

N-Allylaldiminium Cation as a π -Ligand. Synthesis and Crystal Structure of the $[(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{NH}-\text{CH}_2-\text{CH}=\text{CH}_2]\text{Cu}_3\text{Cl}_4$ Compound

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Abstract—The crystals of the $[(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{NH}-\text{CH}_2-\text{CH}=\text{CH}_2]\text{Cu}_3\text{Cl}_4$ compound were prepared by alternating-current electrochemical synthesis from *N*-allyl-4-(*N,N*-dimethylamino)benzaldimine (ADBA) and an ethanol solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in the presence of carbamide and structurally characterized [a DARCh diffractometer, MoK_α radiation, space group $P2_1/n$, $a = 35.267$, $b = 6.511$, $c = 7.587$ Å, $\gamma = 94.64^\circ$, $V = 1736$ Å³, $Z = 4$, $R = 0.035$ for 1030 independent reflections with $F \geq 4\sigma(F)$]. The coordination polyhedron of the Cu(1) atom is a trigonal pyramid formed by three chlorine atoms and the C=C bond; that of Cu(2) is a trigonal pyramid formed by Cl atoms; and that of Cu(3) is a planar triangle formed by chlorine atoms. The length of the coordinated C=C double bond is equal to 1.35(2) Å. The structure is built from the $(\text{Cu}_3\text{Cl}_4)_n^{n-}$ chains π -coordinated to the H^+ADBA cations and oriented along [010]. The geometry of the H^+ADBA cation corresponds to the purely aromatic resonance form, whereas, in the previously studied $[\text{H}^+\text{ADBA}]\text{CuX}_2$ compounds ($X = \text{Cl}, \text{Br}$), it is partially converted into the quinoid form due to the +*M*-effect of the $(\text{CH}_3)_2\text{N}$ group. The calculated effective charges on the atoms indicate that the positive charge on the H^+ADBA cation is stabilized by the hydrogen bonds.

INTRODUCTION

Previous structural studies of the first copper(I) π, σ -complexes with *N*-allyl-substituted Schiff's bases have shown that the efficient Cu–N interaction prevents π -coordination to the σ -coordinated copper atom [1]. One failed to prepare Cu(I) π -complexes with aldimines protonated at the azomethine nitrogen atom (as in the case of mono- and diallylamine [2, 3]) because of their hydrolysis [4]. For this reason, to prepare copper(I) π -complexes with unsaturated derivatives of iminium salts, the *N*-allyl-4-(*N,N*-dimethylamino)benzaldiminium cation (H^+ADBA) stabilized by the +*M*-effect of the $(\text{CH}_3)_2\text{N}$ group was used as a ligand. In the structures of the $[\text{H}^+\text{ADBA}]\text{CuX}_2$ compounds [$X = \text{Cl}$ (**I**) or Br (**II**)] [5], the H^+ADBA cation behaves similarly to the allyl- and diallylammonium cations in the zwitterionic copper(I) π -complexes [6, 7]. Moreover, the geometry of the H^+ADBA cation indicates its partial transition from the aromatic form to the quinoid form as a result of the +*M*-effect of the $(\text{CH}_3)_2\text{N}$ group.

It was of interest to prepare π -complexes with non-protonated *N*-allyl-4-(*N,N*-dimethylamino)benzaldimine and reveal the effect of substitution at the aromatic ring on the efficiency of the Cu–N interaction, which also affects the Cu–(C=C) π -coordination. To prevent the protonation of ADBA (that occurs in the presence of a low amount of water even in a neutral medium), carbamide was used as a proton acceptor [8].

However, the π -complex with protonated ADBA $[\text{H}^+\text{ADBA}]\text{Cu}_3\text{Cl}_4$ (**III**) is formed under these conditions as well. In this work, the results of X-ray structural and quantum-chemical analyses of this compound are reported.

EXPERIMENTAL

ADBA was prepared by the condensation of allylamine with 4-(*N,N*-dimethylamino)benzaldehyde [9]. Complex **III** was prepared as needle-like crystals by the method of alternating-current electrochemical reduction of Cu(II) to Cu(I) ($U = 0.25$ V, $I = 0.13$ mA) on copper electrodes in an ethanol solution (6 ml) containing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (~0.5 mmol), ADBA (~0.4 mmol), and carbamide (~1.0 mmol). The use of low concentrations of the starting substances was necessary for obtaining crystals with satisfactory sizes. The air-stable crystals of compound **III** were formed within a day and during the next 10 days enlarged to the sizes necessary for X-ray experiment. In the case of copper bromide, we failed to obtain crystals suitable for X-ray structural analysis.

After preliminary study by the photographic method, the structure was solved using the experimental data collected on a DARCh single crystal diffractometer; the intensities of reflections were corrected for Lorentz and polarization effects. The structure was solved by the direct method, the light and hydrogen

Table 1. Crystallographic data and details of data collection for complex **III**

| | |
|--|--|
| <i>M</i> | 521.7 |
| <i>F</i> (000) | 1032 |
| Space group | <i>P</i> 2 ₁ / <i>n</i> |
| <i>a</i> , Å | 35.267(8) |
| <i>b</i> , Å | 6.511(2) |
| <i>c</i> , Å | 7.587(2) |
| γ, deg | 94.64(2) |
| <i>V</i> , Å ³ | 1736(1) |
| <i>Z</i> | 4 |
| ρ(meas), g/cm ³ | 2.02 |
| ρ(calcd), g/cm ³ | 1.995(1) |
| μ _{Mo} , cm ⁻¹ | 43.76 |
| Radiation | Mo <i>K</i> _α |
| Diffractionmeter | DARCh |
| Scan technique | θ/2θ |
| No. of reflections: | |
| measured | 1124 |
| independent with <i>F</i> ≥ 4σ(<i>F</i>) | 1030 |
| 2θ _{max} , deg | 48 |
| No. of parameters refined | 258 |
| <i>R</i> | 0.035 |
| <i>R</i> _w | 0.037 |
| Weighing scheme | [σ(<i>F</i> _o) ² + 0.0009 <i>F</i> _o ²] ⁻¹ |
| GOOF | 1.10 |

atoms being located from difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically (hydrogen atoms isotropically) by the full-matrix method. Absorption was corrected (DIFABS program) using the CSD program package [10].

The crystallographic data and details of data collection for structure **III** are presented in Table 1. The coordinates of atoms and their thermal parameters are given in Table 2. The interatomic distances and bond and torsion angles are presented in Table 3.

RESULTS AND DISCUSSION

In the structure under study, the trigonal-pyramidal environment of the copper(I) π-coordinated atom is composed of three Cl atoms and the C=C bond in one of the equatorial positions. The axial elongation [Cu(1)–Cl(2) 2.685(4) Å] is caused by the displacement of the copper atom from the plane of equatorial ligands (Δ = 0.30 Å). The angle between the plane of equatorial ligands and the C=C bond is equal to 16°. A considerable axial deformation of the trigonal-pyramidal chlorine environment of the Cu(2) atom [Cu(2)–Cl(1) 2.962(4) Å] correlates with the smaller Δ value (0.22 Å). A planar-trigonal coordination sphere formed by the chlorine atoms for the Cu(3) atom is rare for the copper(I) complexes. The displacement of the Cu(3) atom from the plane of Cl atoms (Δ = 0.16 Å) is likely caused by the rigidity of the polynuclear inorganic frag-

Table 2. Coordinates of atoms and their thermal parameters* for structure **III**

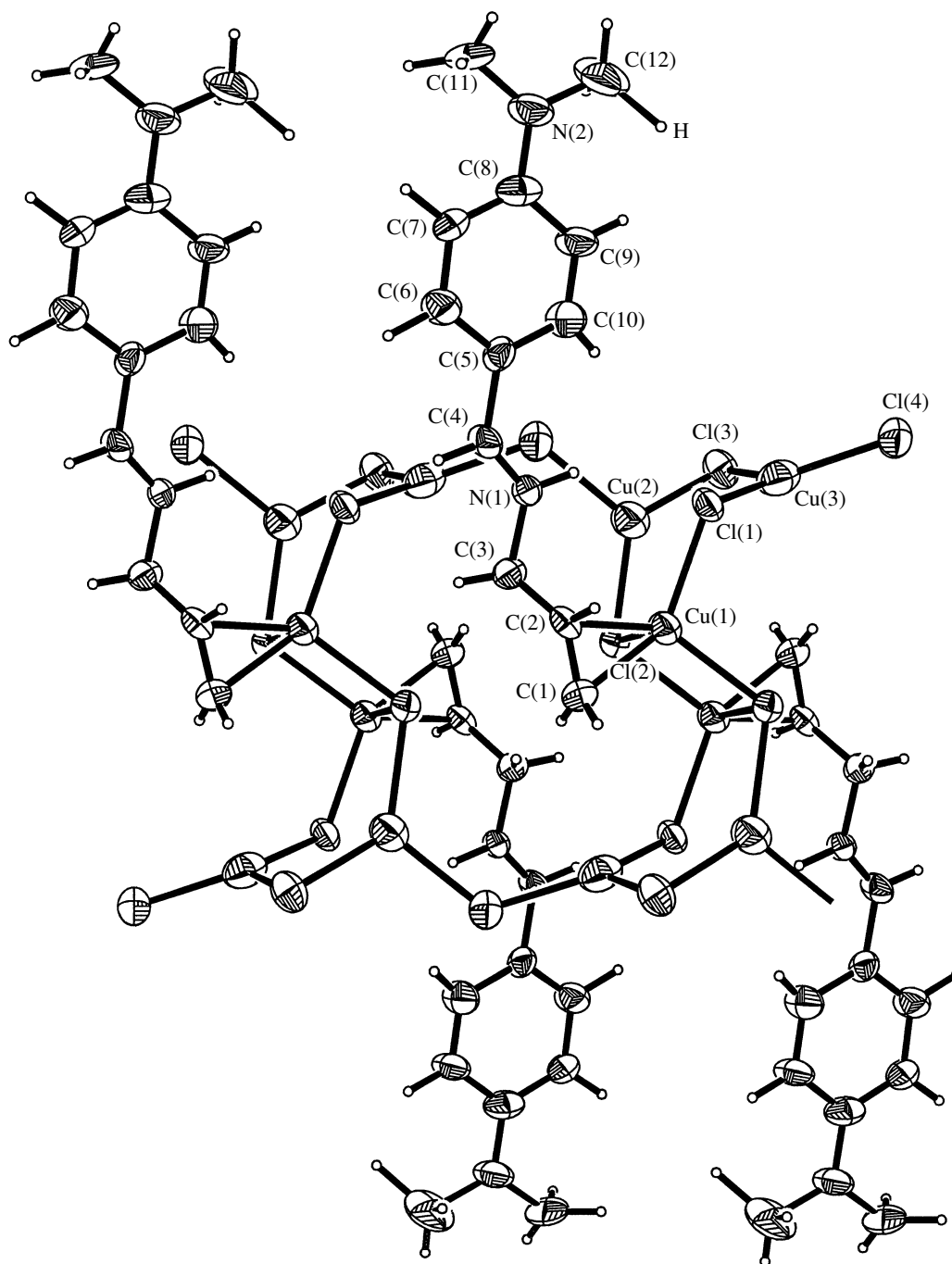
| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> , Å ² | Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> , Å ² |
|-------|------------|------------|-----------|---------------------------|---------|-----------|----------|----------|---------------------------|
| Cu(1) | 0.52567(4) | 0.0531(2) | 0.8080(2) | 3.18(4) | C(11) | 0.8037(3) | 0.630(2) | 0.489(2) | 5.2(4) |
| Cu(2) | 0.57784(4) | 0.2219(2) | 0.1676(2) | 4.42(5) | C(12) | 0.7962(4) | 0.311(2) | 0.670(2) | 6.5(5) |
| Cu(3) | 0.59926(4) | -0.1907(2) | 0.1155(2) | 4.55(5) | H(1.1) | 0.480(2) | 0.31(1) | 0.74(1) | 3(2) |
| Cl(1) | 0.58715(7) | -0.0329(4) | 0.8494(4) | 2.95(8) | H(1.2) | 0.481(2) | 0.18(1) | 0.59(1) | 2(2) |
| Cl(2) | 0.51478(7) | 0.2338(4) | 0.1200(4) | 2.71(8) | H(2.1) | 0.539(2) | 0.206(8) | 0.534(8) | 1(1) |
| Cl(3) | 0.60318(8) | 0.0009(4) | 0.3590(4) | 3.69(9) | H(3.1) | 0.551(2) | 0.59(1) | 0.61(1) | 3(2) |
| Cl(4) | 0.61902(9) | -0.5059(4) | 0.0978(5) | 4.26(9) | H(3.2) | 0.548(2) | 0.50(1) | 0.81(1) | 3(2) |
| N(1) | 0.5957(2) | 0.433(1) | 0.676(1) | 2.9(2) | H(N) | 0.604(2) | 0.32(1) | 0.75(1) | 3(2) |
| N(2) | 0.7794(2) | 0.477(1) | 0.580(1) | 4.1(3) | H(4.1) | 0.611(2) | 0.650(9) | 0.545(9) | 1(2) |
| C(1) | 0.4943(3) | 0.249(2) | 0.663(2) | 3.1(3) | H(6.1) | 0.671(2) | 0.782(9) | 0.435(9) | 1(2) |
| C(2) | 0.5309(3) | 0.293(2) | 0.617(1) | 2.2(3) | H(7.1) | 0.740(2) | 0.76(1) | 0.43(1) | 5(2) |
| C(3) | 0.5546(3) | 0.465(1) | 0.681(2) | 2.8(3) | H(9.1) | 0.728(3) | 0.24(1) | 0.75(1) | 4(2) |
| C(4) | 0.6199(3) | 0.539(2) | 0.595(2) | 2.9(3) | H(10.1) | 0.663(2) | 0.29(1) | 0.74(1) | 1(2) |
| C(5) | 0.6621(3) | 0.519(2) | 0.597(2) | 2.9(3) | H(11.1) | 0.798(2) | 0.62(1) | 0.36(1) | 2(2) |
| C(6) | 0.6848(3) | 0.661(2) | 0.499(2) | 3.7(4) | H(11.2) | 0.801(2) | 0.80(1) | 0.53(1) | 2(2) |
| C(7) | 0.7240(3) | 0.650(2) | 0.496(2) | 3.5(4) | H(11.3) | 0.821(3) | 0.57(2) | 0.46(1) | 5(3) |
| C(8) | 0.7409(3) | 0.494(2) | 0.584(2) | 3.7(4) | H(12.1) | 0.821(3) | 0.30(1) | 0.64(1) | 4(2) |
| C(9) | 0.7167(3) | 0.347(2) | 0.681(2) | 3.8(4) | H(12.2) | 0.772(4) | 0.14(2) | 0.67(2) | 10(4) |
| C(10) | 0.6791(3) | 0.362(2) | 0.682(2) | 3.8(4) | H(12.3) | 0.791(2) | 0.36(1) | 0.75(1) | 1(2) |

* For non-hydrogen atoms, $B_{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j)$.

Table 3. Bond lengths (*d*) and bond (ω) and torsion (ϕ) angles in structure **III**

| Bond | <i>d</i> , Å | Angle* | ω , deg | Bond | <i>d</i> , Å | Angle | ω , deg |
|------------------------|--------------|----------------------------|----------------|-----------------------|--------------|---------------------|----------------|
| Cu(1)–Cl(1) | 2.304(8) | Cl(1)Cu(1)Cl(2) | 99.0(2) | C(5)–C(10) | 1.39(2) | C(4)C(5)C(10) | 124(1) |
| Cu(1)–Cl(2) | 2.685(4) | Cl(1)Cu(1)Cl(2)' | 107.5(2) | | | C(6)C(5)C(10) | 119(1) |
| Cu(1)–Cl(2)' | 2.322(5) | Cl(1)Cu(1) <i>m</i> (1,2) | 122.5(4) | C(6)–C(7) | 1.39(2) | C(5)C(6)C(7) | 120(1) |
| Cu(1)–C(1) | 2.07(1) | Cl(2)Cu(1)Cl(2)' | 92.6(2) | C(6)–H(6.1) | 1.07(7) | C(5)C(6)H(6.1) | 118(4) |
| Cu(1)–C(2) | 2.13(1) | Cl(2)Cu(1) <i>m</i> (1,2) | 101.7(4) | | | C(7)C(6)H(6.1) | 123(4) |
| Cu(1)– <i>m</i> (1,2)* | 1.99(1) | Cl(2)'Cu(1) <i>m</i> (1,2) | 124.2(4) | C(7)–C(8) | 1.39(2) | C(6)C(7)C(8) | 121(1) |
| | | C(1)Cu(1)C(2) | 37.3(4) | C(7)–H(7.1) | 1.02(9) | C(6)C(7)H(7.1) | 119(5) |
| Cu(2)–Cl(1) | 2.962(4) | Cl(1)Cu(2)Cl(2) | 92.5(2) | | | C(8)C(7)H(7.1) | 120(5) |
| Cu(2)–Cl(2) | 2.261(8) | Cl(1)Cu(2)Cl(3) | 95.7(2) | C(8)–C(9) | 1.43(2) | C(7)C(8)C(9) | 118(1) |
| Cu(2)–Cl(3) | 2.277(5) | Cl(1)Cu(2)Cl(4)' | 98.9(2) | C(8)–N(2) | 1.37(2) | C(7)C(8)N(2) | 122(1) |
| Cu(2)–Cl(4)' | 2.262(6) | Cl(2)Cu(2)Cl(3) | 124.1(2) | | | N(2)C(8)C(9) | 120(1) |
| | | Cl(2)Cu(2)Cl(4)' | 120.4(2) | C(9)–C(10) | 1.34(2) | C(8)C(9)C(10) | 120(1) |
| | | Cl(3)Cu(2)Cl(4)' | 112.6(2) | C(9)–H(9.1) | 0.98(9) | C(8)C(9)H(9.1) | 120(6) |
| Cu(3)–Cl(1) | 2.321(4) | Cl(1)Cu(3)Cl(3) | 118.6(2) | | | C(10)C(9)H(9.1) | 120(6) |
| Cu(3)–Cl(3) | 2.227(4) | Cl(1)Cu(3)Cl(4) | 116.0(2) | C(10)–H(10.1) | 0.84(7) | C(9)C(10)C(5) | 123(1) |
| Cu(3)–Cl(4) | 2.224(5) | Cl(3)Cu(3)Cl(4) | 123.9(3) | | | C(9)C(10)H(10.1) | 126(5) |
| Cu(2)⋯Cu(3) | 2.876(4) | Cu(1)Cl(1)Cu(3) | 115.9(2) | | | C(5)C(10)H(10.1) | 111(5) |
| | | Cu(1)Cl(2)Cu(1)' | 87.4(2) | N(2)–C(11) | 1.44(2) | C(8)N(2)C(11) | 120(1) |
| | | Cu(1)Cl(2)Cu(2) | 87.1(2) | N(2)–C(12) | 1.45(2) | C(8)N(2)C(12) | 121(1) |
| | | Cu(1)'Cl(2)Cu(2) | 118.5(2) | | | C(11)N(2)C(12) | 119(1) |
| | | Cu(2)Cl(3)Cu(3) | 79.4(2) | C(11)–H(11.1) | 0.97(9) | N(2)C(11)H(11.1) | 109(5) |
| | | Cu(2)'Cl(4)Cu(3) | 118.7(3) | C(11)–H(11.2) | 1.16(7) | N(2)C(11)H(11.2) | 115(4) |
| C(1)–C(2) | 1.35(2) | C(2)C(1)H(1.1) | 130(6) | C(11)–H(11.3) | 0.8(1) | N(2)C(11)H(11.3) | 105(8) |
| C(1)–H(1.1) | 0.88(9) | C(2)C(1)H(1.2) | 115(6) | | | H(11.1)C(11)H(11.2) | 107(6) |
| C(1)–H(1.2) | 0.80(8) | H(1.1)C(1)H(1.2) | 112(8) | | | H(11.1)C(11)H(11.3) | 81(9) |
| C(2)–C(3) | 1.43(1) | C(1)C(2)C(3) | 125(1) | | | H(11.2)C(11)H(11.3) | 133(9) |
| C(2)–H(2.1) | 0.91(6) | C(1)C(2)H(2.1) | 113(4) | C(12)–H(12.1) | 0.9(1) | N(2)C(12)H(12.1) | 113(6) |
| | | C(3)C(2)H(2.1) | 122(4) | C(12)–H(12.2) | 1.3(1) | N(2)C(12)H(12.2) | 109(6) |
| C(3)–N(1) | 1.48(2) | C(2)C(3)N(1) | 113.4(9) | C(12)–H(12.3) | 0.70(7) | N(2)C(12)H(12.3) | 84(6) |
| C(3)–H(3.1) | 0.96(8) | C(2)C(3)H(3.1) | 110(5) | | | H(12.1)C(12)H(12.2) | 121(8) |
| C(3)–H(3.2) | 0.99(9) | C(2)C(3)H(3.2) | 111(5) | | | H(12.1)C(12)H(12.3) | 121(8) |
| | | N(1)C(3)H(3.1) | 108(5) | | | H(12.2)C(12)H(12.3) | 103(8) |
| | | N(1)C(3)H(3.2) | 107(5) | Angle | ϕ , deg | Angle | ϕ , deg |
| | | H(3.1)C(3)H(3.2) | 107(7) | Cl(2)Cu(1)Cl(1)Cu(3) | –47.2 | C(3)N(1)C(4)C(5) | 175.4 |
| N(1)–C(4) | 1.22(1) | C(3)N(1)C(4) | 125(1) | Cl(2)'Cu(1)Cl(1)Cu(3) | 48.4 | N(1)C(4)C(5)C(6) | –177.5 |
| N(1)–H(N) | 0.95(8) | C(3)N(1)H(N) | 117(5) | Cl(1)Cu(1)Cl(2)Cu(2) | –10.5 | N(1)C(4)C(5)C(10) | –6.2 |
| | | C(4)N(1)H(N) | 117(5) | Cl(3)Cu(2)Cl(2)Cu(1) | 106.6 | C(4)C(5)C(6)C(7) | 179.6 |
| C(4)–C(5) | 1.51(2) | N(1)C(4)C(5) | 127(1) | Cl(1)Cu(3)Cl(3)Cu(2) | –12.7 | C(5)C(6)C(7)C(8) | –2.0 |
| C(4)–H(4.1) | 0.89(6) | N(1)C(4)H(4.1) | 114(4) | CuC(1)C(2)C(3) | –101.1 | C(7)C(8)C(9)C(10) | 1.0 |
| | | C(5)C(4)H(4.1) | 119(4) | C(1)C(2)C(3)N(1) | 154.5 | C(7)C(8)N(2)C(11) | 3.3 |
| C(5)–C(6) | 1.39(2) | C(4)C(5)C(6) | 117(1) | C(2)C(3)N(1)C(4) | –120.2 | C(7)C(8)N(2)C(12) | –178.6 |

* *m*(1,2) is the midpoint of the double C(1)=C(2) bond.

Fragment of structure **III**.

ment representing the $(\text{Cu}_3\text{Cl}_4)_n^{n-}$ chain along [010].

The H^+ADBA cation protonated at the aldimine nitrogen atom is π -coordinated to the chains solely via the $\text{C}=\text{C}$ bond, resulting in its elongation to 1.35(2) Å [$\text{Cu}(1)-m(1, 2)$ 1.99(1) Å, $\text{C}(1)\text{Cu}(1)\text{C}(2)$ 37.3(4)°]. The chains (figure) are joined together by the van der Waals forces between the H^+ADBA cations to form a structure in the [100] direction and by the $\text{C}(4)-$

$\text{H}(4.1)\cdots\text{Cl}(3)$ hydrogen bonds to form a structure along the [001] direction (Table 4).

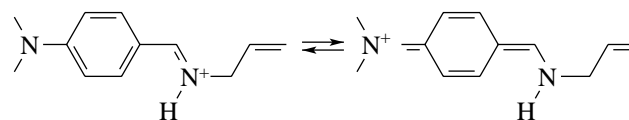
The conformations of the allyl groups in **I**, **II**, and **III** are similar [the $\text{C}(1)=\text{C}(2)-\text{C}(3)-\text{N}(1)$ torsion angles are equal to 156.7°, 152.7°, and 154.5°, respectively], but the structures differ in the $\text{C}(2)-\text{C}(3)-\text{N}(1)=\text{C}(4)$ angles (−91.8° and −97.7° in **I** and **II**, respectively, and −120.2° in **III**). Thus, the geometry of the allylaldimine fragment in structure **III** is closer to

Table 4. Geometry of hydrogen bonds in structure **III**

| A–H...B bond | Distance, Å | | | AHB angle, deg |
|-----------------------|-------------|----------|---------|----------------|
| | H...B | A...B | A–H | |
| N(1)–H(N)...Cl(1) | 2.47(8) | 3.296(9) | 0.95(8) | 144(7) |
| C(2)–H(2.1)...Cl(3) | 3.02(6) | 3.84(1) | 0.91(6) | 149(5) |
| C(4)–H(4.1)...Cl(3) | 2.72(6) | 3.59(1) | 0.89(6) | 166(5) |
| C(6)–H(6.1)...Cl(3) | 2.94(6) | 3.92(1) | 1.07(7) | 151(5) |
| C(12)–H(12.1)...Cl(4) | 3.00(9) | 3.76(2) | 0.9(1) | 143(8) |

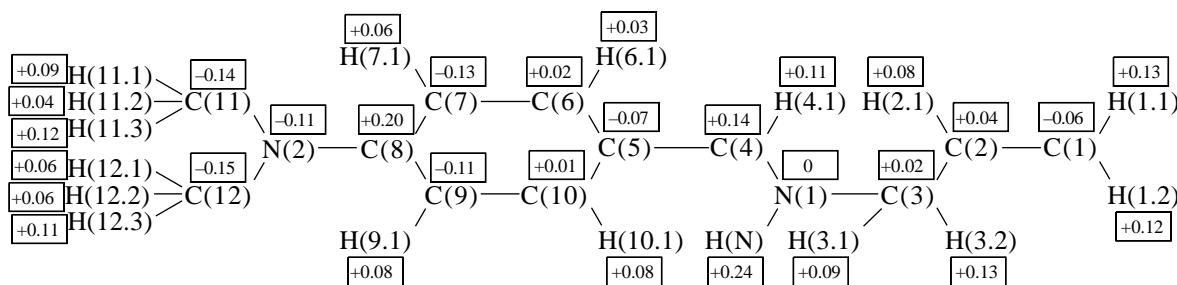
that in the π,σ -complexes of *N*-allyl-2-furylaldimine and *N*-allylbenzaldimine (L) with copper(I) chloride, $2\text{CuCl} \cdot \text{L}$, in which the azomethine nitrogen atom is coordinated to Cu(I) [the C(2)–C(3)–N=C(4) angles are equal to -115.7° and -112.5° , respectively] [1]. The remainder of the H^+ADBA cation in **III** is conjugated and, on the whole, is planar (see torsion angles in Table 3). Due to the conjugation, the cation charge is stabilized by the electron lone pair of the $(\text{CH}_3)_2\text{N}$ group. In structures **I** and **II**, this is manifested by the geometric parameters evidencing a partially quinoid form of the H^+ADBA cation: the bond lengths in the benzene ring are redistributed, the C(4)–C(5) bond is shortened [to 1.42(2) in **I** and 1.41(3) Å in **II**], and the N(1)=C(4)

bond is elongated [to 1.26(1) in **I** and 1.29(2) Å in **III**]. The resonance forms are schematically represented as

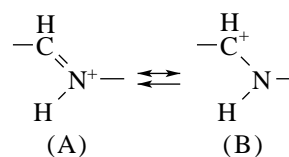


A similar quinoidization with the stabilizing effect of the dimethylamino group, but even to a greater extent, is observed in the related structure of *N,N*-dimethyl-*p*-nitrosoaniline hydrochloride [11]. However, the H^+ADBA cation in compound **III** exhibits a purely aromatic form: the bond lengths in the benzene ring are not redistributed toward the quinoid structure, the C(4)–C(5) bond is not shortened [1.51(2) Å], and the N(1)=C(4) bond [1.22(1) Å] is one of the shortest bonds observed for the copper(I) allylazomethine complexes.

To reveal the special features of the positive charge stabilization on the ligand cation, the charges on the atoms in the structure of π -complex **III** were calculated using the HYPERCHEM program [12] by the modified version of the iterative SCF LCAO MO method in the ZINDO/1 approximation. The calculations were performed for a cluster containing 228 atoms and representing structure **III** (696 initial AOs were taken into account). The charges on the atoms of the H^+ADBA cation are presented below.



The charges on the copper atoms are different: the charge on the Cu(1) atom involved in the π -bonding is equal to $-0.01e$, while the value of $+0.08e$ found for the charges on the Cu(2) and Cu(3) atoms surrounded by the chlorine atoms is close to the values calculated for Cu(I) in the sphalerite structure [3]. This difference is caused by the tangible σ -component $(\text{Cu(I)} \leftarrow \text{L})_\sigma$ of the Cu(1)–(C=C) π -bond. The negative charges on the chlorine atoms are in compliance with the strength of the hydrogen bonds formed with their participation (Table 4): $q_{\text{Cl}(1)} = -0.39e$, $q_{\text{Cl}(2)} = -0.29e$, $q_{\text{Cl}(3)} = -0.37e$, and $q_{\text{Cl}(4)} = -0.36e$. The most significant distinction between **I** and **III** is that the N(1)=C(4) bond in **III** is less polarized (in **I**, $q_{\text{N}(1)} = -0.05e$ and $q_{\text{C}(4)} = +0.20e$), indicating a smaller positive charge transfer to the carbon atom:



The fact that the contribution of form A to **III** is greater than its contribution to **I** is caused by the strengthening of the N(1)–H(N)...Cl(1) bond [2.68(5) Å in **I**, 2.47(8) Å in **III**] polarized according to the $\text{N}^\delta- \text{H}^\delta+ \cdots \text{Cl}^\delta-$ scheme and agrees with the absence of elongation for the N=C bond. In addition, a certain contribution of form B is stabilized, even without conjugation with the aromatic ring, by the strong hydrogen contact C(4)–H(4.1)...Cl(3) (absent in **I**) with an analogous charge transfer to the hydrogen atom. Thus, the positive charge of the H^+ADBA cation in structure **III** is stabilized to a great extent due to the hydrogen bonds, whereas in **I** it

is stabilized owing to the +M-effect of the $(\text{CH}_3)_2\text{N}$ group.

The important role of carbamide in the isolation of the $[\text{H}^+\text{L}]\text{Cu}_3\text{X}_4$ compound is noteworthy. Previously, two such isostructural copper(I) π -complexes were known (with $\text{H}^+\text{L} = \text{sym-triallylguanidinium}$) [13] whose stoichiometry was dictated by the $\text{Cu(I)} : \text{C}=\text{C} = 1 : 1$ ratio, typical of the cuprohalide π -complexes. As for compound **III**, the coordination environments of the two additional copper atoms are comprised of solely the chlorine atoms, and one of them has the planar-trigonal environment.

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