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Synthesis and crystal structure of copper complexes with N,N,N,N',N' - pentaallylethylenediammonium: $[(C_3H_5)_3NC_2H_4N(H^+)(C_3H_5)_2]Cu^{II}Cl_4$ and $[(C_3H_5)_3NC_2H_4N(H^+)(C_3H_5)_2]Cu^{I}Br_3$

Mykhaylo MONCHAK[1]*, Evgeny GORESHNIK[2], Volodymyr DAVYDOV[1], Maryan MYS'KIV[1]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv,*
Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
[2] *Department of Inorganic Chemistry and Technology, Jožef Stefan Institute,*
Jamova 39, SI-1000 Ljubljana, Slovenia
* *Corresponding author. E-mail: mishamonchak@gmail.com*

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N,N,N,N',N'-pentaallylethylenediammonium has been obtained by reaction of ethylenediamine and allyl bromide in benzene +ethanol (1:5) medium in the presence of $NaHCO_3$. After 48 hours of mixing and boiling the mixture was filtered. Good quality crystals of the complexes $[(C_3H_5)_3NC_2H_4N(H^+)(C_3H_5)_2]Cu^{II}Cl_4$ (I) and $[(C_3H_5)_3NC_2H_4N(H^+)(C_3H_5)_2]Cu^{I}Br_3$ (II) were obtained using the alternating-current electrochemical technique and then X-ray investigated. The crystal structures of I and II are monoclinic, for I: space group $P2_1$, a = 7.596(2), b = 18.302(6), c = 8.271(3) Å, β = 103.80(2)°, V = 1116.7(6) Å^3, Z = 2; for II: space group $P2_1/c$, a = 8.328(1), b = 18.377(3), c = 13.854(2) Å, β = 95.31(1)°, V = 2111.1(5) Å^3, Z = 4. In both structures simple ($CuCl_4^{2-}$ and $CuBr_3^{2-}$ respectively) anions occur. Due to the absence of π-interaction in I and II the organic and inorganic moieties are held together by electrostatic interaction and E–H…X (E = N, C; X = Cl, Br) bonds.

Copper complexes / Ethylenediamine / N,N,N,N',N'-pentaallylethylenediammonium bromide / Isolated inorganic anions

Introduction

Ethylenediamine is a classic chelate ligand. Many of its metal complexes have been investigated and their structures solved. Several copper(II) and copper(I) complexes with ethylenediamine [1,2], N,N,N',N'-tetramethylethylenediamine [3], N,N,N',N'-tetraethylethylenediamine [4] and other ligands are described in different literature sources. Since there was no information about N-allyl derivatives of ethylenediamine, we decided to synthesize such ligands and their copper complexes.

We have recently studied Cu(II) and Cu(I) complexes with N,N,N,N',N',N'-hexaallylethylenediammonium dibromide [5,6]. To continue this research, copper(II) and copper(I) coordination compounds with N,N,N,N',N'-pentaallylethylenediammonium bromide were obtained and X-ray studied.

Experimental section

Preparation of N,N,N,N',N' - pentaallylethylenediammonium bromide

N,N,N,N',N'-pentaallylethylenediammonium bromide was obtained from ethylenediamine (1.20 g) and allyl bromide (12.1 g) (1:5) in benzene+ethanol medium in the presence of $NaHCO_3$ (8.4 g). After 48 hours of stirring and boiling the mixture was filtered (NaBr was removed). The excess of solvent was distilled off under reduced pressure and the obtained solution was used to obtain the compounds. The yield of the ligand was 80 %.

Preparation of $[(C_3H_5)_3NC_2H_4N(H^+)(C_3H_5)_2]Cu^{II}Cl_4$

Red crystals of **I** were obtained from 5 ml of ethanol solution of $CuCl_2$ (1 mmol, 0.13 g) and $[(C_3H_5)_3NC_2H_4N(C_3H_5)_2]Br$ (1.2 mmol) (titrated by HCl) on a copper wire after one and a half month.

Table 1 Selected crystallographic parameters and summary of the data collection for compounds **I** and **II.**

	I	**II**
Empirical formula	$C_{17}H_{30}N_2CuCl_4$	$C_{17}H_{30}N_2CuBr_3$
Formula weight	467.77	565.68
Temperature, K	293	200
Wavelength, Å	0.71069 (Mo *K*α)	0.71069 (Mo *K*α)
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $P2_1/c$
Unit cell dimensions		
a, Å	7.596(2)	8.328(2)
b, Å	18.302(6)	18.377(3)
c, Å	8.271(3)	13.854(2)
β, °	103.80(2)	95.31(1)
Volume, Å^3	1116.7(6)	2111.1(5)
Z	2	4
Calculated density	1.391	1.78
Absorption coefficient, mm^{-1}	1.46	6.71
$F(000)$	486	1120
Flack parameter	0.08(3)	–
Crystal size, mm	0.15 × 0.08 × 0.18	0.12 × 0.10 × 0.09
Colour, shape	red, irregular plate	brown, prism
Theta range for data collection, °	2.2-30.0	2.5-29.3
Limiting indices	$-10<h<10$	$-5<h<11$
	$0<k<24$	$-25<k<23$
	$-11<l<9$	$-18<l<17$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Measured reflections	5703	9587
Independent reflections	3337	4919
Observed reflect. $[I > 2\sigma(I)]$	1179	2822
Free parameters	217	208
Weight scheme [a]	$1/[\sigma^2(F_o^2) + (0.0123P)^2]$	$1/[\sigma^2(F_o^2) + (0.0655P)^2 + 7.6249P]$
Goodness-of-fit on F^2	0.998	1.14
Final R indices $[I > 2\sigma(I)]$	R = 0.068, wR = 0.086	R = 0.096, wR = 0.186
R indices (all data)	R = 0.175, wR = 0.099	R = 0.156, wR = 0.223
Residual electron density, e Å^{-3}	0.49, –0.42	1.18, –0.84

[a] $P = (F_o^2 + 2F_c^2)/3$

Preparation of $[(C_3H_5)_3NC_2H_4N(H^+)(C_3H_5)_2]Cu^IBr_3$

Good quality brown crystals of compound **II** were obtained by a 26-month transformation in the mother liquor of initially appeared (under the conditions of the alternating-current electrochemical technique [7]) crystals of copper(I) bromide with N,N,N,N',N'-pentaallylethylenediammonium bromide π-complex $[(C_3H_5)_3NC_2H_4N(H^+)(C_3H_5)_2][Cu^I_4Br_6]$ [8].

X-ray crystal structure determination

Single crystals of **I** and **II** were preliminarily studied by the photometric method and then diffraction data were collected on a CAD-4 (for **I**) or Rigaku AFC7R (for **II**) (graphite monochromated MoK_α radiation; Rigaku AFC7R equipped with a Mercury CCD detector) diffractometer. The structures were solved and refined using the CSD program package [9] and SHELXS-97 and SHELXL-97 [10] software implemented in the program package WinGX [11]. In both structures the nonhydrogen atoms were found by direct methods and the hydrogen ones geometrically.

Full-matrix least-squares refinements based on F^2 were carried out for the positional and thermal parameters of all nonhydrogen atoms. The positions of the H atoms were treated as riding atoms and refined with fixed C–H distances and with U_{iso}(H) equal to $1.2U_{eq}$(C).

Selected crystallographic parameters and a summary of the data collection for the compounds **I** and **II** are given in Table 1. Atomic positional and displacement parameters for **I** and **II** are given in Tables 2 and 3.

The figures were prepared using DIAMOND 3.1 software [12].

Results and discussion

The structure of **I** is built of separate organic cations $[(C_3H_5)_3NC_2H_4N(H^+)(C_3H_5)_2]^{2+}$ and $CuCl_4^{2-}$ anions (Fig. 1 and Fig. 2). The copper(II) atom possesses tetrahedral coordination of chlorine atoms. The distances Cu-Cl vary from 2.241(3) to 2.311(3) Å.

Table 2 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **I.**

Atom	*x*	*y*	*z*	$U_{\mathrm{iso}}/U_{\mathrm{eq}}{}^{a}$
Cu	0.08744(12)	0.00006(6)	0.00902(13)	0.0491(3)
Cl(1)	0.2820(3)	−0.09357(14)	0.0324(3)	0.0642(7)
Cl(2)	0.1222(3)	0.05221(13)	0.2693(3)	0.0563(7)
Cl(3)	−0.2023(3)	−0.03846(16)	−0.0476(3)	0.0728(8)
Cl(4)	0.1274(3)	0.08129(15)	−0.1854(3)	0.0691(8)
N(1)	−0.2523(10)	−0.1307(4)	0.4642(10)	0.050(2)
N(2)	−0.2931(8)	0.0629(4)	0.2822(8)	0.0425(18)
H(2)	−0.1863	0.0555	0.2529	0.051
C(1)	−0.2228(11)	−0.0502(5)	0.4557(11)	0.047(2)
H(1A)	−0.1022	−0.0418	0.4392	0.057
H(1B)	−0.2273	−0.0287	0.5618	0.057
C(2)	−0.3587(10)	−0.0114(5)	0.3190(9)	0.043(2)
H(2A)	−0.3815	−0.0408	0.2187	0.052
H(2B)	−0.4722	−0.0062	0.3522	0.052
C(3)	−0.4484(11)	−0.1493(6)	0.4678(13)	0.058(3)
H(3A)	−0.5291	−0.1317	0.3660	0.069
H(3B)	−0.4614	−0.2019	0.4711	0.069
C(4)	−0.5032(14)	−0.1167(5)	0.6127(13)	0.062(3)
H(4)	−0.4362	−0.1293	0.7185	0.075
C(5)	−0.6407(12)	−0.0709(7)	0.6025(14)	0.092(4)
H(5A)	−0.7108	−0.0571	0.4988	0.111
H(5B)	−0.6671	−0.0526	0.6989	0.111
C(6)	−0.1115(11)	−0.1544(5)	0.6197(11)	0.061(3)
H(6A)	0.0087	−0.1462	0.6022	0.073
H(6B)	−0.1242	−0.1243	0.7128	0.073
C(7)	−0.1294(12)	−0.2334(6)	0.6629(14)	0.060(3)
H(7)	−0.1410	−0.2692	0.5813	0.071
C(8)	−0.1285(13)	−0.2511(6)	0.8135(14)	0.078(3)
H(8A)	−0.1168	−0.2152	0.8949	0.094
H(8B)	−0.1395	−0.2999	0.8411	0.094
C(9)	−0.2216(13)	−0.1705(6)	0.3060(11)	0.069(3)
H(9A)	−0.2618	−0.2207	0.3090	0.083
H(9B)	−0.2994	−0.1476	0.2091	0.083
C(10)	−0.0370(15)	−0.1716(8)	0.2820(12)	0.088(4)
H(10)	0.0194	−0.1270	0.2753	0.106
C(11)	0.0535(16)	−0.2309(7)	0.2694(14)	0.102(5)
H(11A)	0.0010	−0.2764	0.2756	0.122
H(11B)	0.1707	−0.2278	0.2543	0.122
C(12)	−0.2519(11)	0.1131(5)	0.4278(11)	0.049(3)
H(12A)	−0.2121	0.1597	0.3935	0.059
H(12B)	−0.1533	0.0929	0.5127	0.059
C(13)	−0.4213(13)	0.1259(6)	0.5047(17)	0.077(4)
H(13)	−0.5229	0.1478	0.4365	0.092
C(14)	−0.4305(17)	0.1093(8)	0.6488(15)	0.114(6)
H(14A)	−0.3320	0.0874	0.7212	0.137
H(14B)	−0.5358	0.1188	0.6839	0.137
C(15)	−0.4237(10)	0.0935(5)	0.1290(10)	0.048(2)
H(15A)	−0.5382	0.1052	0.1553	0.057
H(15B)	−0.4463	0.0572	0.0410	0.057
C(16)	−0.3463(14)	0.1600(7)	0.0716(13)	0.081(3)
H(16)	−0.2348	0.1551	0.0449	0.097
C(17)	−0.4155(17)	0.2216(7)	0.0557(16)	0.118(5)
H(17A)	−0.5270	0.2292	0.0809	0.142
H(17B)	−0.3560	0.2602	0.0186	0.142

[a] For non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor $U_{\mathrm{eq}} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j)$, for hydrogen atoms U_{iso} was set equal to $1.2U_{\mathrm{eq}}$(C).

Table 3 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **II**.

Atom	*x*	*y*	*z*	U_{iso}/U_{eq} [a]
Cu	−0.27458(15)	0.15160(8)	0.33001(10)	0.0515(4)
Br(1)	−0.02066(13)	0.19444(7)	0.39652(8)	0.0578(4)
Br(2)	−0.52048(12)	0.19512(7)	0.38100(8)	0.0581(4)
Br(3)	−0.28498(12)	0.05664(6)	0.21211(8)	0.0493(3)
N(1)	0.7928(9)	0.4762(5)	0.2523(6)	0.050(2)
N(2)	0.7614(9)	0.6772(5)	0.3191(6)	0.046(2)
H(2)	0.7066	0.6877	0.2563	0.054
C(1)	0.7227(12)	0.5463(5)	0.2837(7)	0.043(2)
H(1A)	0.6475	0.564	0.2326	0.05
H(1B)	0.6611	0.5358	0.3385	0.05
C(2)	0.8404(11)	0.6043(6)	0.3132(7)	0.046(2)
H(2A)	0.9184	0.6064	0.2665	0.058
H(2B)	0.8949	0.5931	0.3748	0.058
C(3)	0.8815(13)	0.4840(7)	0.1629(9)	0.066(3)
H(3A)	0.9729	0.5142	0.178	0.077
H(3B)	0.914	0.4375	0.1443	0.077
C(4)	0.7823(13)	0.5172(7)	0.0786(9)	0.063(3)
H(4)	0.7444	0.5653	0.0875	0.072
C(5)	0.750(2)	0.4837(9)	−0.0053(11)	0.103(6)
H(5A)	0.7813	0.4362	−0.017	0.11
H(5B)	0.6812	0.5092	−0.0565	0.11
C(6)	0.6528(12)	0.4214(6)	0.2306(8)	0.053(3)
H(6A)	0.5877	0.4231	0.2836	0.062
H(6B)	0.5911	0.437	0.1734	0.062
C(7)	0.7079(13)	0.3427(8)	0.2137(11)	0.076(4)
H(7)	0.7581	0.3156	0.2708	0.071
C(8)	0.6883(15)	0.3097(8)	0.1381(11)	0.082(4)
H(8A)	0.7236	0.2627	0.1284	0.088
H(8B)	0.6398	0.3373	0.0814	0.088
C(9)	0.9151(12)	0.4473(6)	0.3335(9)	0.054(3)
H(9A)	0.9483	0.4000	0.3149	0.07
H(9B)	1.0041	0.4786	0.3415	0.07
C(10)	0.8492(13)	0.4393(6)	0.4281(9)	0.056(3)
H(10)	0.8185	0.483	0.4602	0.067
C(11)	0.8227(14)	0.3770(7)	0.4684(9)	0.060(3)
H(11A)	0.7786	0.3741	0.5295	0.062
H(11B)	0.8497	0.3325	0.4373	0.062
C(12)	0.6359(11)	0.6782(6)	0.3897(8)	0.049(3)
H(12A)	0.5998	0.7267	0.3973	0.06
H(12B)	0.5489	0.6484	0.3659	0.06
C(13)	0.6997(13)	0.6510(6)	0.4877(7)	0.051(3)
H(13)	0.793	0.6716	0.5213	0.062
C(14)	0.6299(13)	0.5972(7)	0.5288(8)	0.059(3)
H(14A)	0.6678	0.5804	0.5901	0.068
H(14B)	0.5338	0.5765	0.4952	0.068
C(15)	0.8809(12)	0.7377(6)	0.3368(8)	0.054(3)
H(15A)	0.9059	0.7435	0.4076	0.056
H(15B)	0.9799	0.7265	0.3114	0.056
C(16)	0.8099(18)	0.8109(8)	0.2946(13)	0.087(5)
H(16)	0.7832	0.8192	0.225	0.098
C(17)	0.7881(18)	0.8569(11)	0.3458(13)	0.101(5)
H(17A)	0.8115	0.8551	0.4169	0.102
H(17B)	0.7419	0.9072	0.326	0.102

[a] For non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j)$, for hydrogen atoms U_{iso} was set equal to $1.2U_{eq}$(C).

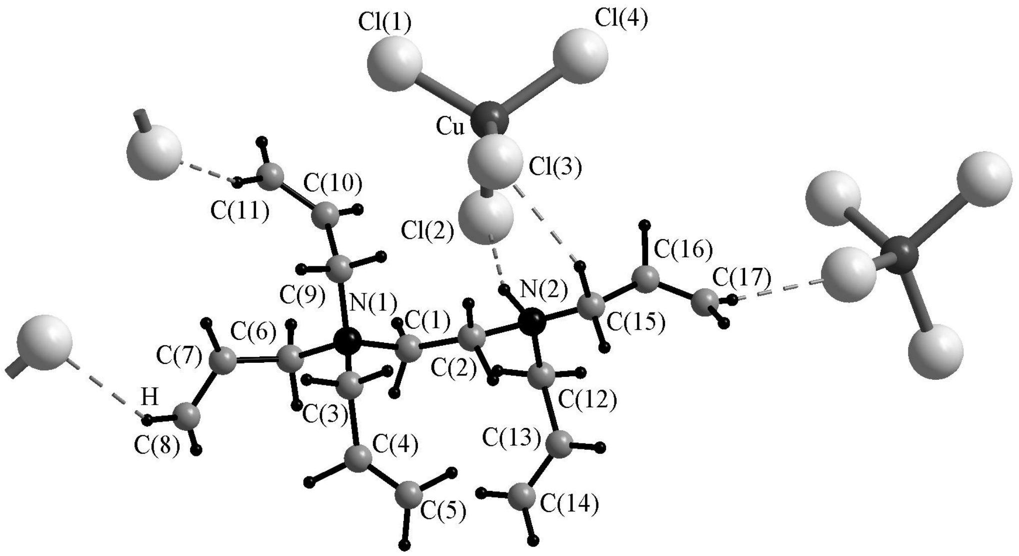

Fig. 1 $[(C_3H_5)_3NC_2H_4N(H^+)(C_3H_5)_2]^{2+}$ and $CuCl_4^{2-}$ ions in the structure of **I**.

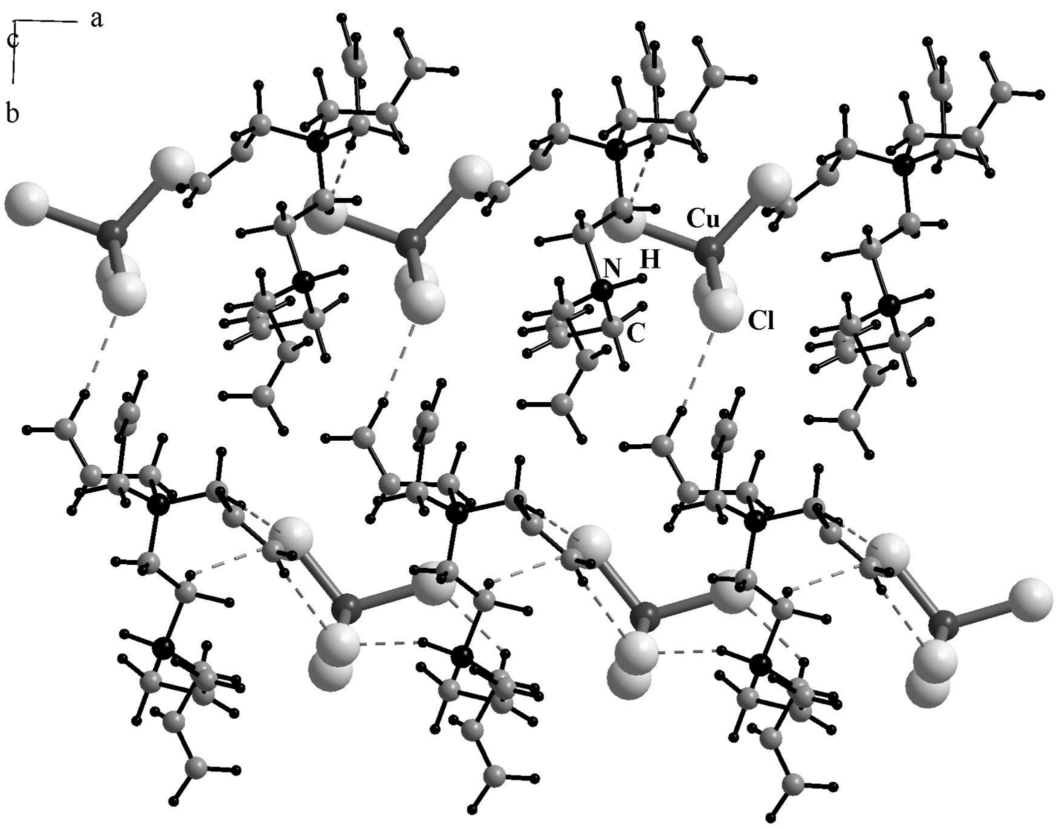

Fig. 2 Projection of the structure of $[(C_3H_5)_3NC_2H_4N(H^+)(C_3H_5)_2]Cu^{II}Cl_4$ (**I**).

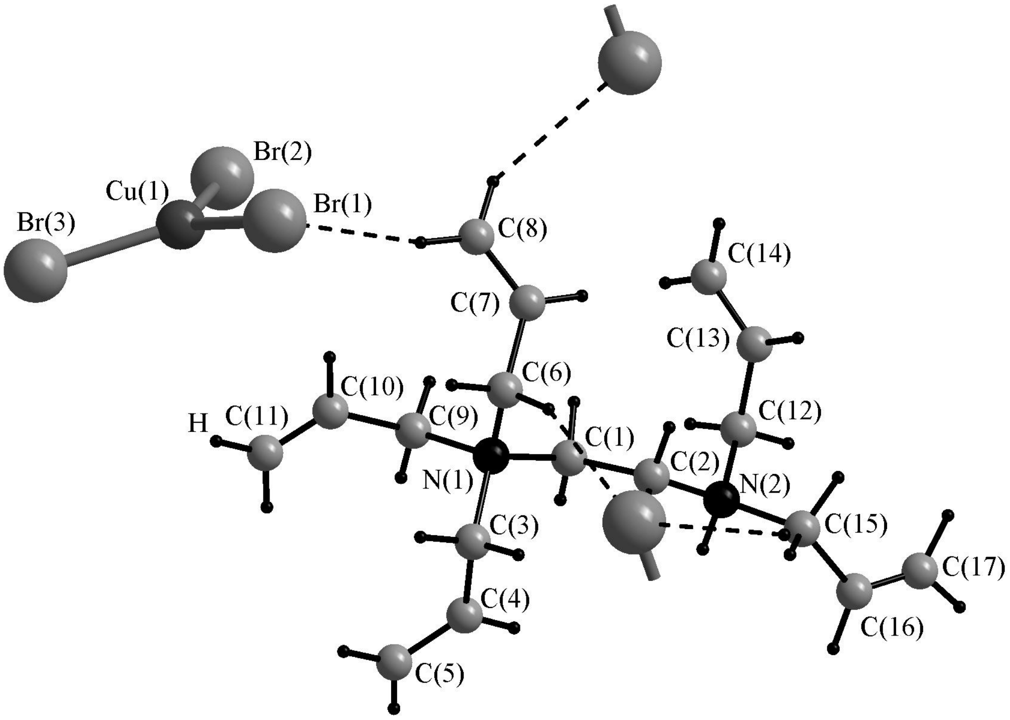

Fig. 3 Fragment of the structure of $[(C_3H_5)_3NC_2H_4N(H^+)(C_3H_5)_2]Cu^IBr_3$ (**II**).

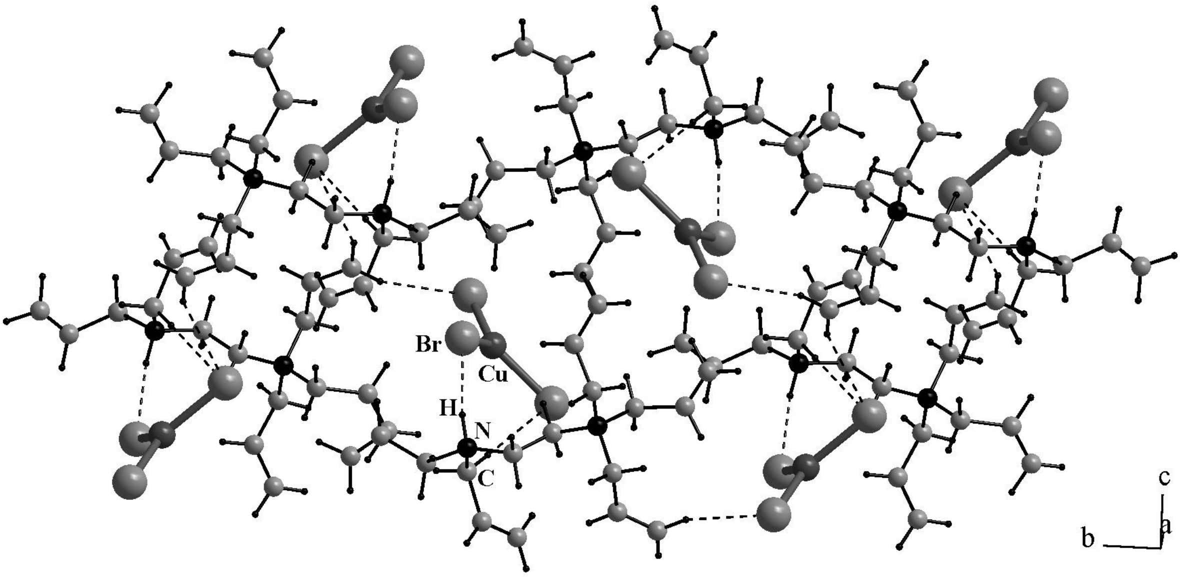

Fig. 4 Projection of the crystal structure of $[(C_3H_5)_3NC_2H_4N(H^+)(C_3H_5)_2]Cu^IBr_3$ (**II**).

Similarly to **I**, the crystal structure of **II** also contains isolated inorganic ($CuBr_3^{2-}$) anions and N,N,N,N',N'-pentaallylethylenediammonium cations, which are held together by electrostatic attraction (Fig. 3 and Fig. 4). The Cu–Br distances range from 2.362(2) to 2.386(2) Å. There are no π-bonds between copper atoms and C=C bonds of any ligand allyl group. Selected bond lengths and angles of **I** and **II** are listed in Table 4.

As for **I** and **II,** in the crystal structure of Cu complexes with N,N,N',N'-tetraethylethylenediammonium chloride $[C_2H_4N_2(H^+)_2(C_2H_5)_4][CuCl_4^{2-}]$ [13] and N,N,N',N'-tetraallylpiperazinium bromide $[C_4H_8N_2(C_3H_5)_4^{2+}][CuBr_3^{2-}]$ [14] analogous inorganic anions occur.

Table 4 Selected bond lengths and angles in the structures of **I** and **II.**

	Bond	*d*, Å	Angle	*ω*, deg
I	Cu–Cl(1)	2.241(3)	Cl(1)–Cu–Cl(2)	107.99(9)
	Cu–Cl(2)	2.311(3)	Cl(1)–Cu–Cl(3)	111.74(11)
	Cu–Cl(3)	2.251(2)	Cl(1)–Cu–Cl(4)	111.48(9)
	Cu–Cl(4)	2.263(3)	Cl(2)–Cu–Cl(3)	102.23(9)
	C(4)–C(5)	1.33(2) [a]	Cl(2)–Cu–Cl(4)	112.68(11)
	C(7)–C(8)	1.29(2) [a]	Cl(3)–Cu–Cl(4)	110.38(10)
	C(10)–C(11)	1.30(2) [a]		
	C(13)–C(14)	1.25(2) [a]		
	C(16)–C(17)	1.24(2) [a]		
II	Cu–Br(1)	2.362(2)	Br(1)–Cu–Br(2)	122.62(7)
	Cu–Br(2)	2.367(2)	Br(1)–Cu–Br(3)	119.03(6)
	Cu–Br(3)	2.386(2)	Br(2)–Cu–Br(3)	118.29(6)
	C(4)–C(5)	1.32(2) [a]		
	C(7)–C(8)	1.21(2) [a]		
	C(10)–C(11)	1.30(2) [a]		
	C(13)–C(14)	1.31(2) [a]		
	C(16)–C(17)	1.13(2) [a]		

[a] Due to disordered atoms of allyl groups imaginary shortened C–C distances occur.

Table 5 Geometry of selected H-contacts in the structures of **I** and **II**.

No.	Contact *D*–H…*A*	Length of the bond, Å			Angle *D*–H…*A*, deg	Atom coordinates of *A*
		D–H	H…*A*	*D*…*A*		
I	N(2)–H(2)…Cl(2)	0.91	2.32	3.19(1)	160	*x*, *y*, *z*
	C(3)–H(3A)…Cl(1)	0.97	2.88	3.83(4)	169	-1+*x*, *y*, *z*
	C(5)–H(5A)…Cl(2)	0.93	2.84	3.69(3)	151	-1+*x*, *y*, *z*
	C(6)–H(6B)…Cl(3)	0.97	2.70	3.67(1)	173	*x*, *y*, 1+*z*
	C(8)–H(8B)…Cl(2)	0.93	2.87	3.67(1)	144	-*x*, -0.5+*y*, 1-*z*
	C(11)–H(11A)…Cl(4)	0.93	2.82	3.71(2)	160	-*x*, -0.5+*y*, -*z*
	C(12)–H(12B)…Cl(4)	0.97	2.88	3.81(4)	160	*x*, *y*, 1+*z*
	C(17)–H(17B)…Cl(1)	0.93	2.79	3.65(2)	156	-*x*, 0.5+*y*, -*z*
II	N(2)–H(2)…Br(2)	0.96	2.34	3.28(2)	165	-*x*, 0.5+*y*, 0.5-*z*
	C(2)–H(2A)…Br(1)	0.96	2.96	3.78(1)	143	1-*x*, 0.5+*y*, 0.5-*z*
	C(3)–H(3A)…Br(3)	0.95	2.99	3.87(2)	155	1-*x*, 0.5+*y*, 0.5-*z*
	C(9)–H(9B)…Br(3)	0.94	2.90	3.78(1)	157	1-*x*, 0.5+*y*, 0.5-*z*
	C(11)–H(11A)…Br(3)	0.96	2.92	3.77(2)	149	1+*x*, 0.5-*y*, 0.5+*z*
	C(11)–H(11B)...Br(1)	0.96	2.84	3.78(1)	164	1+*x*, *y*, *z*
	C(12)–H(12B)…Br(3)	0.94	2.89	3.84(1)	178	-*x*, 0.5+*y*, 0.5-*z*

On the contrary, in the compound of Cu(I) bromide with N,N,N,N',N',N'-hexaallylethylenediammonium dibromide $[C_2H_4N_2(C_3H_5)_6][Cu^{I}_4Br_6]$ an endless complex inorganic fragment $(Cu_4Br_6^{2-})_n$ occurs [5], which contains two crystallographically independent Cu(I) atoms (Fig. 5). Two of the six ligand allyl groups of the centrosymmetric cation are coordinated by metal atoms. Consequently the organic cation plays a bridging role, contrary to the chelate function of ethylenediamine itself.

Since stronger covalent interactions are absent in the structures of **I** and **II**, weak contacts (hydrogen bonds) play a crucial role in the formation of the 3D framework that prevents decomposition. H-bonds are formed between halogen atoms of the inorganic anions and hydrogens at N or C atoms. The geometry of selected H-contacts is presented in Table 5. As it was stated in [15]: “hydrogen bond is the master-key interaction in crystal engineering because it combines directionally with strength”. The hydrogen bonds connect the separate parts of the structures of **I** and **II** into a single whole. They also hinder reeling of parts of the bulky N,N,N,N',N'-pentaallylethylenediammonium cation, in particular of the allyl groups.

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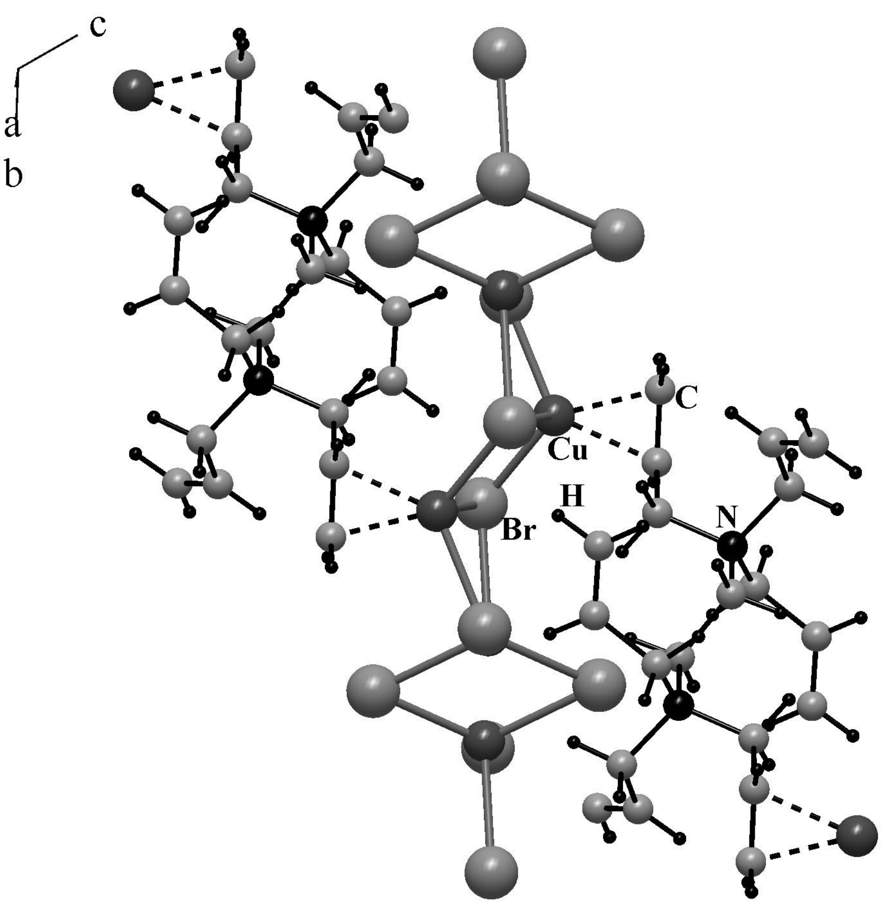

Fig. 5 Structure of the π-complex $[(C_3H_5)_3NC_2H_4N(C_3H_5)_3][Cu^I_4Br_6]$.

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