

**COPPER(I) COMPLEXES WITH
N-ALLYLAZOMETHINES.
THE ROLE OF π - AND σ -COORDINATION
IN STRUCTURE FORMATION OF
 $2\text{CuBr}\cdot\text{R}-\text{CH}=\text{N}-\text{C}_3\text{H}_5$ (R = 2-FURYL) AND
 $\text{CuBr}\cdot\text{R}-\text{CH}=\text{N}-\text{C}_3\text{H}_5$ (R = PHENYL)**

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Crystals of the complexes $2\text{CuBr}\cdot\text{C}_4\text{H}_3(\text{O})-\text{CH}=\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$ (I) and $\text{CuBr}\cdot\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$ (II) were obtained from an ethanol solution of CuBr_2 and N-allyl-2-furylaldimine or N-allylbenzaldimine using the alternating current electrochemical procedure. Their crystal structures were determined (DARCH diffractometer, $\text{MoK}\alpha$ radiation, 1001 ($F \geq 2\sigma F$) and 911 ($F \geq 6\sigma F$) reflections; $R = 0.029$ and 0.063 , respectively, for I and II. π , σ -Complex I crystallizes in space group $A2/a$, $a = 13.698(6)$, $b = 17.679(5)$, $c = 10.247(4)$ Å, $\gamma = 114.03(3)^\circ$, $Z = 8$. Crystal data for σ -complex II: space group $P2_1/a$, $a = 19.016(5)$, $b = 13.876(2)$, $c = 4.0272(9)$ Å, $\beta = 92.90(2)^\circ$, $Z = 4$. The structure of I involves separate π - and σ - coordinations of copper(I) in the form of planar trigons similar to those in the analogous nonisostructural π -complex with copper(I) chloride. The length of the coordinated $\text{C}=\text{C}$ bond is $1.35(1)$ Å. The structure of II consists of infinite $(\text{CuBr})_n$ chains σ -coordinated to the nitrogen atom of the ligand molecules. The noncoordinated allyl group is disordered.

In d -element chemistry, azomethines with a $>\text{C}=\text{N}-$ group of varying nature are rather widespread complexes [1]. Recently, we obtained the first copper(I) π -complexes with olefinic azomethines, namely, 2:1 copper(I) chloride π , σ -complexes with N-allyl-2-furylaldimine (AFA) and N-allylbenzaldimine (ABA) and performed crystal structure determinations [2]. In both compounds, the ligand molecules exhibit similar coordination properties, promoting formation of structurally related compounds. It is of interest to continue investigating the effect of the nature of halogen atoms on the character of coordination bonds and, finally, on structure formation on the whole, especially because in the case of copper(I) bromide [3] the AFA and ABA ligands may differ in behavior. Therefore we have synthesized copper(I) bromide complexes $2\text{CuBr}\cdot\text{AFA}$ and $\text{CuBr}\cdot\text{ABA}$ and studied their crystal structures.

EXPERIMENTAL

The ligands were obtained by allylamine condensation with furfural and benzaldehyde, respectively, with further vacuum distillation [4]. The compounds $2\text{CuBr}\cdot\text{C}_4\text{H}_3(\text{O})-\text{CH}=\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$ (I) and $\text{CuBr}\cdot\text{C}_6\text{H}_5-\text{CH}=\text{N}-\text{CH}_2-\text{CH}=\text{CH}_2$ (II) were synthesized as qualitative single crystals by alternating current ($U = 0.3$ V) electrochemical reduction of Cu(II) to Cu(I) in ethanolic solutions containing CuBr_2 (~1.5 mmole) and the corresponding ligand (~2 mmole). Crystals II shaped as colorless plates grow during one day. In analogous conditions with the use of AFA, electrodes were covered with a tarry substance. The colorless prismatic crystals of complex I suitable for an X-ray experiment formed in the tar on the electrodes during several months. Using even a significant excess of copper(II) bromide relative to the ligand we were unable to obtain a compound with the composition $2\text{CuBr}\cdot\text{ABA}$.

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TABLE 1. Experimental Information and Structure Determination Details

Parameter	I	II
<i>M</i> , au	422.07	288.65
Crystal size, mm	0.35×0.25×0.25	0.45×0.3×0.08
<i>F</i> (000)	1600	568
Space group	<i>A2/a</i>	<i>P2₁/a</i>
<i>a</i> , Å	13.698(6)	19.016(5)
<i>b</i> , Å	17.679(5)	13.876(2)
<i>c</i> , Å	10.247(4)	4.0272(9)
β, deg		92.90(2)
γ, deg	114.03(3)	
<i>V</i> , Å ³	2266(2)	1061.2(4)
<i>Z</i>	8	4
ρ(exp), g/cm ³	2.50	1.83
ρ(calc), g/cm ³	2.474(3)	1.806(1)
μ _{Mo} , cm ⁻¹	113.23	60.73
Scan mode	θ/2θ	θ/2θ
Measured reflections	1075	1334
Unique reflections	1032	1176
Observed reflections (<i>F</i> ≥ <i>nσ</i> (<i>F</i>))	1001	911
<i>n</i>	2	6
2θ _{max} , deg	48	55
No. of parameters refined	164	149
Extinction coefficient	0.00015(2)	—
<i>R</i>	0.0289	0.0629
<i>R_w</i>	0.0291	0.0654
Weighting scheme	σ(<i>F</i> ₀) ² + 0.0006 <i>F</i> ₀ ²] ⁻¹	σ(<i>F</i> ₀) ² + 0.0057 <i>F</i> ₀ ²] ⁻¹
<i>GOOF</i>	0.99	1.03

After a preliminary study by the photomethod, the structures were solved using the diffraction data collected on a DARCH single crystal diffractometer (MoK_α radiation); the intensities were corrected for Lorentz and polarization factors. Crystal data and data collection conditions are listed in Table 1. The structures were solved by direct methods. The light atoms and the H atoms were located from difference Fourier syntheses. During the structure solution for **II** it was found that the double bond of the noncoordinated allyl group is considerably delocalized in one of the directions, due to which pseudoshortening of the C(1)=C(2) distance and deformation of the C(1)=C(2)–C(3) bond angle were observed. Therefore the positions of the carbon atoms of the double bond were split; this led to improved geometry. The hydrogen atoms near the disordered bond were not localized. The nonhydrogen atoms were refined by the full-matrix least-squares anisotropic procedure; the hydrogen atoms and the split carbon atoms in **II** were refined by the isotropic procedure. All calculations including the correction for absorption (DIFABS) were carried out using the CSD package [5]. The atomic coordinates and thermal parameters of **I** and **II** are given in Table 2; interatomic distances and bond and torsion angles are listed in Table 3.

TABLE 2. Atomic Coordinates (×10⁵; ×10⁴ for O, N, C; ×10³ for H) and Thermal Parameters* (×10², Å) for **I** and **II**

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
I					II				
1	2	3	4	5	6	7	8	9	10
Cu(1)	33017(8)	–7863(6)	1770(10)	4.91(5)	Cu	27770(10)	22320(10)	–38740(50)	5.52(8)
Cu(2)	47907(9)	4768(7)	–18000(10)	5.49(5)	Br	30740(10)	13600(10)	–90250(40)	5.50(6)
Br(1)	33727(7)	–12770(6)	23556(9)	5.50(4)	N	2424(10)	3526(8)	–5060(30)	6.3(6)
Br(2)	41751(6)	7054(5)	2849(8)	4.33(3)	C(1.1)**	4010(20)	4810(30)	–3660(90)	7(1)

TABLE 2 (Continued)

1	2	3	4	5	6	7	8	9	10
O	4293(4)	1303(3)	-3868(6)	5.2(3)	C(1.2)**	4160(30)	4460(40)	-4290(130)	5(2)
N	3890(5)	313(4)	-3119(7)	3.9(3)	C(2.1)**	3690(20)	3990(30)	-5060(70)	5(1)
C(1)	2457(7)	-1915(5)	-716(9)	5.2(4)	C(2.2)**	3500(30)	4540(50)	-4840(130)	7(2)
C(2)	2650(6)	-1337(5)	-1656(8)	3.8(3)	C(3)	2953(8)	4112(10)	-6760(40)	4.7(5)
C(3)	33449(7)	-1179(5)	-2715(8)	5.0(4)	C(4)	1859(9)	3910(10)	-4920(40)	5.2(6)
C(4)	3714(6)	-134(5)	-4266(9)	4.4(4)	C(5)	1226(8)	3449(10)	-3460(40)	4.8(6)
C(5)	3989(5)	679(6)	-4749(9)	5.6(4)	C(6)	634(11)	4020(11)	-2990(50)	7.2(7)
C(6)	3953(9)	976(8)	-5938(10)	6.5(6)	C(7)	54(10)	3658(15)	-1710(50)	7.8(8)
C(7)	4266(9)	1826(8)	-5826(12)	6.8(5)	C(8)	26(10)	2720(20)	-840(50)	7.5(7)
C(8)	4445(9)	1988(7)	-4602(14)	7.5(6)	C(9)	589(11)	2150(20)	-1240(60)	7.2(8)
H(1.1)	171(5)	212(4)	-20(6)	4(2)	C(10)	1196(10)	2488(10)	-2660(50)	6.7(7)
H(1.2)	292(5)	-224(4)	-50(6)	4(2)	H(3.1)	304(5)	397(6)	-993(25)	2(3)
H(2)	217(4)	-112(4)	-174(6)	3(2)	H(3.2)	280(5)	464(6)	-775(23)	1(2)
H(3.1)	398(5)	-141(4)	-254(7)	5(2)	H(4)	181(3)	442(4)	-552(15)	1(1)
H(3.2)	318(4)	-145(3)	-348(5)	2(2)	H(6)	71(6)	454(8)	-390(32)	6(4)
H(4)	348(4)	-53(4)	-462(6)	3(2)	H(7)	-38(6)	395(7)	-132(27)	3(3)
H(6)	392(5)	80(4)	-653(6)	1(2)	H(8)	-34(6)	254(7)	5(36)	5(4)
H(7)	436(7)	222(5)	-638(9)	7(3)	H(9)	59(9)	171(9)	-88(40)	4(6)
H(8)	467(5)	235(4)	-416(6)	1(2)	H(10)	168(6)	213(7)	-240(28)	2(3)

For nonhydrogen atoms, $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^ a_j^* (a_i a_j)$.

**Occupation factor is 0.63(9) for C(1.1) and C(2.1), 0.37(9) for C(1.2) and C(2.2).

TABLE 3. Bond Lengths d (Å) and the Bond and Torsion Angles ω and ϕ (deg), Respectively, in **I** and **II**

Bond*	d	Angle*	ω
I			
1	2	3	4
Cu(1)–Br(1)	2.412(4)	Br(1)–Cu(1)–Br(2)	106.0(2)
Cu(1)–Br(2)	2.414(5)	Br(1)–Cu(1)– <i>m</i> (12)	117.7(3)
Cu(1)–C(1)	2.07(1)	Br(2)–Cu(1)– <i>m</i> (12)	136.2(4)
Cu(1)–C(2)	2.136(9)	C(1)–Cu(1)–C(2)	37.4(3)
Cu(1)– <i>m</i> (12)	1.991(9)		
Cu(2)–Br(1)	2.399(6)	Br(1)–Cu(2)–Br(2)	118.0(2)
Cu(2)–Br(2)	2.391(5)	Br(1)–Cu(2)–N	117.3(3)
Cu(2)–N	1.974(8)	Br(2)–Cu(2)–N	124.7(3)
		Cu(1)–Br(1)–Cu(2)	75.8(2)
		Cu(1)–Br(2)–Cu(2)	80.0(2)
C(1)–C(2)	1.35(1)	C(2)–C(1)–H(1.1)	119(4)
C(1)–H(1.1)	1.07(7)	C(2)–C(1)–H(1.2)	126(4)
C(1)–H(1.2)	1.04(7)	H(1.1)–C(1)–H(1.2)	115(5)
C(2)–C(3)	1.49(1)	C(1)–C(2)–C(3)	124.5(9)
C(2)–H(2)	0.89(7)	C(1)–C(2)–H(2)	116(4)
		C(3)–C(2)–H(2)	118(4)
C(3)–N	1.46(1)	C(2)–C(3)–N	111.3(8)
C(3)–H(3.1)	0.98(8)	C(2)–C(3)–H(3.1)	113(4)

TABLE 3 (Continued)

1	2	3	4
C(3)–H(3.2)	0.92(6)	C(2)–C(3)–H(3.2) N–C(3)–H(3.1) N–C(3)–H(3.2) H(3.1)–C(3)–H(3.2)	115(4) 116(4) 103(4) 98(6)
N–C(4)	1.27(1)	C(3)–N–C(4)	119.1(8)
C(4)–C(5)	1.42(1)	N–C(4)–C(5)	125.4(9)
C(4)–H(4)	0.73(6)	N–C(4)–H(4) C(5)–C(4)–H(4)	106(5) 129(5)
C(5)–C(6)	1.34(2)	C(4)–C(5)–C(6)	133(1)
C(5)–O	1.35(1)	C(4)–C(5)–O C(6)–C(5)–O	117.3(9) 110(1)
C(6)–C(7)	1.39(2)	C(5)–C(6)–C(7)	108(1)
C(6)–H(6)	0.67(6)	C(5)–C(6)–H(6) C(7)–C(6)–H(6)	131(6) 120(6)
C(7)–C(8)	1.29(2)	C(6)–C(7)–C(8)	106(1)
C(7)–H(7)	0.87(9)	C(6)–C(7)–H(7) C(8)–C(7)–H(7)	134(6) 121(6)
C(8)–O	1.37(1)	C(7)–C(8)–O	113(1)
C(8)–H(8)	0.74(6)	C(7)–C(8)–H(8) O–C(8)–H(8) C(8)–O–C(5)	140(5) 107(5) 103.9(9)
II			
Cu–Br	2.491(3)	Br–Cu–Br'	112.8(2)
Cu–Br'	2.342(3)	Br–Cu–N	109.3(5)
Cu–N	1.97(1)	Br'–Cu–N Cu–Br–Cu'	137.7(5) 112.8(2)
C(1.1)–C(2.1)	1.39(6)		
C(1.2)–C(2.2)	1.26(9)		
C(2.1)–C(3)	1.54(3)	C(1.1)–C(2.1)–C(3)	117(3)
C(2.2)–C(3)	1.39(7)	C(1.2)–C(2.2)–C(3)	140(6)
C(3)–N	1.49(2)	C(2.1)–C(3)–N C(2.2)–C(3)–N	111(2) 119(3)
N–C(4)	1.20(3)	C(3)–N–C(4)	114(1)
C(4)–C(5)	1.51(2)	N–C(4)–C(5)	124(2)
C(5)–C(6)	1.40(3)	C(4)–C(5)–C(6)	119(1)
C(5)–C(10)	1.37(2)	C(4)–C(5)–C(10) C(6)–C(5)–C(10)	123(2) 118(2)
C(6)–C(7)	1.34(3)	C(5)–C(6)–C(7)	122(2)
C(7)–C(8)	1.35(3)	C(6)–C(7)–C(8)	121(2)
C(8)–C(9)	1.35(3)	C(7)–C(8)–C(9)	120(2)
C(9)–C(10)	1.40(3)	C(8)–C(9)–C(10) C(9)–C(10)–C(5)	122(2) 118(2)
C–H	0.6(1)–1.3(1)		
Torsion angles			
Angle	φ	Angle	φ
I			
Cu(1)Br(1)Cu(2)Br(2)	47.1	C(3)NC(4)C(5)	172.8
Cu(1)Br(2)Cu(2)Br(1)	138.3	NC(4)C(5)C(6)	–172.8

TABLE 3 (Continued)

1	2	3	4
Cu(1)C(1)C(2)C(3)	-105.9	NC(4)C(5)O	-12.0
Cu(2)NC(3)C(2)	67.9	C(4)C(5)C(6)C(7)	176.7
Cu(2)NC(4)C(5)	-10.8	C(5)C(6)C(7)C(8)	-1.3
C(1)C(2)C(3)N	-149.4	C(6)C(7)C(8)O	-1.0
C(2)C(3)NC(4)	-115.3		
II			
BrCuBr'Cu'	-180.0	C(2.2)C(3)NC(4)	107.1
CuNC(3)C(2.1)	-42.5	C(3)NC(4)C(5)	177.2
CuNC(3)C(2.2)	-78.0	NC(4)C(5)C(6)	-170.6
CuNC(4)C(5)	-3.7	NC(4)C(5)C(10)	-11.3
C(1.1)C(2.1)C(3)N	-117.6	C(4)C(5)C(6)C(7)	179.9
C(1.2)C(2.2)C(3)N	110.0	C(5)C(6)C(7)C(8)	-0.2
C(2.1)C(3)NC(4)	142.6	C(6)C(7)C(8)C(9)	-0.5

**m*(12) — the middle of the C(1)–C(2) bond.

RESULTS AND DISCUSSION

Complexes **I** and **II** are built as typical molecular compounds. In **I**, separate π - and σ - coordinations involving two copper(I) atoms are observed; the π -coordinated Cu(1) atom lies in the plane of a triangle formed by the C=C bond and two bromine atoms, and the Cu(2) atom is σ -coordinated with the nitrogen atom and two bromine atoms. As a result of the planar trigonal coordination, the departure of the copper atoms from the plane of ligands in **I** is 0.026 and 0.012 Å, respectively, and the C=C bond forms a small angle $\tau = 1.2^\circ$ with the plane of ligands and is lengthened to 1.35(1) Å.

Structure **I** is built from centrosymmetric dimers $(\text{Cu}_2\text{Br}_2\cdot\text{AFA})_2$ containing inorganic rings Cu_4Br_4 (Fig. 1). The structure of the fragment is rather similar to that in the complexes $2\text{CuCl}\cdot\text{AFA}$ (**III**) and $2\text{CuCl}\cdot\text{ABA}$ (**IV**) [2], but there is a slight difference between them: the Cu(1)X(1)Cu(2) angle equals 75.8° in **I** versus $94.1(1)$ and $95.4(2)^\circ$ in **III** and **IV**. Due to this, the inorganic fragment is more compact in **I** and a contact Cu(2)–Br(2)' is formed, which is absent in **III** and which together with the Cu(2)–O contact forms the trigonal bipyramidal environment of Cu(2). The bond lengths Cu(2)–Br(2)'

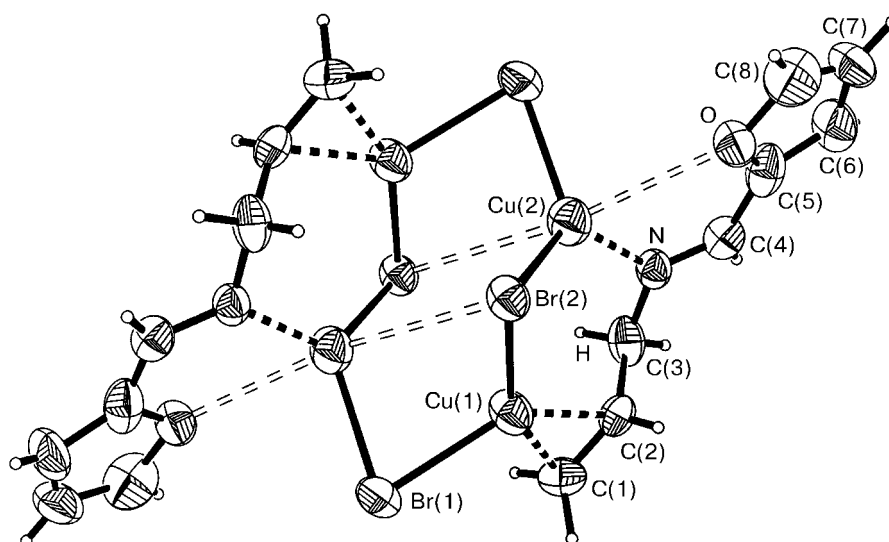


Fig. 1. Structure of the $(\text{Cu}_2\text{Br}_2\cdot\text{L})_2$ dimer in **I**.

3.346(6) Å and Cu(2)–O 2.810(8) Å are close to the values corresponding to the maximal separation of the axial ligands in the trigonal pyramidal sphere of copper(I) in the π -complexes [6]. The maximal deformation of the copper environment involving axial contacts is 68.7(3)° [OCu(2)N angle] and 82.5(2)° [Br(1)Cu(2)Br(2)′ angle]. The angle between the OCu(2)Br(2)′ axial ligands is 158.2(2)°.

Another difference between the structures of $(\text{Cu}_2\text{X}_2\text{AFA})_2$ dimers in **I** and **III** lies in deflection of the Cu(2) atom from the conjugation plane of the furan ring and aldimine N atom as a result of Cl substitution by Br leading to a decreased Cu(1)X(1)Cu(2) angle in structure **I**. Thus in structure **III** the deviation of Cu(2) from the plane of the aromatic nucleus is 0.049 Å, and the nitrogen atom deflects by only 0.003 Å. In structure **I**, these values are 0.746 and 0.090 Å, respectively. The copper atom departing from the plane of the conjugate part of the AFA molecule [Cu(2)NC(4)C(5) angle is -10.8°] breaks the directed Cu(2)–N bond with the electron pair of the nitrogen atom of the Schiff base; Cu(2)–N bond length is 1.974(8) Å in **I** versus 1.932(4) and 1.941(5) Å in **III** and **IV** [in **III** and **IV**, the Cu(2)NC(4)C(5) angle is -2.3 and -0.7°].

In structure **I**, the dimers are linked by intermolecular interactions and hydrogen contacts C(2)–H(2)...Br(2) [H(2)...Br(2) 3.06(6) Å, C(2)H(2)Br(2) 131(5)°]. The latter contacts lead to polarization of atoms in a sequence $\text{Br}^{\delta-} \dots \text{H}^{\delta+} - \text{C}^{\delta-} (= \text{C}) \dots \text{Cu}^{\delta+}$ and to more effective coordination Cu–(C=C). The crystal structure of compound **I** is shown in Fig. 2.

The structure of σ -complex **II** consists of infinite chains $(\text{CuBr})_n$ oriented along [001] and σ -coordinated to the nitrogen atoms of ABA molecules. The phenyl rings and the disordered allyl groups of ABA molecules coordinated to different fragments face each other and are linked by van der Waals forces. The structure of complex **II** is presented in Fig. 3. The coordination sphere of Cu(I) is planar trigonal; the angle of deviation of the copper atom from the ligand plane is only 0.062°. The Cu–N bond length is close to that in **I** [1.97(1) Å; the CuNC(4)C(5) angle is -3.7°]. Although the azomethine nitrogen atom behaves in the same way, the N=C(4) bond length differs between **I** and **II**: 1.27(1) Å in **I** and 1.20(3) Å in **II**. The C(4)–C(5) bond at the aromatic ring in **I** is much shorter [1.42(1) Å] than in **II** (1.51(2) Å). The difference in the degree of N=C conjugation to the aromatic ring between the AFA and ABA molecules is probably caused by the presence of an oxygen atom chelating Cu(2) along with N in AFA. The same, but less pronounced, differences between the geometries of AFA and ABA are also revealed in the isostructural complexes **III** and **IV**.

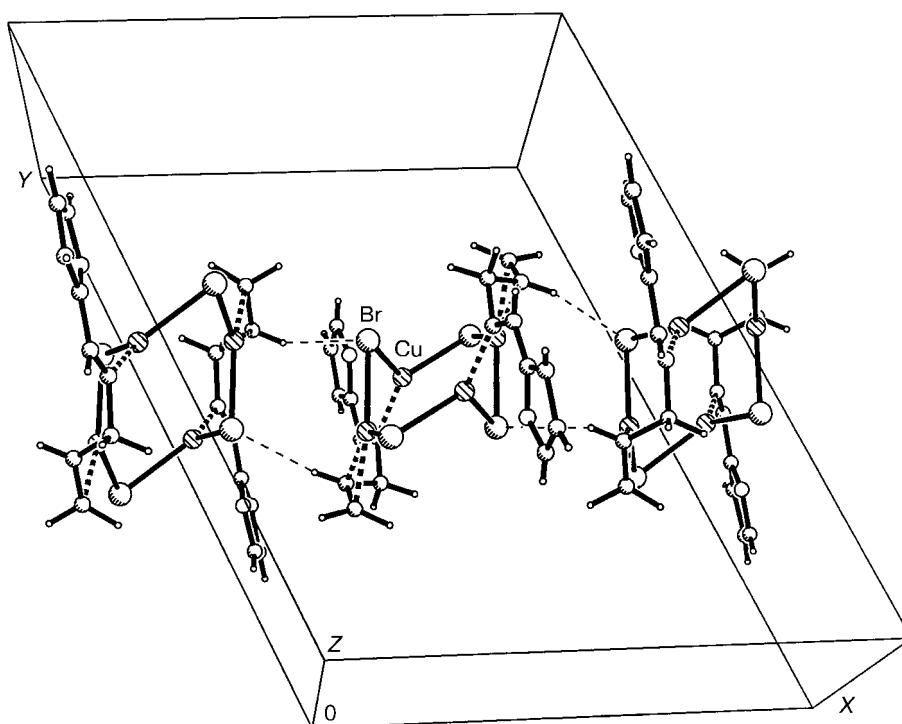


Fig. 2. Crystal structure of compound **I**.

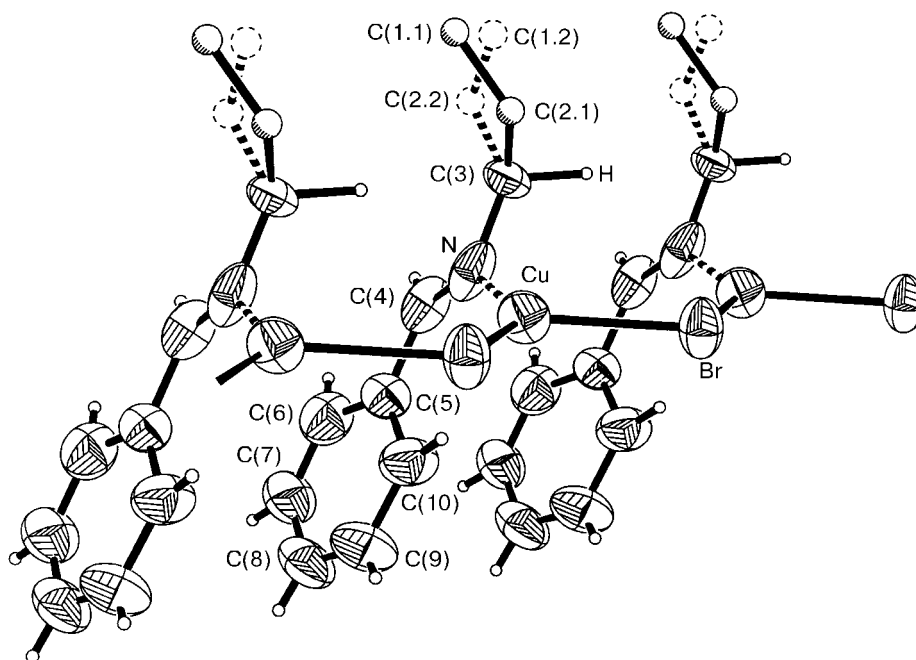


Fig. 3. Structure of complex **II**.

Thus substitution of the furan ring by the phenyl one changes the behavior of the ligand and forms a 1:1 σ -complex CuBr. The type of halogen atom also plays an important role. Replacement of Cl by Br leads to a more compact inorganic fragment and, as a consequence, to the nonisostructural character of **III** and **I**. In the case of complex **II**, the presence of Br atoms in the coordination sphere of Cu(I) promotes formation of only the σ -bond Cu–N.

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