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New π Ligand N,N,N,N',N',N'-Hexaallylethylenediaminium (L^{2+}): Synthesis and Crystal Structures of $LBr_2 \cdot 2H_2O$ and Its Cuprocomplexes $L[Cu^{II}(Br_{0.45}Cl_{3.55})]$, $L[Cu^{I}_4(Br_{4.55}Cl_{1.45})]$, and $L[Cu^{I}_4Br_6]$

M. M. Monchak[a], A. V. Pavlyuk[a,b], V. V. Kinzhibalo[b], and M. G. Mys'kiv[a]

[a] *Franko National University, ul. Kirilla i Mefodiya 6, Lviv, 79005 Ukraine*

[b] *Wroclaw University, ul. F. Joliot-Curie 14, Wroclaw, Poland*

E-mail: myskiv@franko.lviv.ua

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Abstract—The alkylation of ethylenediamine with allyl bromide in the presence of a fourfold (with respect to ethylenediamine) molar amount of $NaHCO_3$ in acetone with an ethanol admixture (15 : 1) affords $LBr_2 \cdot 2H_2O$ (**I**), where L^{2+} is the N,N,N,N',N',N'-hexaallylethylenediaminium cation. Single crystals of complexes $L[Cu^{II}(Br_{0.45}Cl_{3.55})]$ (**II**), $L[Cu^{I}_4(Br_{4.55}Cl_{1.45})]$ (**III**), and $L[Cu^{I}_4Br_6]$ (**IV**) are prepared by ac electrochemical synthesis from an ethanolic solution of $LBr_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$ (or $CuBr_2$) at copper wire electrodes. The crystal structures of compounds **I**–**IV** are determined by X-ray diffraction analysis. The crystals of complex **I** are monoclinic: space group $P2_1/n$, $a = 8.544(3)$, $b = 10.404(3)$, $c = 13.350(4)$ Å, $\beta = 97.29(3)°$, $V = 1177.2(6)$ Å^3, $Z = 2$. The bromine anions in compound **I** are bonded to the L^{2+} cations and water molecules through hydrogen contacts (E)H···Br (E = O, C) of 2.57(3)–2.86(3) Å. The crystals of compounds **II**–**IV** are triclinic: space group $P\bar{1}$. For **II**: $a = 8.762(4)$, $b = 9.163(4)$, $c = 16.500(6)$ Å, $\alpha = 95.62(4)°$, $\beta = 96.39(4)°$, $\gamma = 111.46(4)°$, $V = 1211.4(9)$ Å^3, $Z = 2$; for **III**: $a = 9.074(4)$, $b = 9.435(4)$, $c = 9.829(5)$ Å, $\alpha = 116.12(4)°$, $\beta = 104.14(4)°$, $\gamma = 100.22(4)°$, $V = 692.3(6)$ Å^3, $Z = 1$; for **IV** isostructural **III**: $a = 9.084(4)$, $b = 9.404(4)$, $c = 9.869(4)$ Å, $\alpha = 116.31(3)°$, $\beta = 104.00(3)°$, $\gamma = 100.37(3)°$, $V = 692.1(5)$ Å^3, $Z = 1$. Unlike the isolated tetrahedral CuX_4^{2-} anion in structure **II**, an original chain anion $(Cu_4X_6^{2-})_n$ is observed in the structures of π complexes **III** and **IV**.

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INTRODUCTION

Ethylenediamine (**En**) has been known long ago as a chelate ligand in a number of both copper(II) complexes (for example, $[Cu(En)(Bipy)Cl]OH \cdot H_2O$ [1], $[Cu(En)_2Cl]PF_6$ [2], and $[Cu(En)_2Cl(H_2O)]Cl$ [3]) and copper(I) compounds ($[Cu(En)(CO)][B(Phen)_4]$ [4] and $[Cu_2(En(CH_3)_4)_2I_2]$ [5]). Continuing the studies on the stereochemistry of the copper(I) π complexes with the acyclic allyl-containing ligands [6–8] and regarding the problem of using crystals in technology, it was interesting to study the behavior of ethylenediamine modified by allyl bromide with respect to Cu(I).

This work presents the results of the synthesis and X-ray diffraction analysis of the copper complexes wich contain the N,N,N,N',N',N'-hexaallylethylenediaminium cation ($\mathbf{L^{2+}}$) with the quaternary nitrogen atoms inactive toward copper: $L[Cu^{II}(Br_{0.45}Cl_{3.55})]$ (**II**), $L[Cu^{I}_4(Br_{4.55}Cl_{1.45})]$ (**III**), and $L[Cu^{I}_4Br_6]$ (**IV**), as well as the starting compound $LBr_2 \cdot 2H_2O$ (**I**).

EXPERIMENTAL

Synthesis of complex I was carried out by the interaction of preliminarily dried and distilled ethylenediamine and allyl bromide in the presence of a fourfold (with respect to ethylenediamine) molar amount of $NaHCO_3$ with vigorous stirring and reflux of the mixture in acetone with an ethanol admixture (15 : 1) for 28 h. After a NaBr precipitate was separated, a solution of LBr_2 in acetone was evaporated at room temperature. Light yellow crystals with $T_m = 77°C$ were obtained.

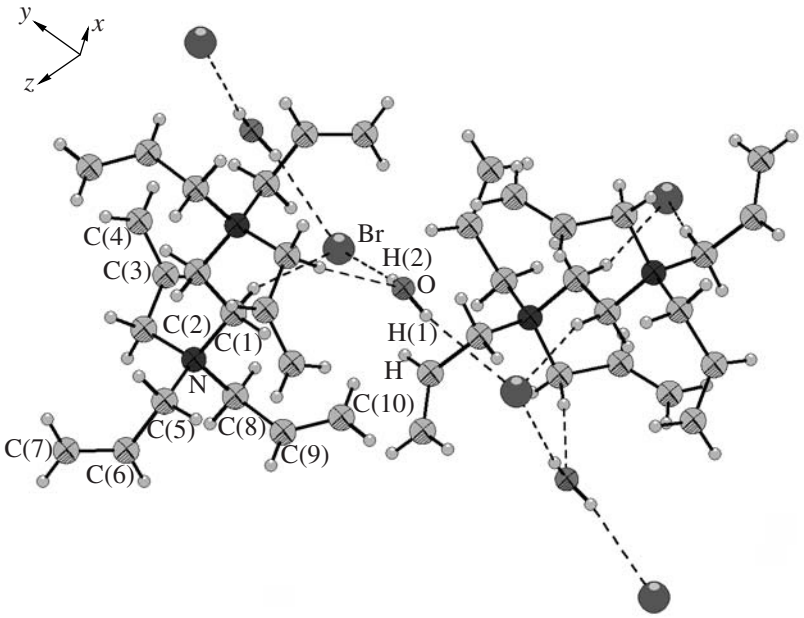

Fig. 1. Fragment of structure **I** and selected geometric characteristics: C(3)=C(4) 1.327(2), C(6)=C(7) 1.323(2), C(9)=C(10) 1.328(2) Å; OH(1)···Br 2.57(3) Å, OH(1)Br 171(2)°, OH(2)···Br 2.64(3) Å, OH(2)Br 167(2)°, C(1)H(1*A*)···Br 2.84 Å, C(1)H(1*A*)Br 162° and C(2)H(2*B*)···O 2.39 Å, C(2)H(2*B*)O 175°.

Red crystals of compound **II** were formed on the copper wire electrodes of the electrochemical reactor containing an alcoholic solution of $CuCl_2 \cdot 2H_2O$ and $LBr_2 \cdot 2H_2O$ for one day without the electric current.

Yellowish crystals of complex **III** grew on the copper electrodes of the reactor containing an ethanolic solution of $CuCl_2 \cdot 2H_2O$ and $LBr_2 \cdot 2H_2O$ as a result of the ac electrochemical synthesis [8] (U = 0.4 V, I_{init} = 0.3 mA) for a week.

Orange crystals of complex **IV** were also obtained by the above described electrochemical method from an alcoholic solution of $CuBr_2$ and $LBr_2 \cdot 2H_2O$ for two days.

X-Ray diffraction analysis. After preliminary studies of compounds **I**–**IV** by the photomethod, diffraction sets obtained on Xcalibur XPS and KUMA-KM4/CCD single-crystal diffractometers (CCD detector, MoK_α radiation, graphite monochromator, ω scan mode, OXFORD-Cryosystem low-temperature attachment) were used to determine their structures. Corrections to the Lorentz and polarization factors were applied to reflection intensities. The X-ray diffraction data were processed using the CrysAlis RED program [9]. Structures **I**–**IV** were solved by direct methods, and light atoms were revealed from the difference Fourier syntheses. An absorption correction was applied by the analytical method [10]. The structures were solved using the SHELX program package [11]. The hydrogen atoms were found in the difference Fourier syntheses and refined in the riding model along with the non-hydrogen atoms. The crystallographic data for compounds **I**–**IV** and details of X-ray experiment are collected in the table. Selected bond lengths and bond angles are listed in the figure captions.

The coordinates of atoms and other parameters for compounds **I**–**IV** were deposited with the Cambridge Structural Database (nos. 695 093, 695 094, 695 095, and 695 096; http://www.ccdc.cam.ac.uk/conts/retrieving.html).

RESULTS AND DISCUSSION

In structure **I**, the electrostatic attraction between the centrosymmetric hexaallylethylenediaminium L^{2+} cations and bromide anions is supplemented by the (O)H···Br hydrogen bonds (2.58–2.65 Å) and weaker (C)H···Br contacts of 2.68 Å lenght (Fig. 1). Due to the bridging function of the H_2O molecules forming the hydrogen bonds with the Br^- anions and the hydrogen atoms of the allyl groups of hexaallylethylenediaminium, no disordering of the C atoms in the C_3H_5 groups of the cation is observed.

The L^{2+} cation contains the inactive nitrogen atoms and, hence, in structure **II** the Cu(II) atoms are localized inside the tetrahedral anion $[CuBr_{0.45}Cl_{3.55}]^{2-}$ (Cu–X 2.260(1)–2.303(1) Å); i.e., only the electrostatic interaction enforced by the (C)H···X hydrogen bonds

Crystallographic data and experimental details for structures **I–IV**

Parameter	Value			
	I	**II**	**III**	**IV**
Empirical formula	$C_{20}H_{38}Br_2N_2O_2$	$C_{20}H_{34}Br_{0.45}Cl_{3.55}CuN_2$	$C_{20}H_{34}Br_{4.55}Cl_{1.45}Cu_4N_2$	$C_{20}H_{34}Br_6Cu_4N_2$
FW	498.34	527.86	971.66	1036.12
Crystal size, mm	0.45 × 0.35 × 0.21	0.28 × 0.24 × 0.19	0.16 × 0.12 × 0.11	0.25 × 0.14 × 0.06
T, K	100(2)	100(2)	100(2)	100(2)
Shape	Blocks	Prisms	Plates	Orange prisms
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell parameters				
a, Å	8.544(3)	8.762(4)	9.074(4)	9.084(4)
b, Å	10.404(3)	9.163(4)	9.435(4)	9.404(4)
c, Å	13.350(4)	16.500(6)	9.829(5)	9.869(4)
α, deg	90	95.62(4)	116.12(4)	116.31(3)
β, deg	97.29(2)	96.39(4)	104.14(4)	104.00(3)
γ, deg	90	111.46(4)	100.22(4)	100.37(3)
V, Å^3	1177.2(6)	1211.4(9)	692.3(6)	692.1(5)
Z	2	2	1	1
ρ(calcd), g/cm^3	1.406	1.453	2.331	2.486
ρ(meas), g/cm^3	1.40	1.43	2.32	2.47
μ, mm^{-1}	3.46	2.04	9.77	11.70
F(000)	258	273	469	494
hkl	$-12 < h < 13$	$-16 < h < 15$	$-17 < h < 16$	$-13 < h < 13$
	$-17 < k < 17$	$-17 < k < 14$	$-17 < k < 17$	$-14 < k < 14$
	$-14 < l < 22$	$-29 < l < 30$	$-18 < l < 17$	$-15 < l < 11$
R_{int}	0.0224	0.037	0.051	0.092
Total number of reflections	4721	16112	9021	5246
Reflections with $F > 4\sigma(F)$*	3457	6152	3625	3785
Refined parameters	126	280	147	145
$2\theta_{max}$, deg	73.6	84.2	84.1	69.6
Weight scheme**	$[\sigma^2(F_o^2) + (0.0428P)^2 + 0.0912P]^{-1}$	$[\sigma^2(F_o^2) + (0.0210P)^2]^{-1}$	$[\sigma^2(F_o^2) + (0.0200P)^2]^{-1}$	$[\sigma^2(F_o^2) + (0.1169P)^2 + 6.5934P]^{-1}$
$R(F^2)$ $(F > 4\sigma(F))$	0.0273	0.0533	0.056	0.073
wR	0.0641	0.0728	0.075	0.202
Goodness-of-fit	1.03	0.99	0.95	1.06
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.93/–0.30	1.10/–0.43	1.97/–0.98	3.81/–3.14

Notes: * The correction to the Lorentz and polarization factors was applied.

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

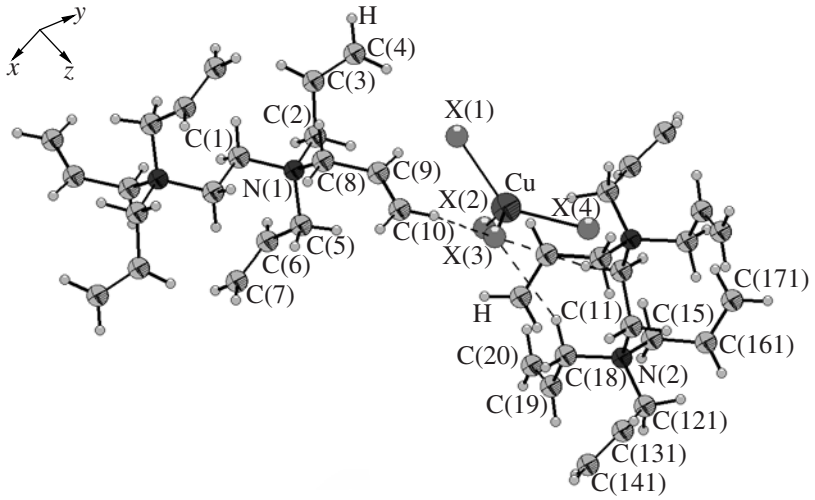

Fig. 2. Fragment of structure **II** and selected geometric characteristics: Cu–X(1) 2.302(1), Cu–X(2) 2.278(1), Cu–X(3) 2.264(1), Cu–X(4) 2.261(1) Å; C(2)H(2*B*)···X(1) 2.87 Å, C(2)H(2*B*)X(1) 147°, C(1)H(1*A*)···X(1) 2.81 Å, C(1)H(1*A*)X(1) 155°, C(11)H(11*A*)···X(3) 2.71 Å, C(11)H(11*A*)X(3) 169°, and C(18)H(18*A*)···X(3) 2.74 Å, C(18)H(18*A*)X(3) 153°.

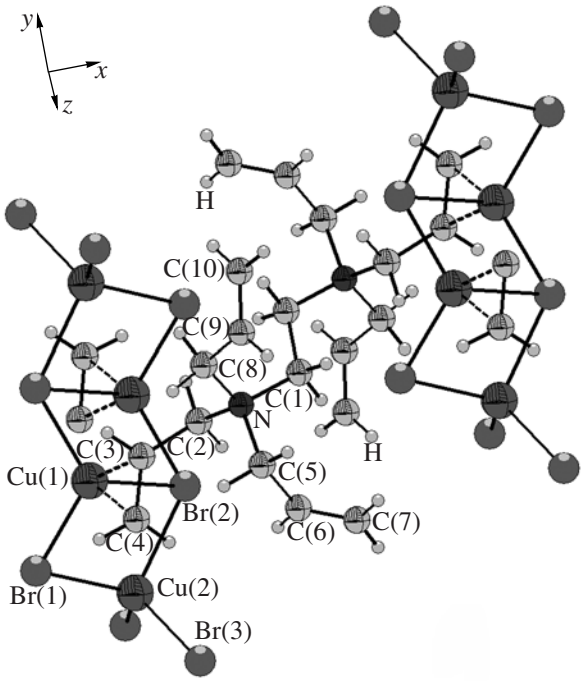

Fig. 3. Fragment of structure **IV** and selected geometric characteristics: Cu(1)–Br(1) 2.390(2), Cu(1)–Br(2)^{ii} 2.372(1), Cu(1)–Br(2) 2.806(2), Cu(1)–*m** 1.964(14), and C(3)=C(4) 1.371(10) Å, C(3)Cu(1)C(4) 38.5(3)°, Cu(2)–Br(3)^{i} 2.453(2), Cu(2)–Br(3) 2.507(1), Cu(2)–Br(2) 2.527(2), and Cu(2)–Br(1) 2.453(1) Å (**m* is the middle of the C=C bond); C(8)H(8*A*)···Br(3) 2.82 Å, C(8)H(8*A*)Br(3) 170° and C(1)H(1*B*)···Br(1) 2.76 Å, C(1)H(1*B*)Br 163°.

exists between the cations and anions in both structures **II** and **I** (Fig. 2). Except for one position with the ratio Cl : Br = 0.786(2) : 0.214(2), other regular systems of points with the halogen atoms contain almost "pure" chlorine atoms: G(Cl) = 0.919(2)–0.965(3).

Isostructural π complexes **III** and **IV** are built-up quite differently than complexes **I** and **II**: each of them contains two of the six C=C bonds of the allyl groups in the L^{2+} centrosymmetric cation, wich are coordinated by two Cu(I) atoms (Fig. 3). Thus, the L^{2+} cation acts as

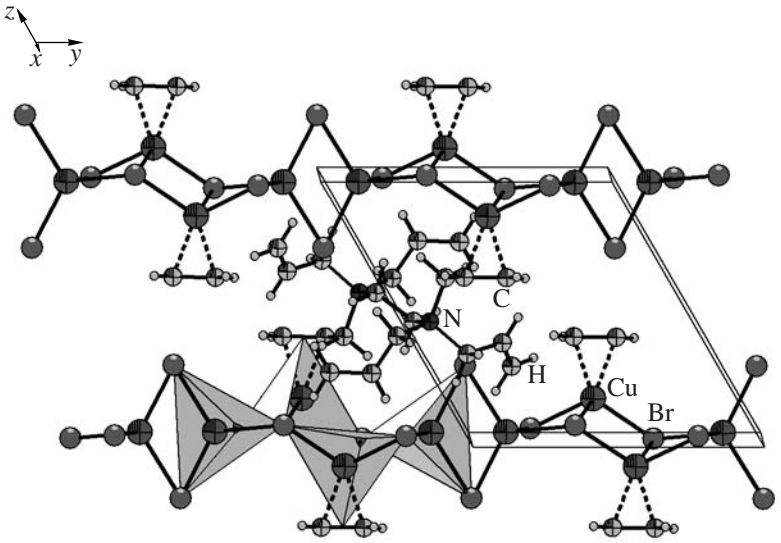

Fig. 4. Packing of the $(Cu_4Br_6^{2-})_n$ anions and hexaallylethylenediaminium cations in structure **IV**.

a bridge between two chain anions $[Cu_4X_6^{2-}]_n$. The centrosymmetric fractal $Cu_4X_6^{2-}$ of the original infinite anion (Fig. 4) contains two independent Cu(I) atoms, one of which π-coordinates the C=C bond of one of the three independent allyl groups of the L^{2+} centrosymmetric cation and another is tetrahedrally coordinated by the halogen atoms. The π-coordinated Cu(I) atom has a trigonal pyramidal environment with the C=C bond in the pyramid base and three X atoms in other vertices of the polyhedron. The C=C coordination bond length is 1.351(5) Å in **III** and 1.371(10) in **IV**.

The L^{2+} centrosymmetric cation in structures **III** and **IV** is a bridging π ligand joining two parallel chains of the anions $(Cu_4X_6^{2-})_n$ through the Cu(I)–(C=C) bond. The $(Cu_4X_6^{2-})_n$ anion is somewhat structurally similar to its stoichiometric analog of the compound [N-allylquinolinium]Cu_2Br_3 (**V**) [12]. However, the $[Cu_4Br_6^{2-}]_n$ anion in **III** and **IV** is somewhat deformed because of the π-coordinated Cu(I) atom. This is a distinction of this anion from the $[Cu_4Br_6^{2-}]_n$ anion in V, where the C=C bond of the allyl group of the organic cation does not interact with the metal atom. Note that in structures **III** and **IV** only two of the six C=C bonds of the hexaallylethylenediaminium cation π-interact with the Cu(I) atoms. This indicates a moderate competitive ability of the C=C bond to incorporate into the coordination trigonal pyramidal environment of the Cu(I) atom compared to the X halogen atoms. A similar situation was observed earlier for the structures of several cuprohalide π complexes, such as [(diallylammonium)CuX_2], where X = Cl [13], Br [14], [(N,N,N',N'-tetraallylpiperazinium)$CuCl_2$] [15]. In these complexes, only 50% of the C=C bonds of the allyl groups are coordinated by the Cu(I) atoms. To the contrary, the both allyl groups are π-coordinated with the Cu^+ ion by the C=C bonds in the structures of the π complexes with the ionic copper(I) salts, namely, [Cu(diallylamine)BF_4] [16], [Cu(diallylamine)NO_3] [17], and [(diallylammonium)$Cu(NO_3)_2$] [18].

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