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Scientific paper

Investigation of the Composition Space Diagram CuCl–Allylamine–dabco. A New Mixed Ligand Compound of $(H_2dabco)_2[Cu_4Cl_9(allNH_3)]$ Composition with Unique $Cu_4Cl_9{}^{5-}$ Cupro(I)-chloride Fragment

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Abstract

The ternary system CuCl–allylamine–dabco (dabco = 1,4-diazabicyclo[2.2.2]octane) with an excess of HCl was explored. Starting from an ethanol solution of $CuCl_2 \cdot 2H_2O$, allylamine and dabco titrated with HCl, copper(I) salts were generated by means of electrochemical alternating current synthesis. In addition to the already known $(H_2dabco)[CuCl_3]$, two modifications of the $(allNH_3)_2[Cu_2Cl_4]$ compound and some Cu(II) by-products, a new mixed ligand compound of the composition $(H_2dabco)_2[Cu_4Cl_9(allNH_3)]$ was synthesized and structurally investigated. Its structure contains unique $Cu_4Cl_9{}^{5-}$ inorganic moiety bound via a η_2-interaction allylammonium moiety and discrete $(H_2dabco)^{2+}$ cations. The structure is stabilized by the system of N–H···Cl hydrogen bonds.

Keywords: copper, chloride, 1,4-diazabicyclo[2.2.2]octane, coordination polymers

1. Introduction

Copper(I) chloride coordination compounds amaze with a variety of inorganic fragments. Starting from the simplest neutral CuCl monomers,[1,2] discrete Cu_2Cl_2 dimers,[3] bicyclic Cu_3Cl_3 trimers,[4] tetramers of cubane[5] and stepped cubane types,[6] prismane-like hexamers[7] and many others were observed. An even broader spectrum of anionic moieties from $CuCl_2{}^-$ dimers to infinite chains, layers and 3D frameworks were reported.[8,9] A comprehensive review of the structural diversity of copper(I) halide aggregates was published nearly a decade ago.[10]

The carbon-carbon double bond successfully competes with the halide ions for the place in the coordination sphere of the Cu(I) ion. On the other hand, protonated organic amines form N–H···Hal hydrogen bonds with halide ions, thereby limiting the bridging ability of the halide ions to the metal centers. We hypothesized that the use of bulky organic amines and amino derivatives of unsaturated hydrocarbons in acidic media could promote the formation of previously unknown copper-halide aggregates. In order to perform a complete study of such a system, we decided to investigate the entire CuCl–allylamine–dabco ternary system in acidic (HCl) medium using the Gibbs diagram.

The electrochemical technique has proven to be an effective tool for the synthesis of copper(I) derivatives.[11,12] The absence of by-products and the possibility to grow high-quality single crystals in one step are the main advantages of such an approach.

It is worth noting that the CCDC contains only 26 entries for 20 compounds containing copper ions and diprotonated H_2dabco cations.[13] Moreover, only six of the above compounds appear to be polymeric, and also six contain monovalent copper ions. On the other hand, only three cupro(I)chloride derivatives of allyl ammonium were found in the CCDC, four other entries contain mixed-anion derivatives.

The phase diagram of CuCl–allylamine–dabco in acidic media was investigated by means of electrochemical synthesis and by varying the ratios of the starting reagents.

A new $(H_2dabco)_2[Cu_4Cl_9(allNH_3)]$ salt with a unique $Cu_4Cl_9^{5-}$ anion was found and characterized by single-crystal X-ray diffraction and Raman spectroscopy. The results are presented in this article.

2. Experimental Section

All chemicals were of commercial origin: $CuCl_2 \cdot 2H_2O$ from Zorka Šabac, p.a., hydrochloric acid from Sigma-Aldrich, ACS reagent, 37%, allylamine from Alfa Aesar, 98+%, 1,4-diazabicyclo[2.2.2]octane (Alfa Aesar, 98%); ethanol (Carlo Erba, p.a) were used without further purification.

2. 1. Syntheses

All experiments were carried out by electrochemical alternating current synthesis in ethanol. 5 mL of ethanol solution containing calculated amounts of $CuCl_2{\cdot}2H_2O$, dabco, allylamine and 1 mL of 37% aqueous HCl were placed in a small test tube. The technical details of the synthetic procedures were described earlier.[10,11] An alternating current of 50 Hz and a voltage of 0.4 V was used. In case of discoloration of the solution and absence of crystals, the test tube was cooled in the refrigerator or the synthesis was repeated with larger amount of reagents.

Table 1. Crystallographic data, details of data collection and structure refinement parameters

	1
Compound	$(H_2dabco)_2[Cu_4Cl_9(allNH_3)]$
Formula	$C_{15}H_{36}Cl_9Cu_4N_5$
M [g mol^{-1}]	859.70
T [K]	150
Crystal system	Triclinic
Space group	$P\bar{1}$
a [Å]	9.3468(4)
b [Å]	12.1301(6)
c [Å]	13.6361(5)
α [°]	112.695(4)
β [°]	91.951(3)
γ [°]	98.337(4)
V [Å^3]	1404.37(11)
Z	2
F(000)	860
ρ_{calcd} [g cm^{-3}]	2.033
Radiation, λ [Å]	MoKα, 0.71073
μ [mm^{-1}]	3.862
Goodness–of–fit on F^2	1.072
Final R_1 $[I > 2\sigma(I)]$	0.0296
Final R_1 (all data)	0.0375
wR_2 $[I > 2\sigma(I)]$	0.0663
wR_2 (all data)	0.0720
Largest diff. peak and hole (e Å^{-3})	0.603, –0.635

2. 2. X-ray Structure Determination

All crystals obtained were examined using the single-crystal X-ray technique. Single-crystal X-ray data for compound **1** were collected on a Gemini A diffractometer with an Atlas CCD detector, using graphite monochromated Mo-Kα radiation. The data were processed using the CrysAlisPro program package.[14] An analytical absorption correction was applied to the data set. The structure was solved using the dual-space algorithm of the program SHELXT[15] and the structure refinement was performed using the software SHELXL-2014,[16] both of which are implemented in the crystallographic software Olex.[17] Hydrogen atoms bound to carbons were set to calculated positions (AFIX commands), their thermal parameters were set to $1.2U_{eq}$ of the corresponding C atoms. The positions of the hydrogen atoms bound to the nitrogen atoms were found on difference Fourier maps and refined freely. In some cases, the N–H bond lengths were constrained using the DFIX command. A summary of the crystallographic data and the structure refinement is given in Table 1. CCDC 2387343 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

3. 1. Influence of Synthetic Conditions on a Formation of Definite Products

The preparation of the starting mixture $CuCl_2 \cdot 2H_2O$–allylamine–dabco–HCl usually resulted in a multicolored – from yellow to brown – solid.

Two series of experiments were carried out in the three-component system $CuCl_2 \cdot 2H_2O$– allylamine–dabco (Fig. 1) in an acidic (HCl) environment. First, five points were selected on a ternary diagram and electrochemical syntheses were carried out. As expected, in dabco-reach region of ternary diagram the formation of H_2dabco salt, namely $(H_2dabco)[CuCl_3]$ was observed.[18] In contrast, an excess of allylamine led to the formation of the $(allNH_3)_2[Cu_2Cl_4]$ salt.[19] The most remarkable result was achieved in a synthesis with 40 mol. % $CuCl_2$, 15 mol. % allylamine and 45 mol. % dabco, in which the formation of earlier unknown yellow-orange crystals of the composition $(H_2dabco)_2[Cu_4Cl_9(allNH_3)]$ was observed. Using the ratio of 40 mol. % $CuCl_2$, 45 mol. % allylamine and 15 mol. % dabco resulted in a mixture of $(H_2dabco)_2[Cu_4Cl_9(allNH_3)]$ and $(allNH_3)_2[Cu_2Cl_4]$ crystals. Further experiments were performed in steps of 10% for each component. In this way, 36 points of definite composition were determined on a Gibbs triangle, and the corresponding ratios of starting materials were used for subsequent syntheses (Table S1). No other mixed

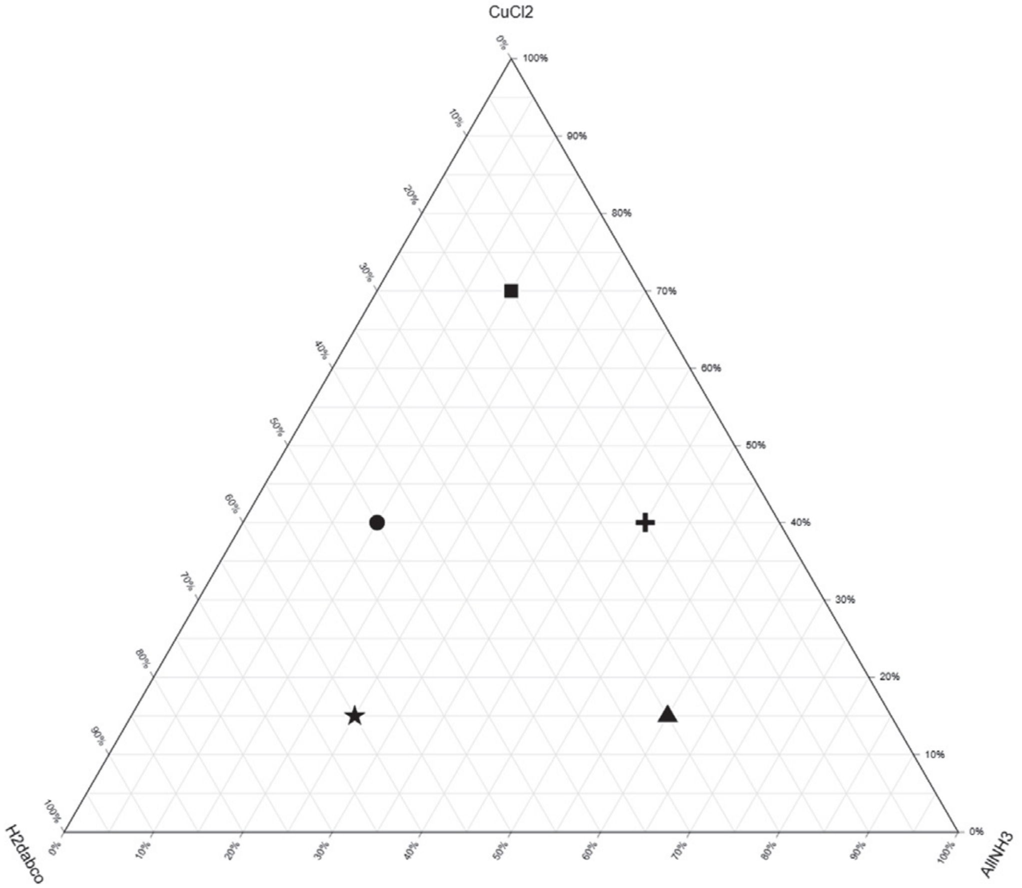

Figure 1. Ternary diagram of CuCl–allylammonium–H_2dabco. Square: region of formation $(allNH_3)_2[Cu_2Cl_4]$, circle – $(H_2dabco)_2[Cu_4Cl_9(allNH_3)]$, cross – $(H_2dabco)_2[Cu_4Cl_9(allNH_3)]$ and $(allNH_3)_2[Cu_2Cl_4]$, star and triangles – $(H_2dabco)[CuCl_3]$.

cation salts were found during this detailed investigation. Crystals of another modification of the compound $(allNH_3)_2[Cu_2Cl_4]$[20] and undesired $(H_2dabco)_2[Cu^{II}Cl_3(H_2O)_2]Cl_3 \cdot H_2O$[21] (copper(II) salt as a result of incomplete electrochemical reduction) were observed.

3. 2. Crystal Structure of 1

The compound $(H_2dabco)_2[Cu_4Cl_9(allNH_3)]$ (**1**) crystallizes in the triclinic space group $P\bar{1}$. Three metal cations and three chloride anions form a six-membered ring with Cu···Cu distances of 2.9252(12)–2.9999(12) Å (Fig. 2). Each pair of copper ions is bound by a μ_2 chloride bridge with Cu–μ_2Cl distances of 2.302(2)–2.352(1) Å. The copper triangle is capped by a μ_3Cl6 center with significantly elongated Cu–Cl bonds with lengths of 2.632(2)–2.705(2) Å. The coordination of each copper center is completed to tetrahedral by another chloride ion: terminal chloride anions for Cu3 and Cu4 and a μ_2 bridge for Cu2. In the last case, the Cl2 bridge connects a Cu_3Cl_7 core with an $(allNH_3)CuCl_2$ fragment involving a π-coordinated Cu1 atom.

All three Cu ions in the Cu_3Cl_7 core are tetra-coordinated. τ_4 parameter values of 0.81, 0.89 and 0.86 for

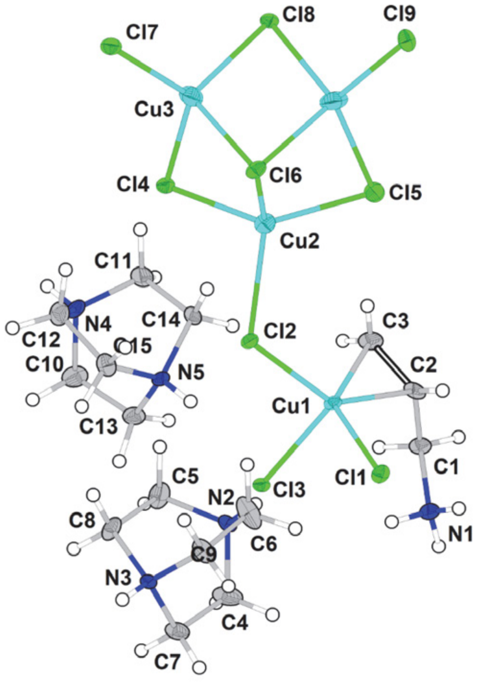

Figure 2. Asymmetric unit of structure **1**. Thermal ellipoids are drawn with 50% probability. Al

Cu2, Cu3 and Cu4 respectively indicate a slightly distorted tetrahedral surrounding in all cases (the value 1.00 corresponds to a perfect tetrahedral geometry, the value 0 to a perfect square planar geometry).[22]

The Dewar-Chatt-Duncanson concept states that an effective Cu–(C=C) interaction leads to a transformation of the Cu coordination polyhedron from tetrahedral to trigonal pyramidal, with the olefin group

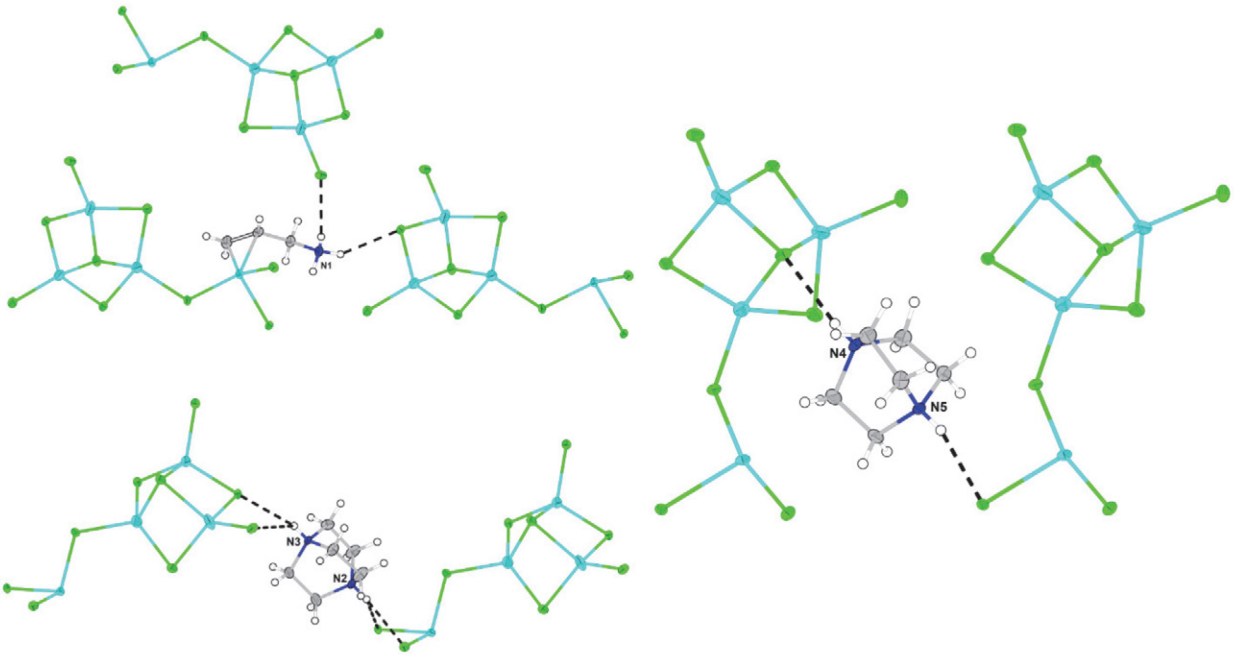

Figure 3. Hydrogen bonds around each organic cation in structure **1**.

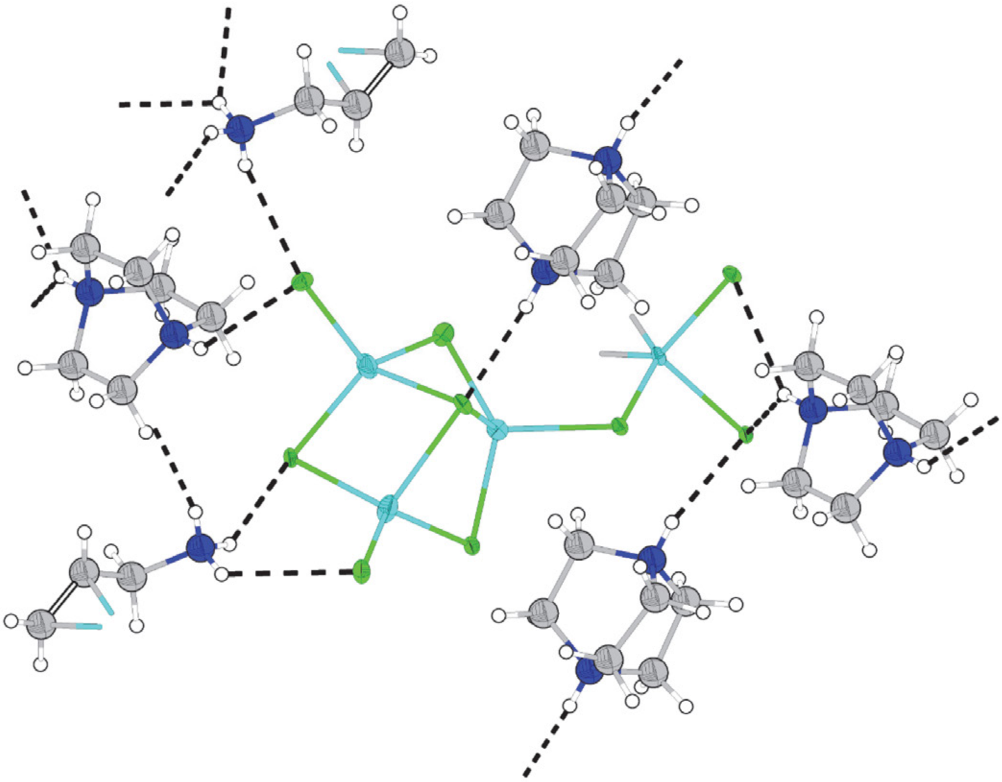

Figure 4. Hydrogen bonds around cupro(I) chloride fragment in structure **1**.

located in the basal plane, and to an increase in the distance between the metal ion and the axial ligand.[23,24] π-coordinated Cu1 center possess well-pronounced trigonal-pyramidal surrounding. The Cu1 ion in structure **1** lies practically in the basal plane (formed by Cl1, Cl2, C2 and C3 atoms) of the coordination polyhedron (distance metal–plane is 0.4 Å), the distance to the Cl3 atom in the apical position is much longer than the length of the Cu1–Cl1 and Cu1–Cl2 bonds (2.4906(6) Å versus 2.2905(7) and 2.3204(7) Å respectively). The C2=C3 bond coordinated to the metal center is tilted by about 2 degrees with respect to the basal plane of the coordination polyhedron. Despite this proper orientation and the relatively short distance Cu–m (m is the center of the C2=C3 double bond) of 1.97 Å, the coordinated C=C-bond is very weakly elongated to 1.344(4) Å. For comparison, the mean length of the coordinated to copper(I) ion C=C bond of 1.360(17) Å was determined with the Mercury software[25] based on 44 records in CCDC[13] containing a C=C + 3Cl environment of the Cu^+ center (four records with a C=C bond length shorter than 1.3 Å or longer than 1.4 Å were excluded as equivocal from the analysis).

Protonated amino-groups of allylammonium and H_2dabco cations form a complex system of N–H···Cl hydrogen bonds (Figs. 3 and 4). Two H-atoms of the allylammonium group are bound to two different Cu_4Cl_9 fragments, and the third H-atom forms an intramolecular N1–H1c···Cl3 bond. Both N4H4 and N5H5 groups from one H_2dabco^{2+} cation form effective H-bonds and connect two chlorocuprate anions. Contrary, the N2H2 and N3H3 groups belong to another H_2dabco unit and form bifurcated hydrogen bonds. This organic cation acts also as a bridge between two Cu_4Cl_9 units.

3. 3. Raman Spectrum

A group of peaks observed in the Raman spectrum of **1** partially match those in the spectra of pure allylamine[26] and dabco[27] (Table 2).

Peaks arising from allylamine were found in **1** at 1207 cm^{-1} (1209, –CH_2 twisting), 1253 cm^{-1} (1283, =CH bending), 1399 cm^{-1} (1423) =CH_2 deformation (the values in parentheses correspond to the frequencies found in the spectrum of solid allylamine). υ_s and υ_{as} modes for =CH_2 were found in **I** in the range between 2909 and 3090 cm^{-1}

An important feature of the Raman spectra of **1** is that the υ_s mode of the C=C-bond is strongly shifted to 1565 cm^{-1} compared to 1636 cm^{-1} in solid allylamine due to the Cu–(C=C) interaction. A similar shift to lower wavenumbers was observed in a number of copper(I) p-complexes.[28]

The broadened peak centered at 246 cm^{-1} in spectrum **1** could be assigned to the υ_s mode of Cu–Cl bonds in $(Cu_4Cl_9)^{5-}$ anion. The corresponding peak was observed at 255 cm^{-1} in [H_2dabco][$CuCl_3$].

4. Concusions

An idea for the synthesis of compound(s) with mixed organic cations and cupro(I) chloride anions was realized by the complete investigation of the CuCl–allylamine–dabco system in acidic media. A new compound of $(H_2dabco)_2[Cu_4Cl_9(allNH_3)]$ composition was obtained and characterized by single crystal X-ray diffraction and Raman spectroscopy. This new compound contains earlier unknown $Cu_4Cl_9^{5-}$ cupro(I)-chloride fragment. The formation of this compound was observed in a rather narrow region of the ternary diagram.

Supplementary Materials

Detailed list of all explored reagents compositions, expanded composition diagram and Raman spectrum of compound **1** are placed as Supplementary Materials.

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Table 2. Originated from the organic part peaks observed in Raman spectra of **1**, pure dabco and $(H_2dabco)[CuCl_3]$ salt.

	in-δ (C–N–C)	out-ν_a (NC_3)	in-ν_s (NC_3)	in-ν_s (NC_3), ν_s (C–C)	ν_a (C–C), in-γ_t (CH_2)	ν_s (C–C), in-ν_s (NC_3), in-δ_s (NC_3)	in-ν_a (NC_3), ν_a (C–C), in-γ_t (CH_2)	in-γ_s (CH_2)
dabco	430	579	598	807	894	972	1061	1459
$(H_2dabco)[CuCl_3]$	406	560	601	803	893	977	1056	1461
1	404	557	606	804	887	979	1056	1456

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Povzetek

Raziskovali smo ternarni sistem CuCl–alilamin–dabco (dabco = 1,4-diazabiciklo[2.2.2]oktan) s presežkom HCl. Iz etanolne raztopine $CuCl_2·2H_2O$, alilamina in dabco titriranega s HCl, so bile s pomočjo elektrokemijske sinteze z uporabo izmeničnega toka generirane bakrove(I) soli. Poleg že znanih $(H_2dabco)[CuCl_3]$, dveh modifikacij spojine $(allNH_3)_2[Cu_2Cl_4]$ in nekaterih Cu(II) stranskih produktov, smo sintetizirali novo spojino $(H_2dabco)_2[Cu_4Cl_9(allNH_3)]$ in jo strukturno analizirali. Njena struktura vsebuje prej neznan anorganski del $Cu_4Cl_9^{5-}$, ki je vezan preko η_2-interakcije z alilamonijem, in diskretnega kationa $(H_2dabco)^{2+}$. Strukturo stabilizira sistem vodikovih vezi N–H···Cl.