29(1) Å] due to lower polarisation. The considerable synergism of the σ and π interactions is also observed in the complexes **54** (Fig. 21), **53** and **55** (Fig. 22), which contain clusters of the types III and IV (see Figs 16 *c*,*d*). Their π- and σ-coordinated Cu(I) atoms are characterised predominantly by the planar-trigonal environment and the C≡C bond is virtually not elongated (see Tables 9 and 10).

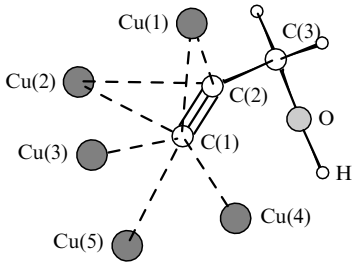


Figure 21. Cluster fragment $[Cu_5(C\equiv CCH_2OH)]$ in the structure of $Rb_3Cu_7Cl_9(C\equiv CCH_2OH)\cdot H_2O$ (**51**).

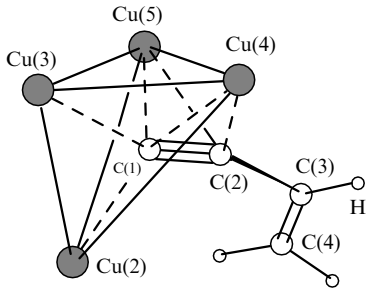


Figure 22. Cluster fragment $[Cu_4(C\equiv CCH=CH_2)]$ in the structure of $Cu_{25}Cl_{17}(C\equiv CCH=CH_2)_8\cdot 14H_2O$ (**55**).

3. Structural aspects of formation of some π-complexes and σ-ethynyl derivatives

Structures of π-complexes and products of their reversible conversions (σ-complexes) are determined both by the structures of the $(Cu_mCl_n)^{(n-m)-}$ anions in solution and the stability of the products, *i.e.*, by the favourable formation of a particular structure. However, the structures of compounds isolated from solution may not be directly associated with the mechanism of their formation because conversions of the initial intermediates of any type lead to the formation of more stable structures, but the least soluble compounds are isolated from solution. Thus, the ethynyl compound with composition $Cu_m(C_2H)$ can be formed by the reaction of $Cu_p(C_2H)$ with Cu_q ($p + q = m$) in solution. At the same time, it is of interest to analyse possible 'genetic' relations between the structures of the initial copper chloride anions and the products formed in the reactions of the latter with RC≡CH.

Let us consider the group of crystalline compounds formed in the $(C_6H_5NH_3)Cl-CuCl-H_2O-HC\equiv CCH_2OH$ system. Colourless crystals of $(C_6H_5NH_3)Cu_4Cl_7$ (**11**), which precipitated from a concentrated almost neutral solution of CuCl (4 mol) and $(C_6H_5NH_3)Cl$ (3 mol) in H_2O (20 mol), rapidly dissolved after addition of propargyl alcohol to give yellow crystals of the ethynyl complex **53**.

$$2\,(C_6H_5NH_3)_3Cu_4Cl_{7(solid)} + HC\equiv CCH_2OH + 2\,H_2O \longrightarrow$$
11
$$\longrightarrow (C_6H_5NH_3)_3Cu_8Cl_{10}(C\equiv CCH_2OH)\cdot 2\,H_2O_{solid} +$$
53
$$+\ 3(C_6H_5NH_3)Cl + HCl.$$

The reaction was accompanied by a decrease in pH to ~ 1.5. Under analogous conditions [but when CuCl and $(C_6H_5NH_3)Cl$ were taken in the molar ratio of 2 : 1], the complex **49** was obtained.

$$4CuCl + 2C_6H_5NH_3Cl + HC\equiv CCH_2OH \longrightarrow$$
$$\longrightarrow (C_6H_5NH_3)_2Cu_4Cl_5(C\equiv CCH_2OH)_{solid} + HCl.$$
49

Unlike the complex **53**, the ethynyl complex **49** was converted into the π-complex **29** upon storage in the mother liquor (pH ⩽ 1). This fact indicates that the process is non-equilibrium in character.

$$(C_6H_5NH_3)_2Cu_4Cl_5(C\equiv CCH_2OH)_{solid} + HCl \longrightarrow$$
49
$$\longrightarrow (C_6H_5NH_3)Cu_2Cl_3(HC\equiv CCH_2OH)_{solid} + (C_6H_5NH_3)Cu_2Cl_3\,.$$
29

Let us consider the relationship between the stereochemistry of compounds **11** and **53** and the possible mechanism of formation of the latter in the solid-phase process (Fig. 23). The subunit of the $(Cu_4Cl_7^{3-})_n$ anion in the structure of **11**, which consists of the Cu coordination polyhedra linked to each other, is shown in Fig. 23 *a*. The molecule of propargyl alcohol can replace the μ-Cl atom (which is hatched in Fig. 23 *a*) in **11** and can be incorporated into the initial macropolyhedron to form the π-complex (η^2-RC≡CH). In this case, the octahedral cavity in the macropolyhedron is transformed into a square-pyramidal cavity. Subsequent deprotonation of the π-ligand with the H_2O molecule affords the expected π-complex with the $^-C\equiv CR$ ligand giving rise to the bridging μ-η^2,μ-η^2-C≡CCH$_2$OH ligand (Fig. 23 *b*). The formation of the π-complex leads to weakening of some Cu–Cl bonds (indicated by dashed lines in Fig. 23 *b*) and to their cleavage accompanied by the formation of two new Cu–C≡ η^1-bonds (Fig. 23 *c*) in the $[Cu_4(C\equiv CCH_2OH)]$ cluster, which is a component of the complex **53**. In the structure of the latter, the $[Cu_8Cl_{10}(C\equiv CCH_2OH)^{3-}]_n$ anions form layers in which the σ,π-coordinated C≡CR group of each propargylium anion is clamped between four Cu atoms inside the square-pyramidal cavity. Due to steric hindrance to the penetration of the H_3O^+ ion into the cavity toward the α-carbon atom of the C≡CCH$_2$OH ligand and the high strength of bonding of the σ- and π-coordinated anion [in the structure of **53**, the length of one of the Cu–C bonds of the acetylenide type is 1.89(2) Å and the Cu–C*

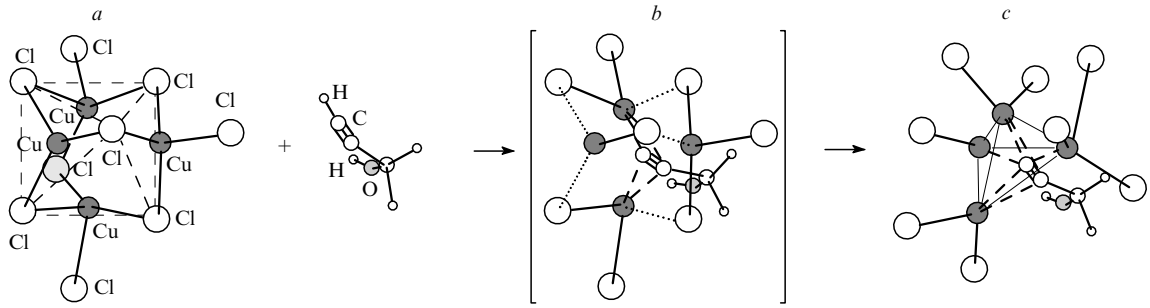


Figure 23. Conversion of the $(C_6H_5NH_3)_3Cu_4Cl_7$ complex (**11**) into the $(C_6H_5NH_3)_3Cu_8Cl_{10}(C{\equiv}CCH_2OH)\cdot 2H_2O$ complex (**53**) in the presence of $HC{\equiv}CCH_2OH$ (the stereochemical aspect).

distance is 1.97(1) Å], the complex **53** is very resistant to decomposition or conversion into the π-complex under the action of HCl.

The formation of the complex **49** differs from the above-considered complex in the structural features. Judging from the stoichiometry of the formation of the complex **29**, the $Cu_2Cl_3^-$ anion is involved in the formation of the complex **49**. This anion was revealed for the first time in the $CsCu_2Cl_3$ complex (**5**) (Fig. 24) and its structure differs fundamentally from that of the $(Cu_4Cl_7^{3-})_n$ anion. The $Cu_2C_3^-$ anion is characterised by the fact that the coordination polyhedra about the Cu atoms are linked to each other exclusively through edges to form infinite $(Cu_2Cl_3^-)_n$ chain fragments within which all metal atoms are virtually in a single plane. In this case, a peculiar sequence of planar (approximately square) $n[Cu_4]$ matrices with Cu ··· Cu contacts [2.81(1) Å] appears. In solution, the complex **5** (Fig. 24) produces the $Cu_2Cl_3^-$ anions (**A**), which interact with alkyne to form the π-complex $[Cu_2Cl_3(RC_2H)]^-$ (**B**).

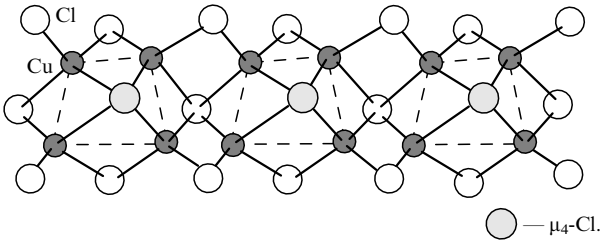


Figure 24. Anion in the structure of the $CsCu_2Cl_3$ complex (**5**).

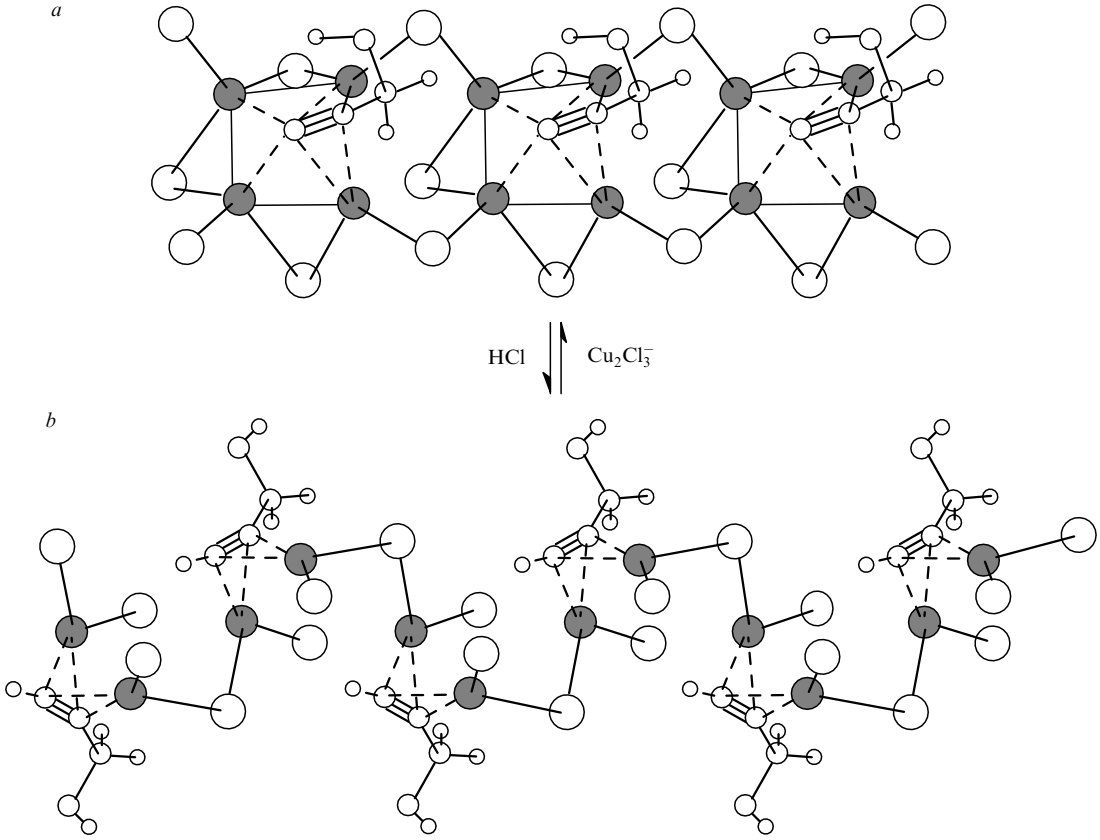
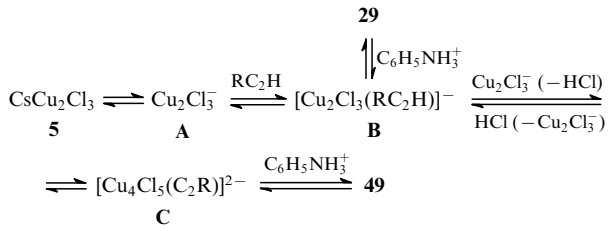


Figure 25. Scheme of formation and conversions of the crystals of the $(C_6H_5NH_3)_2Cu_4Cl_5(C{\equiv}CCH_2OH)$ complex (**49**) into $(C_6H_5NH_3)_2Cu_2Cl_3(HC{\equiv}CCH_2OH)$ (**29**): (*a*) the $[Cu_4Cl_5(C_2R)^{2-}]_n$ anion; (*b*) the $[Cu_2Cl_3(RC_2H)^-]_n$ anion.



R = CH_2OH.

The formation of the complex **49** is a non-equilibrium process and is, most likely, determined by the kinetics of its crystallisation. As a consequence, the π-complex **B** rapidly reacts with the $Cu_2Cl_3^-$ ion in solution to yield the ethynyl complex **C**, which precipitates as the compound **49**. The slow reaction of the complex **49** (through the soluble form **C**) with HCl followed by elimination of $Cu_2Cl_3^-$ to form (through the complex **B**) gives rise to the complex **29**, which is thermodynamically more stable under these conditions.

In the $[Cu_4Cl_5(C{\equiv}CCH_2OH)^{2-}]_n$ anion of the compound **49** (Fig. 25 *a*), the α-carbon atom of the $^-C{\equiv}CCH_2OH$ fragment is accessible to attack by the proton. In addition, the bonds between the σ-coordinated Cu atoms and the α-carbon atom in the structure **49** are weaker [the Cu−C≡ bonds are in the range of 1.95(2)–2.00(2) Å] than those in the complex **53**. Hence, the possibility of the conversion of the $[Cu_4Cl_5(C{\equiv}CCH_2OH)^{2-}]_n$ anion in crystals of the complex **49** accompanied by elimination of the $Cu_2Cl_3^-$ fragments to form the $[Cu_2Cl_3(HC{\equiv}CCH_2OH)^-]_n$ anion of the complex **29** must not be ruled out (Fig. 25 *b*). Crystals of the complex **29** appear in the mother liquor (pH ⩽ 1) immediately after the disappearance of crystals of the complex **49**.

IV. Catalytic conversions of acetylenic compounds in solutions of copper(I) chloride complexes

Studies of the physicochemical properties of the NH_4Cl–CuCl–H_2O system provided the basis for the development of the procedure for investigation of the kinetics of reactions in concentrated aqueous solutions.[13, 118] The principal results of these investigations are considered below.

1. Kinetics of catalytic reactions of acetylene and its derivatives in concentrated aqueous solutions of MCl–CuCl

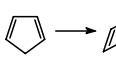
In studies of the kinetics of various reactions of acetylene (and its derivatives) in concentrated aqueous solutions of MCl and CuCl, kinetic models are generally constructed[13] with the use of an empirical dependence of the following type:

$$r = \varphi\,(p_{C_2H_2}, [HCl]_\Sigma, [CuCl]_\Sigma, [NH_4Cl]_\Sigma),$$

where r is the reaction rate and p is the partial pressure.

If the solution contains polynuclear complexes and does not contain an excess of chloride anions with respect to metal, there is no way to express the concentration of free catalytically active complexes (one or several) in terms of $[CuCl]_\Sigma$ (*i.e.*, to account for the material balance with respect to the catalyst in the kinetic equation). Hence, the only approach to a theoretically justified adequate kinetic model and to the elucidation of the reaction mechanism in these systems consists in measuring the concentrations (or activities) of the free reagents and components of the solution (Cu^+ and Cl^-) under stationary conditions of catalytic reactions and in maintaining constant conditions, the partial pressures and concentrations of the reagents being varied, *i.e.*, in maintaining the $[CuCl]_\Sigma : [Cu^+]$ and $[Cl^-]_\Sigma : [Cl^-]$ ratios and, consequently, $[(Cu_mCl_n)^{(n-m)-}]$. In other words, it is necessary to add the initial catalyst (CuCl and, if required, MCl) as the catalyst is trapped by the reagent. The values, which are directly proportional to the activities (and concentrations) of the Cu^+, Cl^- and H_3O^+ ions (see Section II), can be determined by the potentiometric method (under the conditions of constant cationic content).[22, 30, 118]

Table 11. Catalytic reactions in the CuCl–NH_4Cl–H_2O system.

Catalytic reaction	Catalytic system	[CuCl] ($\widetilde{m}$)	Ref.
$C_2H_2 + HCl \longrightarrow CH_2{=}CHCl$ (*1*)	*a*	5–12	119
$C_3H_4 + HCl \longrightarrow MeC(Cl){=}CH_2$ (*2*)	*b*	0.6–12	120
$C_3H_4 + HCl \longrightarrow MeCH{=}CHCl$ (*3*)	*c*	4–12	120
$C_4H_4 + HCl \longrightarrow CH_2{=}CHC(Cl){=}CH_2$ (*4*)	*d*	0.5–8	121
$C_2H_2 + H_2O \longrightarrow MeCHO$ (*5*)	*e*	5–12	119
	f [a]	5–12	122
$C_3H_4 + H_2O \longrightarrow Me_2CO$ (*6*)	*g*	0–12	120
	h [b]	4–12	123
$C_3H_4 + H_2O \longrightarrow MeCH_2CHO$ (*7*)	*i* [b]	4–12	123
$2\,C_2H_2 \longrightarrow HC{\equiv}CCH{=}CH_2$ (*8*)	*j*	5–12	95
$3\,C_2H_2 \longrightarrow CH_2{=}CHC{\equiv}CCH{=}CH_2$ (*9*)	*k*	5–12	124
$3\,C_2H_2 \longrightarrow CH_2{=}CHCH{=}CHC{\equiv}CH$ (*10*)	*l*	5–12	125
$C_2H_2 + HCN \longrightarrow CH_2{=}CHCN$ (*11*)	*m*	5–10	126
C_2H_2 +  (*12*)	*n*	7–12	13
	o	7–21	13

Note. In the reactions (*1*–*11*) $[NH_4Cl] = 12\,\widetilde{m}$; in the reaction (*12*) $[NH_4Cl] = 21\,\widetilde{m}$. [a] In addition to NH_4Cl, Cu_2S_{solid} is present; [b] in addition to NH_4Cl, RSH is present.

This procedure was used for studying 12 reactions of acetylenic compounds in 15 catalytic systems (Table 11). The kinetic equations obtained under conditions of the constant content of NH_4^+ and at the constant a_{Cu^+} and a_{Cl^-} values are given in Table 12. It was found that the type of equation is independent of the concentration of CuCl (in the kinetic equations, only the observed k_{ij} values are a function of this concentration, where i is the number of the reaction and j is the catalytic system) (see Table 12). In essence, k_{ij} is the function of the stationary concentrations of the $(Cu_mCl_n)^{(n-m)-}$ complexes and Cl^- ions or of the stationary activities of Cu^+ and Cl^-

$$k_{ij} = f(a_{Cu^+}, a_{Cl^-}).$$

In the simplest case (the compositions of the initial copper(I) complex and the intermediate of the first irreversible stage are identical in the Cl^- component), the equation is as follows:

$$k_{ij} = \sum_m \sum_n k_{\mathrm{eff}(m,n)}[(Cu_mCl_n)^{(m-n)-}]. \qquad (1)$$

Table 12. Kinetic equations for the reactions of acetylenic compounds in the CuCl–NH_4Cl–H_2O system.

Kinetic equation	Ref.
$r_{1a} = k_{1a}\,p_{C_2H_2}[HCl]$	119
$r_{2b} = k_{2b}\,p_{C_3H_4}[HCl] + k\,p_{C_3H_4}\,a_{Cl^-}$	120
$r_{3c} = k_{3c}\,p_{C_3H_4}[HCl]$	120
$r_{4d} = k_{4d}\,p_{C_4H_4}[HCl] + k\,p_{C_4H_4}[HCl]\,(a^2_{Cl^-}/a_{H_2O})$	121
$r_{5e} = k_{5e}\,p_{C_2H_2}[H_3O^+]/(1 + k\,[H_3O^+]$	119
$r_{5f} = k_{5f}\,p_{C_2H_2}[H_3O^+] + k\,p_{C_2H_2}$	122
$r_{6g} = k_{6g}\,p_{C_3H_4}$	120
$r_{6h} = k_{6h}\,p_{C_3H_4}$	123
$r_{7i} = k_{7i}\,p_{C_3H_4}$	123
$r_{8j} = k_{8j}\,p^2_{C_2H_2}/(k\,p_{C_2H_2} + [H_3O^+])$	95
$r_{9k} = k_{9k}\,p_{C_2H_2}\,p_{C_4H_4}/(k\,p_{C_2H_2} + [H_3O^+])$	124
$r_{10l} = k_{10l}\,p_{C_2H_2}[H_3O^+]/(k\,p_{C_2H_2} + [H_3O^+])$	125
$r_{11m} = k_{11m}\,p_{C_2H_2}\,p_{HCN}/[H_3O^+]$	126
$r_{12n(o)} = k_{12n(o)}\,p_{C_2H_2}\,p_{C_3H_6}/[H_3O^+]$	13

Note. The subscript in the kinetic equation denotes the number of the reaction and the letter denotes the catalytic system (see Table 11).

The $k_{\text{eff}(m,n)}$ values can be determined only if all complexes present in the system are taken into account, *i.e.*, by solving the system of equations of the same type (1). However, taking into account the presence of a large number of complexes in solution, the large error in the determination of k_{ij} (10% – 15%) and the errors in the determination of the total set of complexes, one cannot expect that the coefficients of this system thus obtained reflect the true contributions of individual complexes to the reaction rate. In this connection, the average composition of the complexes, which make the major contribution to k_{ij} both due to the large $k_{\text{eff}(m,n)}$ values and the high concentrations of $(Cu_mCl_n)^{(n-m)-}$, was estimated. From Eqn (1) it follows:

$$k_{ij} = \sum_m \sum_n k_{\text{eff}(m,n)} \beta_{m,n} a^m_{Cu^+} a^n_{Cl^-} = \sum_m \sum_n k_{m,n} a^m_{Cu^+} a^n_{Cl^-} . \quad (2)$$

The a_{Cl^-} value decreases as $[CuCl]_\Sigma$ increases, because a_{Cu^+} and a_{Cl^-} are interdependent:

$$[CuCl]_\Sigma = \sum_m \sum_n m\beta_{m,n} a^m_{Cu^+} a^n_{Cl^-} ,$$

$$[Cl^-]_\Sigma = [Cl^-] + \sum_m \sum_n n\beta_{m,n} a^m_{Cu^+} a^n_{Cl^-} ,$$

due to which the independent determination of m and n is impossible. It was demonstrated [126, 127] that the a_{Cu^+} and a_{Cl^-} values determined by the potentiometric method are related to each other by the empirical dependence throughout the a_{Cu^+} range met in the systems under consideration ($a_{Cu^+} = 10^{-8} - 10^{-6}$):

$$a_{Cl^-} = \frac{a^0_{Cl^-}}{b a^g_{Cu^+}} . \quad (3)$$

The b and g coefficients were determined experimentally for each case represented in Table 12. From Eqns (2) and (3) it can be shown that

$$k_{ij} = \sum_m \sum_n k_{m,n} a^m_{Cu^+} a^n_{Cl^-} = \sum_m \sum_n \frac{k_{m,n} (a^0_{Cl^-})^n}{b^n} a^{m-ng}_{Cu^+} = \sum_k k_k a^{l_k}_{Cu^+} . \quad (4)$$

The average observed order ($\hat{l}$) with respect to a_{Cu^+} can be determined by approximating Eqn (4) by Eqn (5)

$$k_{ij} = k_{\text{eff}(i,j)} a^{\hat{l}}_{Cu^+} , \quad (5)$$

where $\hat{l} = \hat{m} - \hat{n}g$ is the weighted-mean value, which accounts for the l_k values for each complex and the fraction of the reaction rate (θ_k) determined by the participation of the kth complex

$$\frac{d \ln k_{ij}}{d \ln a_{Cu^+}} = \hat{l} = \sum_k l_k \theta_k . \quad (6)$$

From Eqn (6) it follows that the $\hat{n}$ and $\hat{m}$ values are also weighted-mean. In the general case, the $\hat{l}$ value should be variable because θ_k can change as the $[CuCl]_\Sigma$ changes. The fact that the $\hat{l}$ value for all processes is constant throughout the range of CuCl concentrations under study indicates that the $m(n)$ values for the complexes, which make the major contribution to k_{ij}, are similar. To estimate the m and n values and the compositions of the initial $(Cu_mCl_y)^{(y-m)-}$ complexes ($y \neq n$ upon elimination or addition of Cl^- ions in the individual stages of the reaction), the following equation was used:

$$\hat{m} = \frac{\hat{l}}{1-g} + \frac{\hat{q}g}{1-g} = \hat{m}_{\min} + \frac{\hat{q}g}{1-g} , \quad (7)$$

where $\hat{q} = \hat{n} - \hat{m}$.

It was assumed that multiply-charged complexes, which are formed in insignificant amounts in concentrated CuCl solutions,[22, 30, 31, 33] are not involved in the reactions with acetylenic compounds, and hence analysis of the compositions of the $(Cu_mCl_y)^{(y-m)-}$ complexes was restricted to $y - m = 1$ or 2. In addition, it was assumed that acetylene replaces the water molecule upon the formation of a π-complex, thus retaining the charge of the complex. Then the parameter $\hat{q}$ in Eqn (7) can take the values 0, 1, 2 and 3 depending on the presence of stages of elimination of one Cl^- ion ($y = n + 1$, $\hat{q} = 0$ or 1) and stages of conversion of intermediates with the participation of one Cl^- ion ($y = n - 1$, $\hat{q} = 2$ or 3) as well as on the presence of mechanisms in which $y = n$ ($\hat{q} = 1$ or 2). In this case, the $\hat{m}$ values change from $\hat{m}_{\min}$ ($\hat{q} = 0$) to $\hat{m}_{\min} + 3g/(1-g)$. On these assumptions, $\hat{m} \geqslant 1$ and $\hat{n} \geqslant \hat{m}$ have a physical meaning.

The dependence of k_{ij} on $[CuCl]_\Sigma$ is shown in Fig. 26. Although the k_{ij} value increases as [CuCl] increases in all cases, the character of $k_{ij} = f[CuCl]$ is substantially different for different reactions (see Table 11). For dimerisation (*8*) of acetylene, hydrocyanation (*11*) of acetylene, hydration of methylacetylene (*6h* and *7i*) and acetylene (*5f*) and the reactions with cyclopentadiene (*12*), the k_{ij} value sharply increases only at $[CuCl]_\Sigma \geqslant 5\ \tilde{m}$, *i.e.*, in the concentration range in which polynuclear complexes ($Cu_3Cl_4^-$, $Cu_3Cl_5^{2-}$, $Cu_4Cl_5^-$, $Cu_4Cl_6^{2-}$, *etc.*) appear in noticeable amounts. The observed order with respect to $[CuCl]_\Sigma$ is smaller than unity only for the reaction with HCl (*4d*). The observed orders with respect to a_{Cu^+} ($\hat{l}$) are given in Table 13.

The $(Cu_mCl_nCN)^{(n-m+1)-}$ and $[Cu_mCl_n(C \equiv CH)]^{(n-m+1)-}$ complexes are involved in hydrocyanation (*11*) and diene condensation (*12*) of acetylene possessing rate-determining stages. These complexes are formed due to the replacement of the Cl^- ion.

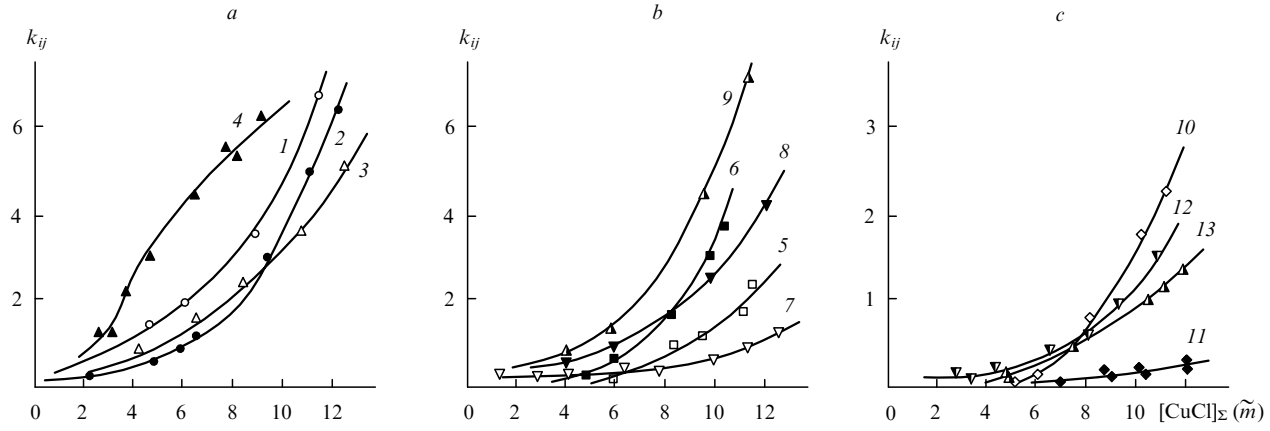


Figure 26. Dependence of k_{ij} on the concentration of CuCl: (*1*) $k_{1a} \times 10^3$; (*2*) $k_{2b} \times 10^5$; (*3*) $k_{3c} \times 10^7$; (*4*) $k_{4d} \times 0.5 \times 10^5$; (*5*) $k_{5e} \times 10^3$; (*6*) $k_{5f} \times 10^2$; (*7*) k_{6g}; (*8*) $k_{6h} \times 0.5 \times 10^5$; (*9*) $k_{7i} \times 0.5 \times 10^5$; (*10*) $k_{8j} \times 10^4$; (*11*) $k_{9k} \times 10^7$; (*12*) k_{11m}; (*13*) $k_{12n} \times 10^6$.

Table 13. The $\hat{m}$ values and the probable compositions of the initial $(Cu_mCl_y)^{(y-m)-}$ complexes.

k_{ij}	$\hat{I}$	g	$\hat{m}_{min}$ ($\hat{q}=0$)	$\hat{m}$ ($\hat{q}=1$)	$(Cu_mCl_y)^{(y-m)-}$ ($\hat{q}=1$)	$\hat{m}$ ($\hat{q}=2$)	$(Cu_mCl_y)^{(y-m)-}$ ($\hat{q}=2$)	$\hat{m}$ ($\hat{q}=3$)
k_{1a}	0.73	0.29	1.03			1.85	$CuCl_2^-$, $Cu_2Cl_3^-$	2.25
k_{2b}	0.88	0.33	1.31			2.30	$Cu_2Cl_3^-$, $Cu_3Cl_4^-$	2.79
k_{3c}	1.10	0.33	1.64			2.65	$Cu_2Cl_3^-$, $Cu_3Cl_4^-$	3.12
k_{4d}	0.71	0.33	1.06			2.26	$Cu_2Cl_3^-$, $Cu_3Cl_4^-$	2.54
k_{5e}	0.63	0.32	—	1.49	$CuCl_2^-$, $Cu_2Cl_3^-$	1.96	$Cu_2Cl_4^{2-}$	
k_{5f}	1.16	0.29	1.64	2.04	$Cu_2Cl_3^-$	2.45	$Cu_2Cl_4^{2-}$, $Cu_3Cl_5^{2-}$	
k_{6g}	0.67	0.33	1.00	1.49	$CuCl_2^-$, $Cu_2Cl_3^-$	1.99	$Cu_2Cl_4^{2-}$	
k_{6h}	0.77	0.47	1.45	2.34	$Cu_2Cl_3^-$, $Cu_3Cl_4^-$	3.23	$Cu_3Cl_5^{2-}$, $Cu_4Cl_6^{2-}$	
k_{7i}	0.99	0.47	1.87	2.75	$Cu_2Cl_3^-$, $Cu_3Cl_4^-$	3.64	$Cu_3Cl_5^{2-}$, $Cu_4Cl_6^{2-}$	
k_{8j}	2.60	0.32	3.83	4.30	$Cu_4Cl_5^-$, $Cu_5Cl_6^-$	4.76	$Cu_4Cl_6^{2-}$, $Cu_5Cl_7^{2-}$	
k_{9k}	0.13	0.33	—	—	—	1.18	$CuCl_3^{2-}$, $Cu_2Cl_4^{2-}$	
k_{10l}	0.64	0.33	—	1.45	$Cu_2Cl_3^-$, $CuCl_2^-$	1.94	$Cu_2Cl_4^{2-}$	
k_{11m}	2.21	0.39	3.62	4.26	$Cu_4Cl_6^{2-}$, $Cu_5Cl_7^{2-}$			
k_{12n}	1.52	0.60	3.80	5.30	$Cu_5Cl_7^{2-}$, $Cu_6Cl_8^{2-}$			
k_{12o}	2.02	0.60	5.05	6.55	$Cu_7Cl_9^{2-}$			

Note. At $\hat{q}=0$, the $(Cu_mCl_y)^-$ complexes with $m=3$ and 4 (catalytic systems *m* and *n*) and $m=5$ (catalytic system *o*) are involved in the reactions (*11*) and (*12*), respectively.

$$(Cu_mCl_y)^{(y-m)-} + HC\equiv CH \rightleftharpoons$$
$$\rightleftharpoons [Cu_mCl_n(C\equiv CH)]^{(n-m+1)-} + H_3O^+ + Cl^-.$$

Hence, $y=n+1$ (at $\hat{q}=0$ or 1) and $\hat{m}_{min}=3.6-5.0$ for the reactions (*11*) and (*12*). In the reactions (*8*)–(*10*), which proceed without rate-determining stages, $\hat{q}$ reflects the composition of the transition state ($y=n$). Polynuclear complexes with $m=3-7$ are involved in the reactions (*8*), (*9*) and (*12*) (see Table 3).

The participation of polynuclear Cu(I) complexes in the dimerisation of acetylene (*8*) was confirmed by spectrophotometric studies of the dependence of the dimerisation rate on the concentration of the 'yellow' complexes $[Cu_4Cl_4(C\equiv CH)^-$ and $Cu_4Cl_5(C\equiv CH)^{2-}]$ and on their compositions as a function of a_{Cu^+}, a_{Cl^-}, $p_{C_2H_2}$ and $[H_3O^+]$ [58] (see Section III) and was additionally supported by isolation of crystalline copper chloride and ethynyl complexes formed in the catalytic Nieuwland system (the structures of these complexes are considered in Sections II and III).

2. Kinetics and crystal-chemical aspects of the mechanism of Nieuwland oligomerisation of acetylene

Comprehensive investigations of the kinetics of dimerisation [58, 95, 125, 128–131] and trimerisation [124, 125] of acetylene made it possible to state the major features of the mechanism of these reactions. Let us consider dimerisation of acetylene (*8*) (see Table 11) giving rise to vinylacetylene (VA) in detail. At constant activities of Cu^+ and Cl^-, *i.e.*, at constant concentrations of catalytically active complexes, the reaction rate r_{VA} is described by the equation

$$r_{VA}=\frac{k_H p_{C_2H_2}^2}{k p_{C_2H_2}+[H_3O^+]}. \quad (8)$$

A two-stage mechanism without a rate-determining stage corresponds to this equation, where the copper chloride complex is denoted by [Cu]

$$(1)\ [Cu] + C_2H_2 \rightleftharpoons [Cu]C_2H^- + H_3O^+,$$
$$(2)\ [Cu]C_2H^- + C_2H_2 \xrightarrow{k_2} \mathbf{X_1},$$
$$(3)\ \mathbf{X_1} + H_3O^+ \xrightarrow{k_3} [Cu] + C_4H_4.$$

The stages 1 and 2, which follow unambiguously from the kinetics, are supplemented by the stage 3, which is required to obtain the final stoichiometric equation for the catalytic reaction (*8*). It was also found that the k constant in the denominator is independent of $[CuCl]_\Sigma$ (and a_{Cu^+}), but depends on a_{Cl^-} ($k=k'/a_{Cl^-}$). This fact leads to the equation

$$r_{VA}=\frac{k'_H p_{C_2H_2}}{k' p_{C_2H_2}+[H_3O^+][Cl^-]}, \quad (9)$$

according to which Cl^- and H_3O^+ are eliminated in the same stage (the stage 1 or the following quasi-equilibrium stage).

Data on the composition of the intermediate $\mathbf{X_1}$ (and to some extent on its nature) were obtained in studies of the kinetics of the preparation of vinylacetylene and 2-chlorovinylacetylene (CVA) in systems containing additionally small concentrations ($\sim 10^{-3}$ mol litre^{-1}) of $CuCl_2$.[132, 133] In the presence of $CuCl_2$, the conversion of the intermediate $\mathbf{X_1}$ takes two competitive paths, *viz.*, the stages 3 and 4

$$(4)\ \mathbf{X_1} + CuCl_2 \xrightarrow{k_4} \mathbf{X_2} \xrightarrow{CuCl_2} CH_2=C(Cl)-C\equiv CH + 2\,CuCl.$$

Under these conditions, the sum of the rates r^*_{VA} and r_{CVA} is equal to the rate of formation of $\mathbf{X_1}$ (*i.e.*, r_{VA}). The rate ratio is described by the equation

$$\frac{r^*_{VA}}{r_{CVA}}=\bar{K}\frac{[H_3O^+]}{[CuCl_2]}, \quad (10)$$

where $\bar{K}=k_3/k_4$.

As a result, the equation for the rate of formation of vinylacetylene includes the concentration of the H_3O^+ ion, which is involved in the stage 3 after the irreversible stage 2

$$r^*_{VA}=\frac{k_H p_{C_2H_2}^2}{k p_{C_2H_2}+[H_3O^+]}\cdot\frac{\bar{K}[H_3O^+]}{\bar{K}[H_3O^+]+[CuCl_2]}. \quad (11)$$

As a consequence, the rate of formation of vinylacetylene (r^*_{VA}) passes through a maximum as $[H_3O]^+$ changes. It was

suggested that the intermediate $\mathbf{X_1}$ with composition $[Cu]C_4H_3$ was formed due to the insertion of acetylene at the $Cu-C\equiv CH$ bond, *i.e.*, this intermediate is the β-ethynylvinyl derivative of copper ($CuCH=CHC\equiv CH$). The reaction of $\mathbf{X_1}$ (successively with two $CuCl_2$ molecules) afforded only chlorovinylacetylene. An analogous process took place in the reaction of $CuCH=CHCl$ with two $CuCl_2$ molecules to form $CH_2=CCl_2$ (acidolysis yielding $CH_2=CHCl$ was the competitive process).[134,135] The formation of chlorovinylacetylene from the intermediate $\mathbf{X_1}$ (it is the intermediate common to vinyl- and chlorovinylacetylenes) is also confirmed by the fact that none of such compounds as vinylacetylene, diacetylene, vinylidene chloride or vinyl chloride in these systems is converted into chlorovinylacetylene under the above-mentioned conditions.[132,133] Investigation of the effect of the addition of $HgCl_2$ on the synthesis of vinylacetylene demonstrated[131] that an increase in the acidity of the $CuCl-NH_4Cl-H_2O$ systems upon the addition of $HgCl_2$ is associated with an exchange reaction giving rise to the organomercury derivative $ClHgCH=CHC\equiv CH$, which is stable to HCl. Vinylacetylene can be isolated from this derivative only under the action of concentrated HCl.

Let us consider the stages 1–3 in more detail. Activation of acetylene resulting in its deprotonation (stage 1) occurs, most likely, in the course of several reactions the first of which involves the formation of π-complexes **B**

$$\underset{\mathbf{A}}{(Cu_mCl_n)^{(n-m)-}} + C_2H_{2(aqueous)} \rightleftharpoons \underset{\mathbf{B}}{[Cu_mCl_n(C_2H_2)]^{(n-m)-}} + H_2O.$$

Kinetic studies demonstrated that replacement of Cl^- in this stage is contradictory to Eqn (9). The formation of the π-complex can occur either in the course of the replacement of the coordinated water molecule or as a result of the cleavage of the μ-Cl bond without the replacement of Cl^-. The replacement of the bridging chlorine atom accompanied by its migration to other coordination vacancies can also occur. Based on the assumption that the short-range order of complexes dissolved in concentrated solutions (which is similar to that in a melt), for example, of $Cu_3Cl_5^{2-}$ (see Refs 48 and 49), corresponds to the structure of the complex **9a** in the crystalline state ($T_{m.p.} \approx 80$ °C), the process of replacement of the water molecules can be represented by the scheme shown in Fig. 27. In this process, the formation of the intermediate **B** is accompanied by the migration of the bridging chlorine atom in the complex **A** to the coordination site, which was previously occupied by the water molecule of crystallisation (this molecule is hatched in Fig. 27). The intermediate **B** (more precisely, the coordination π-unit) is structurally similar to one of the π-complexes (**20**, **21a**,**b**, **22** or **23**).

The reaction of the π-complex (**B**) with a water molecule affords the acetylenide (ethynyl) intermediate **C**. In this case, the Cl^- ion can be eliminated simultaneously with H_3O^+, but it can also be eliminated in the following quasi-equilibrium stage, the type of the kinetic equation being the same

$$\underset{\mathbf{B}}{[Cu_mCl_n(C_2H_2)]^{(n-m)-}} + H_2O \rightleftharpoons \underset{\mathbf{C}}{[Cu_mCl_{n-1}(C_2H)]^{(n-m)-}} + H_3O^+ + Cl^-.$$

Among a wide diversity of the structures of ethynyl compounds (see Section III), the complexes **43** and **44** (see Fig. 13) correspond to the intermediate **C** whose existence was suggested in the study[96] without convincing reasons.

As mentioned above, variations in the partial pressure of acetylene ($p_{C_2H_2}$) and $[H_3O^+]$ with the maintenance of constant a_{Cu^+} and a_{Cl^-}, *i.e.*, the concentrations of the active copper chloride complex, allows one to solve the question as to what particular σ-organometallic compound, which is present in the solution, serves as an intermediate in the catalytic reaction. In the synthesis of vinylacetylene, an unsymmetrical ethynyl complex serves as such an intermediate. In solution, other 'yellow' complexes, for example, the symmetrical acetylenide complex $[(Cu_2C_2)Cu_pCl_q)]^{(q-p)-}$ existing in equilibrium with the $[(Cu_mCl_{n-1})(C_2H)]^{(n-m)-}$ ion, are present in solution depending on pH. The above-mentioned inactive complex enters into the material balance with respect to $[CuCl]_\Sigma$. Hence, the reaction rate of the formation of vinylacetylene passes through a maximum as the concentration of HCl changes if the concentration of $(Cu_mCl_n)^{(n-m)-}$ is not maintained constant.[128] The maximum rate is observed in the range pH = 1.5–0.9 ([HCl] = 0.05–0.15 $\widetilde{m}$). In this case, an increase in the acidity of the solution (pH < 1.5) leads to destruction of symmetrical acetylenide and to an increase in the concentration of unsymmetrical $[Cu]C_2H$ acetylenide. A further increase in the acidity leads to the disappearance of this intermediate and to a decrease in the rate to zero. The formation of a complex containing the Cu_2C_2 fragment of the type **45** at pH = 4 and low temperature is in complete agreement with the above reasoning and observations.

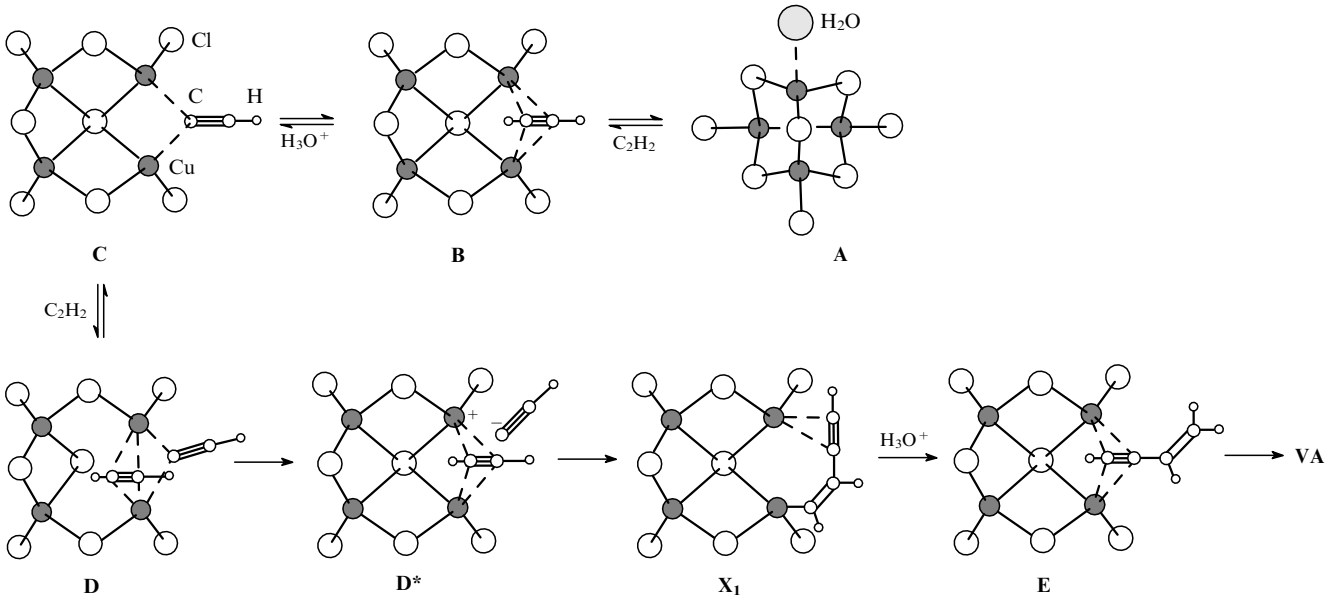


Figure 27. Structural changes in the course of catalytic oligomerisation of acetylene.

Evidently, the subsequent stage of the Nieuwland process (stage 2) giving rise to the intermediate $\mathbf{X_I}$ involves the insertion of acetylene at the $Cu-C_2H$ bond to form the $CuCH=CHC\equiv CH$ fragment whose acidolysis affords C_4H_4. Below are represented the stages of the conversion of the intermediate **C** into the intermediate $\mathbf{X_I}$ (see Fig. 27).

$$[Cu_mCl_{n-1}(C_2H)]^{(n-m)-} + C_2H_2 \rightleftharpoons$$
$$\mathbf{C}$$
$$\rightleftharpoons [Cu_mCl_{n-1}(C_2H_2)(C_2H)]^{(n-m)-} + H_2O,$$
$$\mathbf{D}$$
$$[Cu_mCl_{n-1}(C_2H_2)(C_2H)]^{(n-m)-} + H_2O \longrightarrow [Cu_mCl_{n-1}(C_4H_3)]^{(n-m)-}.$$
$$\mathbf{D} \qquad\qquad \mathbf{X_I}$$

The stage of acidolysis of the intermediate $\mathbf{X_I}$ (the electrophilic replacement of the Cu atom by the H^+ ion in the $Cu-CH=$ fragment) is beyond question. This stage was confirmed by the kinetic data [Eqn (11)]. The reaction proceeds very readily even with water.[136, 137] Stages of this type were also observed in hydration, hydrochlorination and hydrocyanation of acetylene.[13]

$$[Cu_mCl_{n-1}(C_4H_3)]^{(n-m)-} + H_3O^+ \longrightarrow$$
$$\mathbf{X_I}$$
$$\longrightarrow [Cu_mCl_{n-1}(CH_2=CHC\equiv CH)]^{(n-m+1)}.$$
$$\mathbf{E}$$

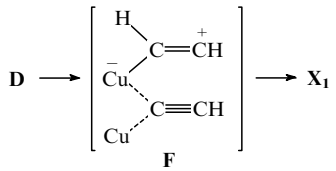
The intermediate **E** decomposes to form vinylacetylene (it can be replaced by acetylene) or is involved in trimerisation of acetylene to give hexa-1,5-dien-3-yne [divinylacetylene (DVA)].

The insertion of acetylene giving rise to the intermediate $\mathbf{X_I}$ is the most important and intricate stage of the process. The fact of insertion is beyond a doubt because the reactions of cuprates $R_2Cu\cdot MgX$ and $RCu\cdot MgX_2$ with alkynes are well known [136, 137] and proceed stereoselectively (100% *syn*-addition) under mild conditions. However, the question about the mechanism of the process of insertion remains open. In the mononuclear case, the stage of insertion

$$HC\equiv CH \longrightarrow CuCH=CHR$$
$$\downarrow$$
$$Cu-R$$

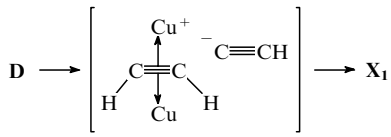
is not an elementary concerted process because it is symmetry-forbidden due to the d^{10} configuration and sp^3 hybridisation of the atomic orbitals of Cu(I).[138] Three alternative paths are formally possible.

1. The formation of the metallocarbenium ion (**F**) followed by the rapid migration of the ethynyl group giving rise to the intermediate $\mathbf{X_I}$ in the first irreversible stage.

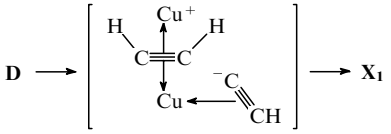


F

2. Dissociation of the [Cu](μ-η¹-C≡C) bond to form the contact ionic pair followed by the addition of the carbanion to the η²-coordinated acetylene.



3. Dissociation of the bridging [Cu](μ-η¹-C≡C) bond accompanied by the conversion of the ethynyl group into the η²-state followed by the addition of the η²-$HC\equiv C^-$ carbanion to η²-alkyne.



Path 1 was considered [13] for the reactions of cationic Pt(II) complexes with alkynes. This path was assumed[13] for reactions with the participation of Hg^{2+}, but it is less probable for Cu(I) halides. Path 3 is more interesting because a softer nucleophile and a weak base (η²-$HC\equiv C^-$) are involved in the reaction. In addition, paths 2 and 3 provide a more adequate explanation for the high stereoselectivity of the insertion of alkynes. To discuss these alternatives, let us use the data on the structures of the complexes $(PyH)_4Cu_9Cl_{12}(C\equiv CH)$ (**44**) and $NH_4Cu_8Cl_9(HC\equiv CH)_4\cdot 2/5\{[Cu(H_2O)_2]\cdot[CuCl_2]\cdot H_2O\}$ (**23**). Crystal-chemical analysis demonstrated that these compounds are genetically related (Fig. 28). The subunit Cu_8Cl_9 (Fig. 28 *b*) is common to both complexes. This subunit contains four pairs of $[Cu_2]$ 'matrices' with the $Cu\cdots Cu$ distance of ~ 2.8 Å. The η²,η²-coordination of one C_2H_2 molecule at the $[Cu_2]$ matrix each affords the structural fragment shown in Fig. 28 *c*. The coordination of the η¹,η¹-C≡CH ligand at the $[Cu_2]$ matrix gives rise to the fragment shown in Fig. 28 *a*. The relation between the fragments (*a*) and (*c*) suggests the possible stereochemistry of the second and third paths of conversions of the intermediate **D** into $\mathbf{X_I}$. Probably, the intermediate **D** is formed by the replacement of the σ-coordinated μ₄-Cl ligand in the complex with acetylene (μ-η²,η²-C_2H_2). The resulting complex **D** (see Fig. 27) contains simultaneously several ligands coordinated at the $[Cu_2]$ matrix, *viz.*, η¹,η¹-C≡CH and η²,η²-C_2H_2. The intermediate **D** can be converted into $\mathbf{X_I}$ *via* two paths. From the viewpoint of the stereochemistry, the path 2 is the most favourable and involves the cleavage of the $Cu-C$ η¹-bond to form the contact ionic pair **D*** (see Fig. 27). The ^-C_2H ion rapidly attacks one of the $C^{\delta+}$ atoms of the π-bonded C_2H_2 molecule. In the case of the path 3, the η¹,η¹-C≡CH ligand should be converted into the η¹,η²-C≡CH ligand. Then the $Cu-C$ η¹-bond can be cleaved followed by the attack of the η²-coordinated anion on the η²-acetylene. Protolysis of the intermediate $\mathbf{X_I}$ affords π-coordinated vinylacetylene (Fig. 27, the intermediate **E**).

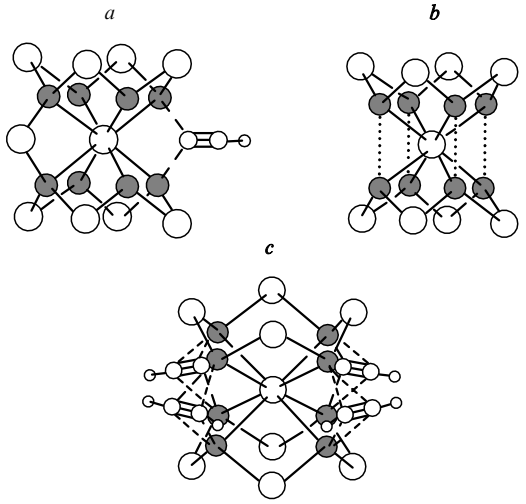


Figure 28. Structural fragment of the $(PyH)_4Cu_9Cl_{12}(C\equiv CH)$ complex (**44**) (*a*), the Cu_8Cl_9 subunit (*b*) and the structural fragment of the $NH_4Cu_8Cl_9(HC\equiv CH)_4\cdot 2/5\{[Cu(H_2O)_2]\cdot[CuCl_2]\cdot H_2O\}$ complex (**23**) (*c*).

The $[Cu_mCl_n(C_4H_4)]^{(n-m)-}$ complex (**E**) can be deprotonated to form the intermediate **G** (of the type **55**, see Fig. 22). Judging from the kinetic data, the latter is converted into divinylacetylene.

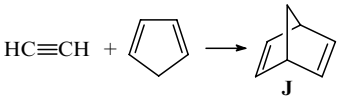
$$[Cu_mCl_n(C\equiv CCH=CH_2)]^{(n-m)-} \xrightarrow{C_2H_2} \underset{\mathbf{G}}{} \longrightarrow [Cu_mCl_n(C_4H_3)C_2H_2)]^{(n-m)-} \underset{\mathbf{H}}{} \longrightarrow \mathbf{X_3} \xrightarrow{H_3O^+}$$
$$\longrightarrow Cu_2Cl_2(CH_2=CHC\equiv CCH=CH_2) + (Cu_{m-2}Cl_{n-2})^{(n-m)-}.$$
$$\underset{\mathbf{I}}{}$$

Protolysis of the intermediate $\mathbf{X_3}$ (an analogue of $\mathbf{X_1}$) yields the intermediate **I** (complex **34**).

The intermediate $\mathbf{X_1}$ can interact with yet another acetylene molecule (through the π-complex), which can be inserted at the Cu–CH= bond, because the insertion of alkynes at the Cu(I)–alkenyl bond occurs rather readily.[137] As a result, hexa-1,3-dien-5-yne (the isomer of divinylacetylene) is formed. On certain assumptions, the scheme of its formation agrees with the kinetic data.[13]

3. Addition of cyclopentadiene and HCN to acetylene

The Diels–Alder reaction (*12*) of acetylene with cyclopentadiene to form norbornadiene **J** proceeds efficiently in highly concentrated solutions of CuCl.

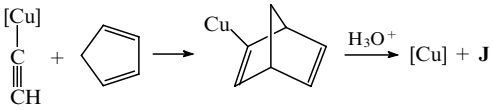


The polynuclear complexes Cu_5, Cu_6 and Cu_7 also participate in this reaction. The process involves the rate-determining stage because the reaction

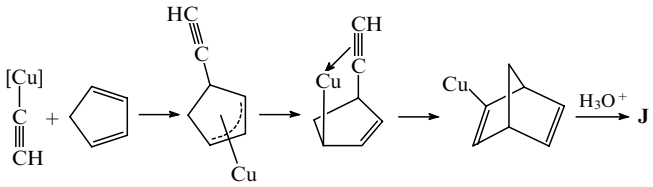
$$[Cu]C\equiv CH + C_5H_6 \longrightarrow \mathbf{X_4} \xrightarrow{H_3O^+} C_7H_8 + [Cu]$$

proceeds more slowly than the reaction of the ethynyl intermediate with C_2H_2. Two possible mechanisms of formation and conversion of $\mathbf{X_4}$ should be considered.

1. The classical diene synthesis, *viz.*, [4 + 2]-cycloaddition, with the participation of an active (polarised) dienophile.



2. The insertion of diene at the Cu–C bond to form the η^3-allylic intermediate followed by the repeated intramolecular insertion of C≡CH at the Cu–C bond.



Hydrocyanation of acetylene (*11*, see Table 12) to form acrylonitrile proceeded in more acidic solutions of CuCl (the HCl content was up to 3 mass %). The process involves the rate-determining stage. At constant a_{Cu^+} and a_{Cl^-}, the process is described by the equation

$$r_{11m} = \frac{k_{11m}\, p_{C_2H_2}\, p_{HCN}}{[H_3O^+]}. \qquad (12)$$

If the concentrations of the active components are not maintained constant, the reaction rate passes through a maximum both as p_{HCN} and the concentration of H_3O^+ change.[126] Although the conclusion about the participation of the free CN^- ion or a complex containing the ~CuCN fragment cannot be made because of the presence of the rate-determining stage, the experimental data give grounds to suggest that the the mechanism is analogous to that of dimerisation of acetylene. The concentration of free cyanide ions in acidic solutions of CuCl cannot be higher than 10^{-9}–10^{-10} mol litre^{-1} due to which the attack of the free cyanide ion present in solution on the π-coordinated acetylene ligand is improbable, as in the case of the $HC\equiv C^-$ anion in the dimerisation of acetylene.

Catalysis of hydrocyanation of acetylene in concentrated solutions makes it possible to achieve high concentrations of the copper cyanide complex ~CuC≡N. Thus the concentration of dissolved CuCN in the CuCl–NH_4Cl–H_2O system can reach 15 mass %. If HCN is passed through these systems, different mono- and polycyanide complexes of copper, *viz.*, $[Cu_mCl_{n-1}(CN)]^{(n-m)-}$ and $[Cu_mCl_{n-x}(CN)_x]^{(n-m)-}$, can be formed depending on the concentration of HCl. High reactivities of polynuclear cyanide complexes are also associated with their bridging structures analogous to those of the complex $NH_4Cu_2(CN)_3\cdot H_2O$[139] (Fig. 29 *a*) or $KCu_2(CN)_3\cdot H_2O$.[140] In addition, due to the bridging structure, CN^- can be held as an anion in the coordination sphere of the ($Cu^+C^-\equiv NCu$) complex in the course of insertion of acetylene at the Cu–CN bond. Acrylonitrile formed after acidolysis of the intermediate CuCH=CHC≡NCu can be coordinated to form the π-complex of the type $2CuCl\cdot CH_2=CHCN$.[141] In the latter, the acrylonitrile molecule serves as the bridging η^2- (at the C=C bond) and η^1- (at the N atom) ligand. Interestingly, the CN^- ion can be replaced in the structure of the cyanide complex $KCu_2(CN)_3\cdot H_2O$ by the C_2^{2-}

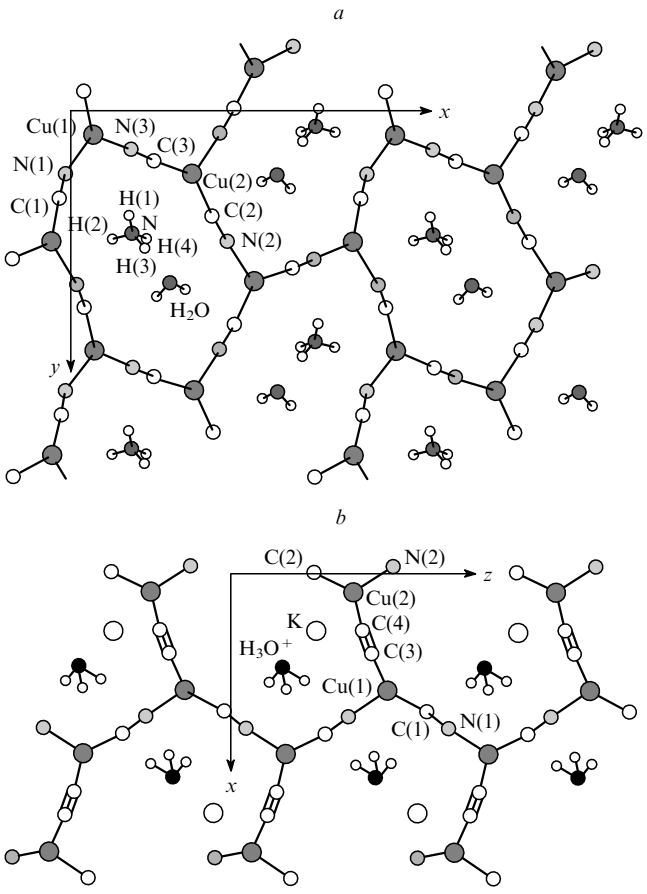


Figure 29. The $[Cu_2(CN)_3^-]_n$ anions in the structure of the $NH_4Cu_2(CN)_3\cdot H_2O$ complex[139] (*a*) and the $[Cu_2(CN)_2(C\equiv C)^{2-}]_n$ anions in the structure of the $[K(H_3O)^+]Cu_2(CN)_2(C\equiv C)$ complex[18] (*b*).

dianion (Fig. 29 *b*) to form the complex $[K(H_3O^+)]\cdot[Cu_2(CN)_2(C\equiv C)]$.[18]

4. Participation of ethynyl copper complexes in homogeneous oxidative conversions of alkynes in the CuCl – MCl – $CuCl_2$ systems

Many oxidative conversions of acetylene and alkynes proceed in concentrated solutions of CuCl in the presence of $CuCl_2$.[13, 142] As mentioned above, 2-chlorobut-1-en-3-yne,[132, 133] *trans*-1,2-dichloroethylene and 1,1-dichloroethylene[134, 135] formed from acetylene in these systems. Soluble σ-ethynyl derivatives are also involved in oxidative dehydrocondensation of alkynes yielding substituted diacetylenes **K**[13, 143] and in substituting oxidative chlorination giving rise to chloroalkynes **L**.[144–147]

$$\sim CuC\equiv CR \xrightarrow{2\,CuCl_2} \begin{cases} \xrightarrow{} RC\equiv CC\equiv CR \quad \mathbf{K} \\ \xrightarrow{} ClC\equiv CR \quad \mathbf{L} \end{cases}$$

The CuCl – $CuCl_2$ catalytic systems ($CuCl_2$ is a catalyst in the presence of O_2 or in an electrochemical system) are characterised by the formation of heterovalent polynuclear complexes very typical of copper.[148] The structure of the simplest representative of these complexes, *viz*., $[(C_2H_5)_4N]Cu_2Cl_4$, has been described.[15] The Cu(I) and Cu(II) centres in the polynuclear chain $(Cu_2Cl_4)_n^{n-}$ differ in symmetry.

Concentrated solutions, which enable one to achieve high concentrations of intermediates ($\sim CuC\equiv CR$, $\sim CuCN$ or $\sim CuCH=CHX$), play an important role in the catalysis of addition at the C≡C bonds of the HC≡CH, HCl, HOH, HCN and C_5H_6 molecules. In oxidative conversions of alkynes, electron transfer from CuR to $CuCl_2$ in mixed complexes occurs so rapidly ($k = 0.5\times10^8$ mol^{-1} litre s^{-1})[149] that the reaction rates are high even in solutions dilute with respect to CuCl (for example, at the concentrations of LiCl, CuCl and $CuCl_2$ equal to 5, 0.2 and 0.5 mol litre^{-1}, respectively). The kinetic equations for some reactions proceeeding in these systems under conditions of constant high concentration of the cations (Li^+) {when $[CuCl]_\Sigma \propto [(CuCl_n)^{(n-1)-}]$ and $[CuCl_2]_\Sigma \propto [(CuCl_n)^{(n-2)-}]$} were obtained. Thus, the rate of oxidative dimerisation of methylacetylene (MA) is described by the equation[142]

$$r_{DDA} = \frac{k_{DDA}\,p_{MA}[CuCl_2][CuCl]^2}{[H_3O^+]}, \qquad (13)$$

where DDA is dimethyldiacetylene.

The process occurs through the intermediate CuC≡CMe and involves the rate-determining stage whose transition state includes Cu(I) and Cu(II) ions $[2Cu(I)\cdot Cu(II)(^-C\equiv CR)]^{\#}$. It should be noted that two CuCl molecules enter into in the reaction even in rather dilute solutions. Apparently, these molecules are required for stabilisation of the assumed intermediate, *viz*., the ethynyl complex of copper(II) (ClCuC≡CMe). The kinetic data[142] demonstrate that two molecules of the intermediate decompose to form dialkyne

$$\underset{\mathbf{M}}{2\,ClCuC\equiv CMe\cdot 2\,CuCl} \longrightarrow MeC\equiv CC\equiv CMe + 6\,CuCl.$$

It may be suggested that the ethynyl group in the **M** complex acts as the μ_3-η^1,η^2,η^2-ligand. It is also conceivable that two CuCl molecules act as catalysts in the formation of $ClCu^{II}C\equiv CMe$

$$ClCuC\equiv CMe\cdot 2CuCl \longrightarrow ClCuC\equiv CMe + 2CuCl,$$

$$2ClCuC\equiv CMe \longrightarrow MeC\equiv CC\equiv CMe + 2CuCl.$$

The reaction of $\sim Cu^IC\equiv CMe$ with two $CuCl_2$ molecules affords 1-chloroprop-1-yne (CP). The latter is formed in two stages the first of which is rate-determining.

$$CuC\equiv CMe + 2\,CuCl_2 \longrightarrow CuCl_2(ClCu^{II}C\equiv CMe) + CuCl,$$

$$CuCl_2(ClCu^{II}C\equiv CMe) \longrightarrow ClC\equiv CMe + 2\,CuCl.$$

The reaction rate is described by the equation

$$r_{CP} = \frac{k_{CP}\,p_{MA}[CuCl_2]^2[CuCl]}{[H_3O^+]}. \qquad (14)$$

It should be noted that heterovalent copper complexes with organic ligands (of the σ- and π-types) are as yet unknown although the complex **15** may be assigned to heterovalent organometallic complexes because its structure contains Cu^{2+} ions occupying octahedral cavities and CuC≡CH species as 'guests' along with the 'host' complexes.

V. Conclusion

Analysis of the experimental data obtained in studies of the compositions and structures of the complexes $M_{(n-m)}Cu_mCl_n$ in solutions and in the solid phase, copper(I) π-complexes with acetylene and its derivatives and σ-ethynyl compounds, and information gained from investigations of the kinetics of the catalytic conversions of alkynes in the MCl – CuCl – H_2O and MCl – CuCl – $CuCl_2$ – H_2O systems reveals the specific features of the coordination chemistry of copper(I) halide complexes and the peculiarities of the behaviour of copper(I) as a catalyst of conversions of acetylenic compounds.

The formation of coordination polyhedra through bridging chloride (bromide) ligands in which Cl^- acts as the μ_2-, μ_3- or μ_4-ligand gives rise to low-charged polynuclear associates $(Cu_mCl_n)^{(n-m)-}$, which can efficiently interact with acetylene and alkynes to form various π- and σ-organometallic compounds.

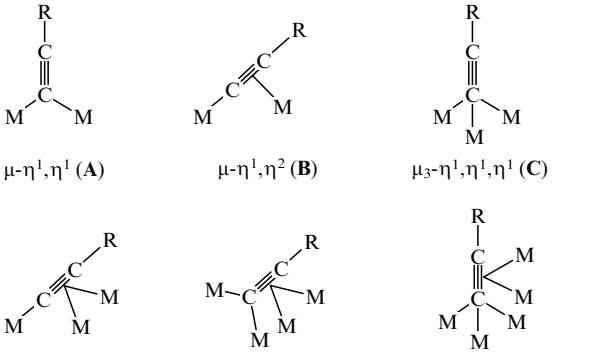
The geometric characteristics of the π-coordination polyhedra about the Cu(I) atoms and of the triple C≡C bond π-activated at the metal centre in the CuCl π-complexes with acetylene and its derivatives and the higher efficiency of the Cu(I) – (C≡C) π-interaction compared to that of Cu(I) – (C=C) are consistent with the statement that two degenerate π-MOs are split into two MOs with different energies ($\pi_\parallel$ and $\pi_\perp$) in the course of π-bonding with Cu(I) due to which the reactivities of alkynes increase. Using the copper(I) halide π-complexes of organic compounds containing the C≡C bond as an example, two qualitatively different modes of π-coordination of the C≡C groups to the Cu(I) atoms were revealed. These modes differ in the efficiency of the π-interaction. Thus, the first mode of coordination occurs in the case of the probable simultaneous participation of $\pi_\parallel$-, $\pi^*_\parallel$ and $\pi^*_\perp$-MOs to form the Cu(I) – (C≡C) π-unit. The second mode of coordination occurs if two individual π-MOs of the C≡C bond interact with the Cu(I) atom idependently of one another giving rise to the bridging Cu(I) – (C≡C) – Cu(I) π-unit (η^2,η^2-HC≡CR). In the latter case, each π-MO of the acetylene group behaves analogously to that of the ethylene group and is independently coordinated to one metal atom. The participation of the higher $\pi_\parallel$-MO and two π*-MOs is favourable for an increase in the contribution both of the donor-acceptor and dative components of the bond due to which Cu(I) – alkyne bonding in the first case is more efficient.

In the crystalline anionic π-complexes of CuCl with acetylene and its monosubstituted derivatives, the efficiency of the Cu(I) – (C≡C) π-interaction, which is manifested in the elongation of the π-coordinated C≡C bond, is substantially affected by ≡C H···Cl hydrogen bonds (the length of the π-coordinated C≡C bond depends linearly on the H···Cl distance). The reason is that the Cl atoms whose electron-withdrawing properties depend substantially on the strength of the $M^+\cdots Cl^-$ ionic interaction can affect the polarisation of the ≡C – H bond of the π-coordinated molecule of terminal alkyne through the C(H)···Cl contact due to which the electron density on the carbon atoms can increase or decrease resulting in the corresponding decrease or increase of the contribution of the dative transfer

Cu(I) → (HC≡CR). In this case, the C≡C bond is subjected to an insignificant or substantial elongation, respectively.

The high efficiency of π-interactions in copper(I) complexes of the ethynyl type (σ,π-complexes) whose formation in the MCl–CuCl–H_2O systems (according to the kinetic data) plays a decisive role in many conversions of C_2H_2 and alkynes is associated with the mutual strengthening of individual types of interactions, *viz*., of Cu(I)–(η^1-C≡CR) and Cu(I)–(η^2-C≡CR). This effect of mutual strengthening (synergism) of acetylenide and π-types of interactions, which was revealed in cluster acetylenides and ethynyl complexes of Cu(I), is often accompanied by unusual structural manifestations and by the appearance of qualitatively new properties of the C≡C group π-activated at the metal centre [the $^{-}C{\equiv}C^{-}$ dianion in the compound **45** can be π-coordinated simultaneously to three Cu(I) atoms].

In addition to the modes of coordination of ethynyl groups (C≡CR) to the copper(I) atom (**A**, **B**, **C** and **D**) known in organometallic chemistry,[96–117] new types of clusters (**E** and **F**) were found in the case of copper chloride complexes.



μ-η^1,η^1 (**A**) μ-η^1,η^2 (**B**) μ_3-η^1,η^1,η^1 (**C**)

μ_3-η^1,η^2,η^2 (**D**) μ_4-η^1,η^1,η^2,η^2 (**E**) μ_5-η^1,η^1,η^1,η^2,η^2 (**F**)

The polydentate character of coordination of acetylene in π-complexes and of ethynyl ligands in σ-organometallic compounds (as well as of cyanide groups) is the governing factor responsible for the catalytic activity of polynuclear Cu(I) complexes, which is characterised by the following features.

1. The high rate of cleavage of the bridging Cu–Cl (μ,μ_3,μ_4-Cl)-bonds to form the initial π-complexes (in some cases, the μ-Cl atom is isolobally replaced by alkyne).

2. The high solubility of such molecules as Cu≡CH, CuC≡CR and CuCN due to reactions with polynuclear $(Cu_mCl_n)^{(n-m)-}$ anions and, consequently, the high concentration of intermediates in solutions (the concentration of 'yellow' acetylenide complexes in the Nieuwland reaction reaches 0.1 mol litre^{-1}).

3. The bridging nature of the coordinated ethynyl and cyanide groups provides various stereochemical possibilities for the appearance of carbanionic ($RC{\equiv}C^{-}$) and cyanide ($N{\equiv}C^{-}$) nucleophiles in the complex.

4. The tendency for cluster-formation in polynuclear σ,π-ethynyl complexes has a particular effect on the course of catalytic processes.

5. All stages of the process, including coordination of the products, can occur on the 'matrix' of one complex formed from the [Cu_n] cluster.

6. The formation of polynuclear heterovalent complexes in oxidation reactions is favourable for the electron transfer in multiple-electron processes.

7. Hydration and hydrochlorination of alkynes in which the σ-organometallic intermediate is formed in the course of the attack of the nucleophile (Cl^- or H_2O), which is present in the solution of the copper(I) π-complex, can also occur without the participation of polynuclear complexes and, correspondingly, need not be catalysed by concentrated solutions.

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