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Copper(I) Halide Complexes with N,N'-Diallyl-N,N,N',N'-Tetramethylethylenediaminium (L^{2+}). Synthesis and Crystal Structures of the Complexes [$L_{0.5}CuCl_2$], [$L_{0.5}CuCl_{0.72}Br_{1.28}$], and [$L_{0.5}CuBr_2$]

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Abstract—The Eschweiler–Clarke reaction of ethylenediamine with formaldehyde and formic acid yielded N,N,N',N'-tetramethylethylenediamine, which was alkylated with allyl chloride or allyl bromide to give the corresponding N,N'-diallyl-N,N,N',N'-tetramethylethylenediaminium (L^{2+}) dihalides. In methanolic solutions of copper(II) halide and an appropriate ligand, ac electrochemical synthesis with copper wire electrodes afforded single crystals of Cu(I) complexes with L^{2+}: [$L_{0.5}CuCl_2$] (**I**), [$L_{0.5}CuCl_{0.72}Br_{1.28}$] (**II**), and [$L_{0.5}CuBr_2$] (**III**). The crystal structures of complexes **I**–**III** were determined by X-ray diffraction study. The isostructural crystals of **I** and **II** are monoclinic, space group $P2_1/n$, $Z = 4$. For **I**: $a = 7.632(4)$ Å, $b = 11.318(5)$ Å, $c = 10.635(5)$ Å, $\beta = 98.551(7)^\circ$, $V = 908.4(7)$ Å^3. For **II**: $a = 7.7415(7)$ Å, $b = 11.4652(9)$ Å, $c = 10.7267(10)$ Å, $\beta = 98.351(4)^\circ$, $V = 942.0(2)$ Å^3. The organic cation L^{2+} acts as a bridge linking a pair of separate cuprous halide fragments Cu_2X_4. Although being isostoichiometric with **I** and **II**, complex **III** has a different structure. The crystals of **III** are monoclinic, space group $P2_1/c$, $a = 6.519(2)$ Å, $b = 9.060(3)$ Å, $c = 16.284(6)$ Å, $\beta = 97.219(4)^\circ$, $V = 954.2(6)$ Å^3, $Z = 4$. In structure **III**, the inorganic fragment forms infinite polymer chains $(CuBr_2^-)_n$. The organic and inorganic parts are held together only by electrostatic interactions. Structures **I**–**III** are stabilized by hydrogen bonds (C)H···X (2.6–2.9 Å).

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Our previous investigations have dealt with the synthesis and X-ray diffraction study of copper complexes with N,N,N,N',N',N'-hexaallylethylenediaminium (**L⁶**) – [$\{L^6\}_{0.5}Cu_2Br_3$] [1], N,N,N,N',N'-pentaallylethylenediaminium (**L⁵**) – [$L^5(H^+)Cu_4Br_6$], and N,N,N',N'-tetraallylethylenediaminium (**L⁴**) – [$\{L^4(H^+)_2\}_{0.5}Cu_2Cl_3$] [2]. To understand better the complexation between N-allyl derivatives of ethylenediamine and copper(I) halides, here we obtained Cu(I) complexes with N,N'-diallyl-N,N,N',N'-tetramethylethylenediaminium (**L^{2+}**) – [$L_{0.5}CuCl_2$] (**I**), [$L_{0.5}CuCl_{0.72}Br_{1.28}$] (**II**), and [$L_{0.5}CuBr_2$] (**III**)) and examined their structures using X-ray diffraction.

EXPERIMENTAL

Synthesis. N,N,N',N'-Tetramethylethylenediamine (**L**) was prepared by the Eschweiler–Clarke reaction of ethylenediamine with formaldehyde and formic acid according to a general procedure for the synthesis of tertiary amines from primary or secondary ones [3]:

$$H_2NC_2H_4NH_2 + 4CH_2O + 4HCOOH \xrightarrow{T,\,^\circ C} (CH_3)_2NC_2H_4N(CH_3)_2 + 4CO_2 + 4H_2O.$$

Formaldehyde (35% solution, 38 ml) and 90% formic acid (52 ml) were added to ethylenediamine (6.65 ml, 6.0 g). The reaction mixture was refluxed on a water bath. After vigorous evolution of CO_2 ceased, the heating was continued for several hours (the total time of the synthesis was ~11 h). Then an excess of 36% HCl (18 ml) was added; the unreacted formaldehyde and formic acid were removed. The free ligand was liberated from its hydrochloride by adding an excess of concentrated aqueous KOH to the residue and extracted with benzene. The solvent and other volatile impurities were removed to give virtually pure ligand L in ~80% yield, which then was distilled under reduced pressure (40 mmHg/80°C).

N,N'-Diallyl-N,N,N',N'-tetramethylethylenediaminium dichloride **LCl_2** was obtained from L and allyl chloride in a molar ratio of 1 : 2.2. The reaction mixture was refluxed in benzene with vigorous stirring for 17 h. The resulting white precipitate of the ligand was filtered off.

N,N'-Diallyl-N,N,N',N'-tetramethylethylenediaminium dibromide **LBr_2** was obtained from L and

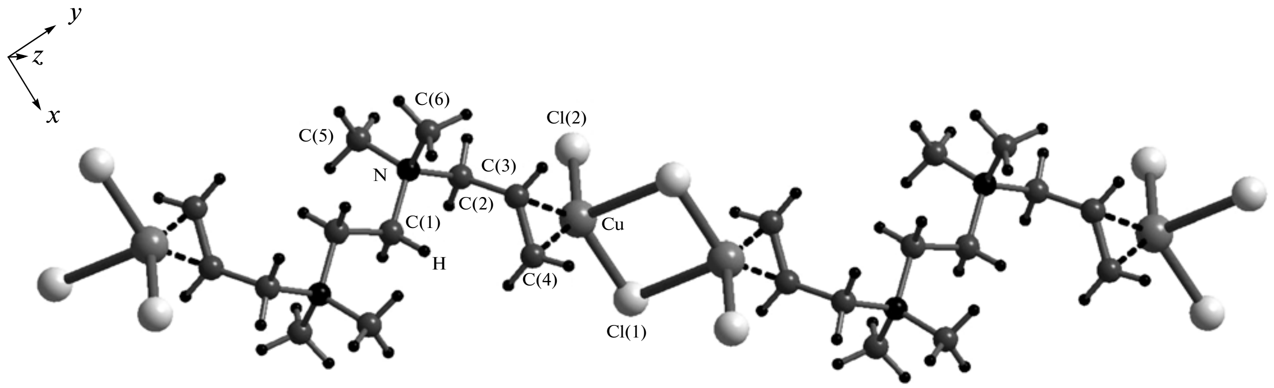

Fig. 1. Bridging function of N,N'-diallyl-N,N,N',N'-tetramethylethylenediaminium in structure **I**: Cu-Cl(1), 2.261(2) Å; Cu-Cl(2), 2.242(2) Å; Cu-*m**, 1.953(1) Å; C(4)CuC(3), 38.6(2)°; C(3)–C(4), 1.368(9) Å (*m** is the midpoint of the C(3)–C(4) bond).

allyl bromide in a molar ratio of 1 : 2.2. Because the reaction is exothermic, allyl bromide was slowly added dropwise. The reaction mixture was refluxed in benzene with vigorous stirring for 10 h. The resulting white precipitate of LBr_2 was filtered off.

Colorless prismatic crystals of complexes **I** and **II** were obtained by an ac electrochemical synthesis [4] with copper wire electrodes in methanolic solutions of $CuCl_2 \cdot 2H_2O$ containing LCl_2 or LBr_2, respectively. Crystals of complex **I** grew after 24 h. Small crystals of complex **II** formed after three days grew up to a required size for three weeks.

Colorless prismatic crystals of complex **III** were obtained by an ac electrochemical synthesis with copper wire electrodes in a methanolic solution of $CuBr_2$ and LBr_2 for three days. The crystals grew up to a required size for three and half weeks.

X-ray diffraction analysis. After a preliminary photometric study, structures **I**–**III** were identified using arrays of reflection intensities collected on a Rigaku AFC7R single-crystal diffractometer (CCD detector, MoK_α radiation, graphite monochromator, ω scan mode, a low-temperature attachment) and corrected for the Lorentz and polarization factors. The data obtained were processed with the Rigaku CrystalClear program package [5]. Structures **I**–**III** were solved by the direct methods. Light atoms were located from difference electron-density maps. An absorption correction was applied analytically [6]. Structures **I**–**III** were solved with the SIR-92 program [7] and refined with the SHELX program package [8]. All hydrogen atoms were located geometrically. Crystallographic parameters and the data collection statistics for structures **I**–**III** are summarized in Table 1. Selected bond lengths and bond angles are given in the figure captions.

The atomic coordinates and other parameters of complexes **I**–**III** have been deposited with the Cambridge Crystallographic Data Collection (nos. 780362, 780363, and 780364, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

In the isostructural crystals of complexes **I** and **II**, both allyl groups of N,N'-diallyl-N,N,N',N'-tetramethylethylenediaminium are π-coordinated by the copper atoms (Fig. 1). The structure contains a centrosymmetric inorganic island fragment Cu_2X_4. The coordination polyhedron of copper(I) is a trigonal pyramid with two halogen atoms and the allyl C=C bond the alkyl group of ligand L^{2+} in the base and an apical halogen atom. The length of the coordinated C=C bond is 1.368(9) Å in **I** and 1.364(9) Å in **II**. Earlier, the fragment Cu_2X_4 has been found in copper complexes with asymmetric alkyl derivatives of ethylenediamine: $[(CH_3)_2NC_2H_4NH(CH_3)Cu_2^{II}Cl_4]$ [9] and $[(C_2H_5)_2NC_2H_4NH(C_2H_5)Cu_2^{II}Cl_4]$ [10], as well as with allyl onium derivatives of aliphatic amines [11, 12]. The anion $Cu_2Br_4^{2-}$ is also contained in a copper π-complex with N,N,N,N',N',N'-hexaallylethylenediaminium bromide, $[\{L^6\}_{0.5}CuBr_2]$ [13]. In other copper complexes with tetra- (L^4), penta- (L^5), and hexaallylethylenediamines (L^6), the inorganic fragment has a more complicated structure: either an island-type structure (but with a different composition) as in $[\{L^4(H^+)_2\}_{0.5}Cu_2Cl_3]$ [2] or a polymeric one as in $[L^5(H^+)Cu_4Br_6]$ [1] and $[\{L^6\}_{0.5}Cu_2Br_3]$ [2]. The C=C bonds of the allyl groups of the organic cation L^{2+} in complexes **I** and **II** are coordinated by the metal atoms of two anions $Cu_2X_4^{2-}$. Thus, the ligand acts as a bridge, which is also characteristic of other allyl derivatives of ethylenediamine [1, 2]; in contrast, N,N,N',N'-tetramethylethylenediamine forms chelate complexes with copper(I) halides [14]. Structures **I** and **II** are built from infinite chains of interconnected cations and anions (Fig. 2). The chains are

Table 1. Crystallographic parameters and the data collection statistics for structures **I–III**

Parameter	Value		
	I	**II**	**III**
Empirical formula	$C_6H_{13}NCl_2Cu$	$C_6H_{13}NCl_{0.72}Br_{1.28}Cu$	$C_6H_{13}NBr_2Cu$
M	233.62	290.52	322.52
Crystal size, mm	0.13 × 0.07 × 0.06	0.12 × 0.10 × 0.09	0.1 × 0.07 × 0.06
Temperature, K	296	200	200
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
Unit cell parameters:			
a, Å	7.632(4)	7.7415(7)	6.519(2)
b, Å	11.318(5)	11.4652(9)	9.060(3)
c, Å	10.635(5)	10.7267(10)	16.284(6)
β, deg	98.551(7)	98.351(4)	97.219(4)
V, $Å^3$	908.4(7)	942.0(2)	954.2(6)
Z	4	4	4
ρ_{calcd}, g/cm^3	1.708	2.048	2.245
ρ_{exp}, g/cm^3	1.70	2.04	2.23
μ, mm^{-1}	2.92	7.90	10.60
F(000)	476	567.8	620
Ranges of h, k, and l indices	$-9 < h < 10$	$-7 < h < 10$	$-8 < h < 6$
	$-14 < k < 9$	$-15 < k < 15$	$-11 < k < 6$
	$-13 < l < 11$	$-13 < l < 8$	$-21 < l < 20$
R_{int}	0.049	0.037	0.039
Number of measured reflections	4007	3966	4190
Number of reflections with $F > 4\sigma(F)$*	1485	1590	1699
Number of parameters refined	91	93	92
$2\theta_{max}$, deg	58.0	58.0	58.4
Weighting scheme**	$[\sigma^2(F_o^2) + (0.0743P)^2 + 1.886P]^{-1}$	$[\sigma^2(F_o^2) + (0.052P)^2 + 1.5641P]^{-1}$	$[\sigma^2(F_o^2) + (0.0392P)^2 + 0.7846P]^{-1}$
$R(F^2)(F > 4\sigma(F))$	0.070	0.054	0.043
wR	0.1645	0.135	0.098
GOOF	1.12	1.11	1.18
$\Delta\rho_{max}/\Delta\rho_{min}$, $e\,Å^{-3}$	0.67/–0.63	0.83/–0.97	0.76/–1.01

* A correction for the Lorentz and polarization factors was applied.

** $P = (F_o^2 + 2F_c^2)/3$.

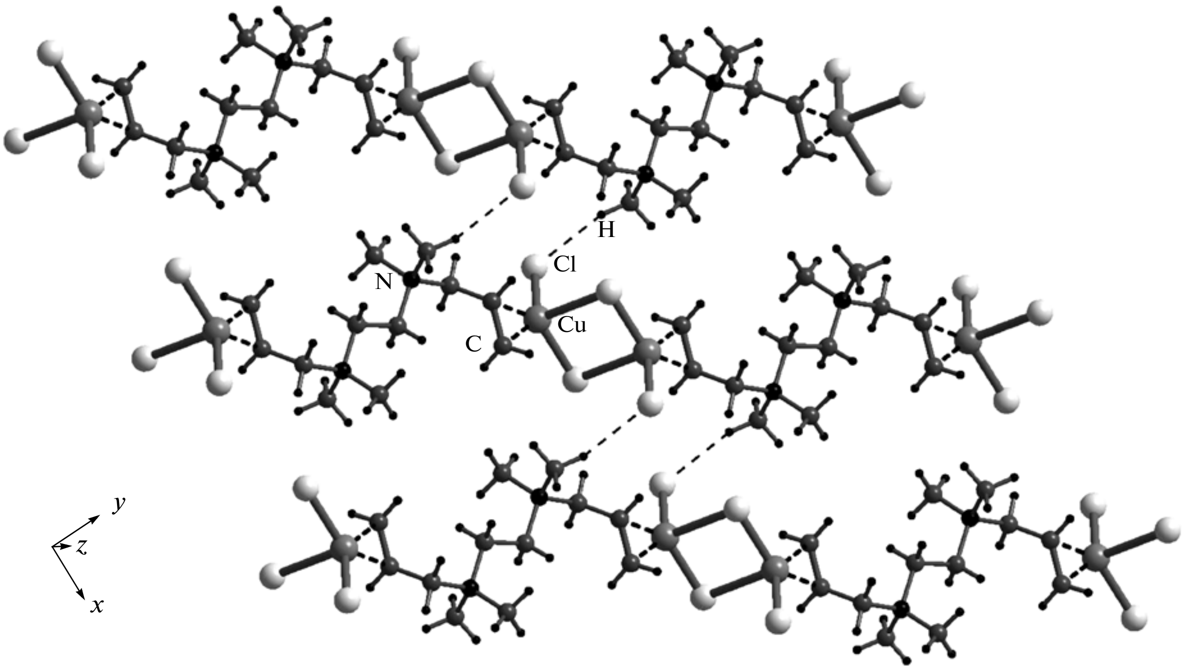

Fig. 2. Fragment of structure **I**.

united, both within a layer and between adjacent layers, through a branched system of hydrogen bonds (C)H···X (Table 2).

Complex **III** has a different structure (Fig. 3). The allyl groups are not π-coordinated by the copper(I) atoms. A similar pattern has been noted for N-allyl

Table 2. Geometrical parameters of the hydrogen bonds in structures **I**–**III**

Contact D–H···A	Bond lengths, Å			D–H···A angle, deg	Coordinates of atom A
	D–H	H···A	D···A		
			I		
C(1)–H(12)···Cl(2)	0.97	2.81	3.71(2)	154	$2.5 - x, -0.5 + y, 0.5 - z$
C(2)–H(22)···Cl(1)	0.97	2.86	3.73(1)	149	$-1 + x, y, z$
C(5)–H(52)···Cl(1)	0.96	2.61	3.53(2)	161	$2.5 - x, -0.5 + y, 0.5 - z$
C(6)–H(61)···Cl(1)	0.96	2.77	3.72(2)	174	$-0.5 + x, 0.5 - y, 0.5 + z$
C(6)–H(63)···Cl(2)	0.96	2.73	3.55(1)	144	$2 - x, 1 - y, 1 - z$
			II		
C(5)–H(53)···Cl(2)	0.96	2.87	3.68(2)	142	$1 + x, y, z$
C(6)–H(62)···Br(1)	0.96	2.88	3.82(2)	167	$0.5 + x, 1.5 - y, -0.5 + z$
C(2)–H(22)···Cl(2)	0.97	2.94	3.80(1)	149	$1 + x, y, z$
C(1)–H(12)···Br(1)	0.97	2.91	3.81(2)	155	$1.5 - x, -0.5 + y, 0.5 - z$
			III		
C(1)–H(12)···Br(2)	0.97	2.89	3.82(2)	161	x, y, z
C(1)–H(11)···Br(2)	0.97	2.94	3.85(2)	156	$1 + x, y, z$
C(2)–H(22)···Br(1)	0.97	3.01	3.86(1)	147	$x, 1 + y, z$
C(5)–H(53)···Br(1)	0.96	2.83	3.74(2)	159	$x, 1 + y, z$

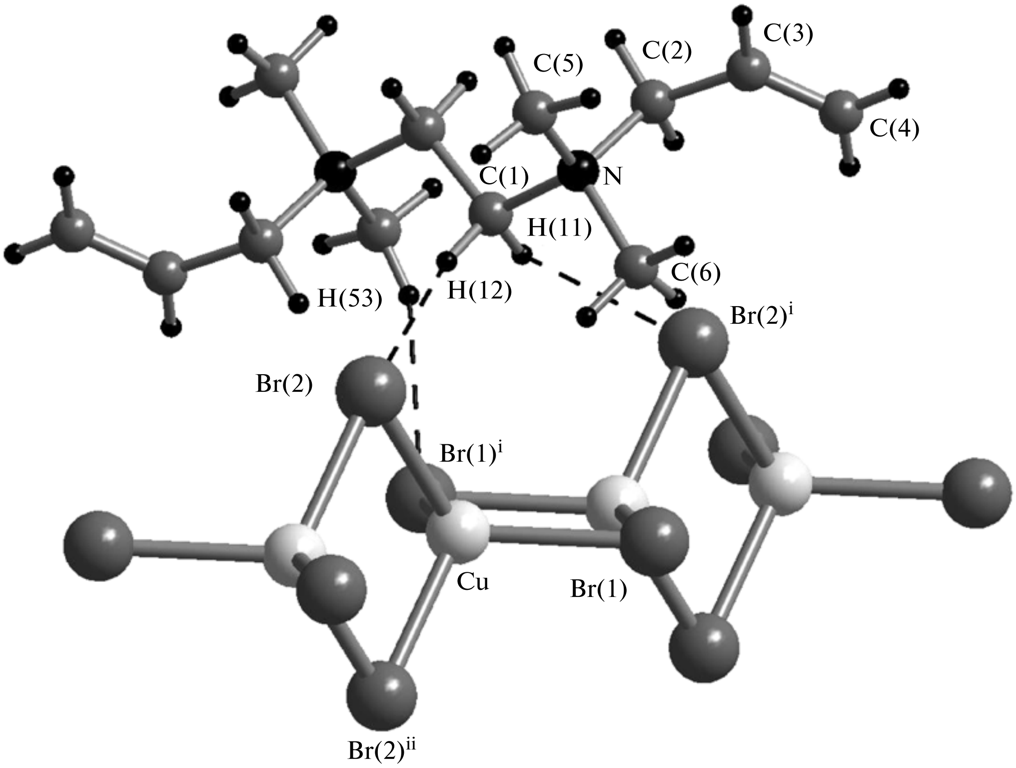

Fig. 3. Geometry of the coordination entity in structure **III**: Cu–Br(1), 2.487(2) Å; Cu–Br(2), 2.512(2) Å; Cu–Br(1)^{i}, 2.520(2) Å; Cu–Br(2)^{ii}, 2.523(2) Å (^{i} $-x + 1, -y, -z + 1$; ^{ii} $-x, -y, -z + 1$).

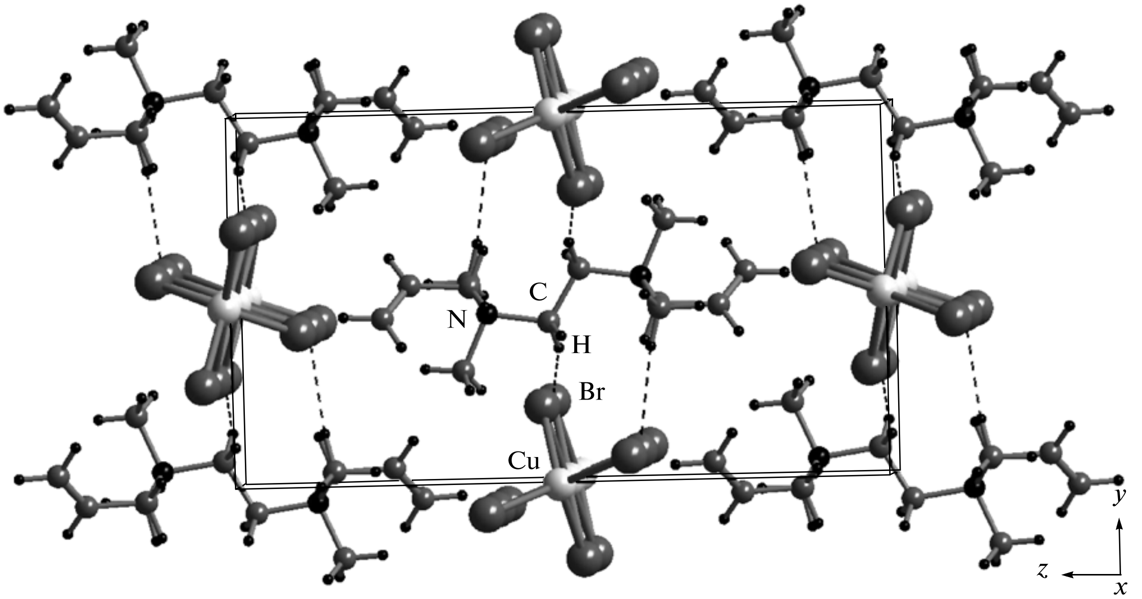

Fig. 4. Fragment of structure **III**.

derivatives of piperazinium, in which even the partial presence of a Br atom in the environment of Cu(I) precludes the formation of the bond Cu(I)–(C=C) [15, 16]. The organic and inorganic parts in structure **III** are held together by electrostatic interactions (Fig. 4). Structure **III** contains the polymeric inorganic anion $\left(\mathrm{CuBr}_2^-\right)_n$, which is similar to that in copper(I) complexes with the ethylenediaminium cation [2]. The tetrahedral environment of the copper atom consists of bromine atoms (Cu–Br, 2.487(2)–2.523(2) Å). The determining role in structure **III** is played by hydrogen bonds C(H)···X (Table 2) which crosslink the organic and inorganic parts of the structure, thus ordering the arrangement of the methyl and allyl groups of the cation L^{2+}.

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