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Copper(I) complexes with 3-(allylamino)-, 3-(diallylamino)-, 3-[(2-hydroxyethyl)(allyl)amino]- and 3-[(2-hydroxyethyl)amino]- propanenitriles. Synthesis and crystal structure of $[\{C_3H_5NH(H^+)C_2H_4CN\}Cu_2Br_3]$, $[\{(C_3H_5)_2N(H^+)C_2H_4CN\}CuCl_{1.94}Br_{0.06}]$, $[\{HOC_2H_4NH(H^+)C_2H_4CN\}CuCl_2]$ and $[\{HOC_2H_4(C_3H_5)N(H^+)C_2H_4CN\}CuCl_2]$

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Four crystalline copper(I) complexes with N-derivatives of propanenitrile: $[\{C_3H_5NH(H^+)C_2H_4CN\}Cu_2Br_3]$ (I), $[\{(C_3H_5)_2N(H^+)C_2H_4CN\}CuCl_{1.94}Br_{0.06}]$ (II), $[\{HOC_2H_4NH(H^+)C_2H_4CN\}CuCl_2]$ (III) and $[\{HOC_2H_4(C_3H_5)N(H^+)C_2H_4CN\}CuCl_2]$ (IV), have been obtained (by the alternating current electrochemical technique from alcohol solutions of the organic ligand and $CuCl_2{\cdot}2H_2O$ or $CuBr_2$) and investigated by X-ray diffraction. Crystals of compound I are triclinic, space group *P*-1, *Z* = 2, *a* = 6.5520(7), *b* = 7.8642(8), *c* = 11.2370(12) Å, *α* = 90.694(6), *β* = 94.427(6), *γ* = 93.690(6)°, *V* = 575.99(10) Å^3. Crystals of compounds II-IV are monoclinic. For II and IV the space group is $P2_1/c$, *Z* = 4. For II: *a* = 11.6518(4), *b* = 7.0086(2), *c* = 14.6765(5) Å, *β* = 100.965(13)°, *V* = 1176.64(7) Å^3; IV: *a* = 11.001(3), *b* = 7.017(2), *c* = 14.653(4) Å, *β* = 97.19(3)°, *V* = 1122.2(5) Å^3. For III the space group is *P*2/c, *Z* = 4, *a* = 7.452(2), *b* = 7.642(2), *c* = 15.867(5) Å, *β* = 95.43(3)°, *V* = 899.5(4) Å^3. The structures of the coordination compounds I-IV possess distinct polymer anionic chains $(CuX_2)_n^{n-}$ or $(Cu_2X_3)_n^{n-}$ (X = Cl, Br), which are joined together by organic cations (H^+L) (I) or surrounded by them (II-IV). Hydrogen bonding play a significant role in the stabilization of the structures.

Copper(I) / π- and σ-Complexes / β-Aminonitriles / Crystal structure / Electrochemical technique

Introduction

Aminonitriles form a large class of organic compounds with diverse representatives that find their application in various spheres. More than 150 years have passed since the first synthesis of compounds of this class was mentioned by Strecker [1,2], but the topicality and challenges remain inexhaustible [3] and the chemistry of nitriles is a traditional subject of intensive research in terms of theory and practice. Attempts to systematize nitrile compounds have been made by E.N. Zil'berman [4] but, as mentioned by the author himself, some specific classes have been left untouched since there has never been a substantial basis for a sustained development of a complex methodology [5]. Efforts are underway to expand the scope of efficient methods for the synthesis of these compounds, with growing emphasis on copper(I) compounds with N-derivatives of aminopropanenitrile with further practical potential of explaining the mechanism of interaction of copper(I) salts with aminonitriles [6].

The present paper also reports results on new Cu(I) halide π-complexes with N-allyl derivatives of aminonitriles.

Experimental section

Synthesis of 3-(allylamino)propanenitrile ($C_3H_5NHC_2H_4CN$, L1)

This ligand was obtained from acrylonitrile (6.8 mL, 0.1 mol) and allylamine (11.2 mL, 0.15 mol). The mixture of reagents was continuously stirred and cooled (5 h, 20°C), maintaining the temperature not higher than 30°C [7], then it was heated for 1 h in a water bath with a reflux condenser at 60°C. The product (orange liquid) was purified by distillation in vacuum produced by a water-jet pump (85°C / 40 mm Hg). The yield of *L1* was 88% (15 mL).

Synthesis of 3-(diallylamino)propanenitrile ($(C_3H_5)_2NC_2H_4CN$, L2)

To obtain 3-(diallylamino)propanenitrile a mixture of acrylonitrile (7 mL, 0.11 mol) and diallylamine (16 mL, 0.13 mol) was heated with a reflux condenser in a water bath at 50-60°C for 8 h and then kept at room temperature for 24 h [7]. A small amount of unreacted initial substances was distilled off in vacuum produced by a water-jet pump; the red-orange liquid was distilled at 130°C (20 mm Hg). The yield of *L2* was 75% (13 mL).

Synthesis of 3-({2-hydroxyethyl}amino)propanenitrile ($(HOC_2H_5)NHC_2H_4CN$, L3) and 3-({2-hydroxyethyl}allylamino)propanenitrile ($(HOC_2H_5)C_3H_5NC_2H_4CN$, L4)

3-({2-hydroxyethyl}amino)propanenitrile (*L3*) was synthesized from monoethanolamine (3 mL, 0.05 mol) and acrylonitrile (3.5 mL, 0.05 mol). After 24 h at 25°C, the mixture was kept at room temperature (19°C) for 12 h. The resulting colorless liquid was used for further syntheses of *L4* and complex III. The yield of *L3* was ~75%.

To obtain 3-({2-hydroxyethyl}allylamino)-propanenitrile an ethanol-benzene (1:1) solution of *L3* and allyl bromide (1.11 g, 0.0128 mol) in the presence of $NaHCO_3$ (1.465 g, 0.0128 mol) was stirred and heated in a reflux condenser (80°C) for 72 h. Then the mixture was filtered (NaBr was removed) and the excess of solvents was distilled off under reduced pressure. A yellow liquid was obtained (17 mL). The yield of *L4* was ~90%.

Preparation of ($[(C_3H_5NH(H^+)C_2H_4CN)Cu_2Br_3]$ (I)

Colorless needle-like crystals of complex **I** appeared from an ethanol (4 mL) solution of $CuBr_2$ (1 g, 4.5 mmol) and *L1* (0.6 mL, 5 mmol, titrated with a concentrated water solution of 48% HBr to pH = 3) under conditions of the alternating current electrochemical technique [8]. The initial solution was placed into a small test-tube and copper-wire electrodes in cork were inserted. After applying 0.65 V of alternating current (frequency 50 Hz) tension for 7 days, crystals of **I** were formed on the copper electrodes. The yield of the complex was 70%.

Preparation of $[(C_3H_5)_2N(H^+)C_2H_4CN\}CuCl_{1.94}Br_{0.06}]$ (II)

Good quality crystals of the mixed halide complex **II** were obtained in a similar way (alternating current, U = 0.4 V, I_{init} = 1 mA, time of synthesis 22 h) starting from an ethanol (4 mL) solution of 0.7 mL (4.3 mmol) of *L2* (titrated with a concentrated water solution of 48% HBr to pH = 4) and 0.70 g (4.1 mmol) of $CuCl_2{\cdot}2H_2O$. The yield was 50%.

Preparation of $[(HOC_2H_4NH(H^+)C_2H_4CN)CuCl_2]$ (III)

Colorless prismatic crystals of compound **III** appeared on the copper wire electrodes after 3 h (U = 0.45 V, I_{init} = 0.5 mA) from a benzene-ethanol (0.5 mL C_6H_6 and 4.5 mL C_2H_5OH) solution of $CuCl_2{\cdot}2H_2O$ (0.65 g, 3.8 mmol) and *L3* (0.68 mL, 4 mmol, titrated with 36% HCl to pH = 4). The yield was 70%.

Preparation of $[\{HOC_2H_4(C_3H_5)N(H^+)C_2H_4CN\}CuCl_2]$ (IV)

Crystals of the π-complex **IV** grew from a solution of $CuCl_2{\cdot}2H_2O$ (0.70 g, 4.1 mmol) and *L4* (0.72 mL, 4.5 mmol, titrated with 36% HCl to pH = 4.5-5) in a mixture of C_6H_6 (0.5 mL), C_2H_5OH (2.5 mL) and C_3H_7OH (1.5 mL) after 10 h under conditions of an alternating current electrochemical synthesis (U = 0.45 V, I_{init} = 0.5 mA). The product yield was 70%.

X-ray crystal structure determination

The crystallographic parameters and summaries of the data collections for **I-IV** are presented in Table 1. Single crystals of **I-IV** were preliminarily studied by the photographic method and then diffraction data were collected on a Rigaku AFC7R (for **I-II**) or KUMA-KM4/CCD (for **III-IV**) diffractometers (graphite monochromated Mo K_α radiation). Lorentz and polarization corrections were applied.

The X-ray data were processed using the Rigaku CrystalClear program [9] for compounds **I** and **II**. The CrysAlisRED program was used for processing the X-ray data for complexes **III** and **IV** [10]. An absorption correction was applied by the analytical method [11].

Table 1 Crystallographic data and experimental details for structures **I-IV**.

	I	**II**	**III**	**IV**
Empirical formula	$C_6H_{11}Br_3Cu_2N_2$	$C_9H_{15}Br_{0.06}Cl_{1.94}CuN_2$	$C_5H_{11}Cl_2CuN_2O$	$C_8H_{15}Cl_2CuN_2O$
Formula weight	477.98	288.45	249.60	289.66
Temperature, K	200	200	100	100
Wavelength, Å	0.71073 (Mo K_α)	0.71069 (Mo K_α)	0.71073 (Mo K_α)	0.71073 (Mo K_α)
Crystal system, space group	Triclinic, *P*-1	Monoclinic, $P2_1/c$	Monoclinic, *P*2/c	Monoclinic, $P2_1/c$
Diffractometer	Rigaku AFC7	Rigaku AFC7	KUMA-KM4/CCD	KUMA-KM4/CCD
Unit cell dimensions				
a, Å	6.5520(7)	11.6518(4)	7.452(2)	11.001(3)
b, Å	7.8642(8)	7.0086(2)	7.642(2)	7.017(2)
c, Å	11.2370(12)	14.6765(5)	15.867(5)	14.653(4)
α, °	90.694(6)	90	90	90
β, °	94.427(6)	100.965(13)	95.43(3)	97.19(3)
γ, °	93.690(6)	90	90	90
Volume, Å^3	575.99(10)	1176.64(7)	899.5(4)	1122.2(5)
Z	2	4	4	4
Calculated density, g·cm^{-3}	2.756	1.628	1.843	1.714
Absorption coefficient, mm^{-1}	14.05	2.47	2.97	2.39
F(000)	448	587.6	504	592
Crystal size, mm	0.10 × 0.05 × 0.04	0.10 × 0.09 × 0.03	0.20 × 0.18 × 0.16	0.10 × 0.08 × 0.05
Colour, shape	Colorless, prism	Colorless, chunk	Colorless, prism	Colorless, prism
Theta range for data collection, °	1.8-29.0	2.8-28.2	3.0-37.0	2.8-35.1
Limiting indices	$-8 \le h \le 8$, $-10 \le k \le 10$, $0 \le l \le 14$	$0 \le h \le 15$, $-9 \le k \le 5$, $-18 \le l \le 18$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-23 \le l \le 26$	$-15 \le h \le 16$, $-10 \le k \le 10$, $-23 \le l \le 19$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Measured reflections	2431	3614	14333	11972
Independent reflections	2431	2430	4030	4243
Observed reflections [$I > 2\sigma(I)$]	1880	2301	2374	3403
Refined parameters	118	189	183	114
Weighting scheme [a]	$[\sigma^2(F_o^2) + (0.0355P)^2]^{-1}$	$[\sigma^2(F_o^2) + (0.0506P)^2+3.3037P]^{-1}$	$[\sigma^2(F_o^2) + (0.0455P)^2+0.1706P]^{-1}$	$[\sigma^2(F_o^2) + (0.048P)^2]^{-1}$
Goodness-of-fit on F^2	0.97	1.15	1.03	1.10
Final *R* indices [$I > 2\sigma(I)$]	$R = 0.043$, $wR = 0.099$	$R = 0.047$, $wR = 0.115$	$R = 0.040$, $wR = 0.099$	$R = 0.028$, $wR = 0.083$
Residual electron density, e Å^{-3}	1.72 and -0.79	0.45 and -0.83	1.14 and -1.35	0.86 and -0.79

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

Structures **I-IV** were solved by direct methods and the light atoms were revealed from difference Fourier syntheses, using the SHELX program package [12]. Full-matrix least-squares refinements based on F^2were carried out for the positional and thermal parameters of all non-hydrogen atoms. The hydrogen atoms in structures **I-III** were revealed from difference Fourier syntheses and refined in the riding model along with the non-hydrogen atoms (fixed C–H distances and with U_{iso}(H) equal to 1.2U_{eq}(C)); for **IV** the H-atoms were refined independently.

Atomic positional and displacement parameters for **I-IV** are given in Tables 2-5. The figures were prepared using DIAMOND 3.1 software [13].

Results and discussion

The π-complex [{$C_3H_5NH(H^+)C_2H_4CN$}Cu_2Br_3] (**I**) is isostructural to the previously studied copper(I) chloride complex [{$C_3H_5NH(H^+)C_2H_4CN$}Cu_2Cl_3] [6]. In the crystal structure of **I** the *L1*(H^+) cation is coordinated by two copper(I) atoms through the C=C-bond of an allyl group and an N atom of a nitrile group. As a result of the bridging function of the organic cations (they are coordinated by metal atoms from parallel inorganic chains) the structure consists of 2D coordination layers (Fig. 1). Two crystallographically independent Cu(I) atoms possess trigonal-pyramidal coordination environment: Cu(1) is surrounded by a C=C-bond and three Br atoms, Cu(2) by one N atom and three halogen atoms. In both cases the apical position of the metal coordination polyhedron is occupied by a halogen atom (Table 6). The infinite metal halide chain $(Cu_2Br_3)_n^{n-}$ of the compound is similar to those in the structure of the related complex [H^+(*diallylamin*)Cu_2Br_3] [14]. Bonds [15] (N)H…Br and (C)H…Br, formed by H atoms of the amino-group of *L1*(H^+), connect the polymeric coordination layers mentioned above into a 3D-framework (Table 7).

In the structure of **II**, the organic cation *L2*(H^+), which possesses two allyl groups, does

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

Atom	*x*	*y*	*z*	U_{iso}/U_{eq} [a]	Atom	*x*	*y*	*z*	U_{iso}/U_{eq} [a]
Cu(1)	0.77442(12)	0.26878(10)	0.85467(7)	0.0363(2)	H(1N)	−0.1206	0.0644	0.2407	0.037
Cu(2)	0.40281(13)	0.25313(10)	0.67075(7)	0.0416(2)	H(2N)	0.0706	0.1653	0.2709	0.037
Br(1)	0.65575(10)	0.49036(8)	0.71833(5)	0.03659(19)	H(2A)	−0.2555	0.3388	0.4702	0.041
Br(2)	1.14215(10)	0.24439(8)	0.83787(5)	0.03569(19)	H(2B)	−0.2529	0.1446	0.4387	0.041
Br(3)	0.60876(10)	0.00760(8)	0.72155(6)	0.0398(2)	H(3A)	−0.3110	0.2974	0.2656	0.037
N(1)	0.1767(11)	0.2456(8)	0.5443(5)	0.0489(15)	H(3B)	−0.1058	0.4092	0.2948	0.037
N(2)	−0.0570(8)	0.1686(6)	0.2356(4)	0.0310(11)	H(4A)	0.0115	0.3278	0.0997	0.039
C(1)	0.0180(11)	0.2494(8)	0.4971(5)	0.0377(16)	H(4B)	0.0513	0.1376	0.0714	0.039
C(2)	−0.1787(9)	0.2545(9)	0.4324(5)	0.0341(14)	H(51)	−0.2868	0.0820	0.0069	0.041
C(3)	−0.1720(9)	0.2962(7)	0.3020(5)	0.0305(13)	H(6A)	−0.3216	0.4296	0.0420	0.044
C(4)	−0.0433(9)	0.2109(8)	0.1056(5)	0.0325(14)	H(6B)	−0.4886	0.3009	−0.0310	0.044
C(5)	−0.2418(10)	0.1900(8)	0.0365(5)	0.0339(14)					
C(6)	−0.3634(10)	0.3204(8)	0.0134(5)	0.0366(15)					

[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 U_{iso} was set equal to $1.2U_{eq}$(C)

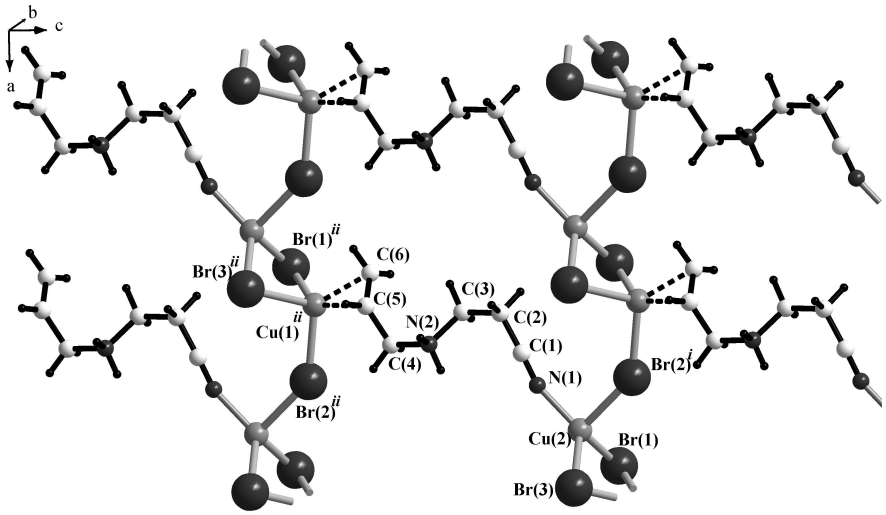

Fig. 1 Projection of the structure of [{$C_3H_5NH(H^+)C_2H_4CN$}Cu_2Br_3] (**I**).
Symmetry codes: (*i*) −1+*x*, *y*, *z*, (*ii*) −1+*x*, *y*, −1+*z*.

not demonstrate its multiple coordination possibilities (bridging or chelate behaviour is not present). It is coordinated to copper(I) by the C=C bond of only one allyl group. The nitrile group and the C=C bond from the other allyl radical do not take part in the metal coordination (Fig. 2). The copper atom possesses trigonal pyramidal coordination, formed by one C=C bond and three halogen atoms. The distance Cu–(C=C) is 1.945(5) Å, d(Cu–X_{ap})= 2.8505(10) Å; the distances Cu–X are 2.2549(9) and 2.2853(10) Å, the angles X–Cu–X/X–Cu–*m* are in the range 92-101° (Table 8). Due to the bridging role of the halogen atoms, copper(I) halide units are connected into polymeric $(CuX_2)_n^{n-}$ chains, which are orientated along the *b*-axis. π-coordinated monodentate cations *L2*(H^+) are attached to the anionic copper(I) halide fragments, forming 1D coordination polymers. A branched system of H-bonds [16,17] connects the separate "chains" into a framework (Fig. 3).

In the case of compound **III**, the organic ligand

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	0.52101(4)	0.05441(7)	0.36225(3)	0.02458(18)
X(1) [b]	0.71705(7)	0.07566(13)	0.40437(7)	0.0295(3)
X(2) [b]	0.47908(7)	−0.24784(13)	0.30748(6)	0.0249(3)
N(1)	0.1219(4)	0.0584(6)	−0.0842(3)	0.0432(10)
N(2)	0.2429(3)	−0.0285(5)	0.2454(2)	0.0207(6)
C(1)	0.1785(4)	0.0620(6)	−0.0123(3)	0.0287(9)
C(2)	0.2490(3)	0.0640(6)	0.0816(3)	0.0246(8)
C(3)	0.1720(3)	0.0005(6)	0.1494(3)	0.0232(7)
C(4)	0.2723(3)	0.1597(6)	0.2944(3)	0.0212(7)
C(5)	0.3588(3)	0.1424(6)	0.3840(2)	0.0225(7)
C(6)	0.4403(3)	0.2789(6)	0.4142(3)	0.0266(8)
C(7)	0.1791(3)	−0.1650(6)	0.3002(3)	0.0255(8)
C(8)	0.0598(3)	−0.0950(6)	0.3063(3)	0.0293(9)
C(9)	0.0306(4)	−0.0496(8)	0.3855(3)	0.0392(11)
H(1N)	0.311(4)	−0.093(7)	0.242(3)	0.030(12)
H(2A)	0.309(4)	−0.028(7)	0.079(3)	0.036(13)
H(2B)	0.273(4)	0.196(8)	0.090(3)	0.038(13)
H(3A)	0.110(4)	0.090(6)	0.153(3)	0.025(11)
H(3B)	0.139(4)	−0.117(7)	0.130(3)	0.020(10)
H(4A)	0.299(4)	0.235(7)	0.257(3)	0.023(11)
H(4B)	0.199(4)	0.206(6)	0.305(3)	0.021(10)
H(51)	0.345(4)	0.058(7)	0.430(4)	0.038(13)
H(6A)	0.446(3)	0.387(6)	0.385(3)	0.014(9)
H(6B)	0.480(5)	0.285(8)	0.476(4)	0.053(16)
H(7A)	0.179(4)	−0.284(7)	0.267(3)	0.023(11)
H(7B)	0.228(4)	−0.184(7)	0.360(3)	0.028(11)
H(81)	0.007(5)	−0.094(7)	0.252(4)	0.035(12)
H(9A)	−0.050(5)	−0.013(9)	0.391(4)	0.057(16)
H(9B)	0.087(5)	−0.058(8)	0.446(4)	0.055(17)

[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 U_{iso} was set equal to $1.2U_{eq}$(C).

[b] X(1) ≡ (0.959(4)Cl+0.041(4)Br); X(2) ≡ (0.979(4)Cl+0.021(4)Br).

Table 4 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **III**.

Atom	*x*	*y*	*z*	U_{iso}/U_{eq} [a]	Occ. (<1)
Cu	0.24472(4)	0.34383(4)	0.162448(17)	0.03562(9)	
Cl(1)	0	0.34116(9)	¼	0.02612(13)	
Cl(2)	0.29078(7)	0.05214(7)	0.13757(3)	0.03635(13)	
Cl(31)	½	0.478(3)	¼	0.032(2)	0.45(5)
Cl(3)	0.4868(8)	0.4402(10)	0.2698(9)	0.0202(12)	0.27(3)
O(1)	0.3907(3)	1.2914(3)	−0.08896(15)	0.0361(7)	0.661(3)
O(11)	0.4111(6)	1.2922(6)	−0.1273(3)	0.0261(10)	0.339(3)
N(1)	0.2254(7)	0.5114(7)	0.0612(3)	0.0306(10)	0.661(3)
N(11)	0.2019(14)	0.5033(11)	0.0861(5)	0.0256(16)	0.339(3)
N(2)	0.2696(5)	0.9585(4)	−0.1535(2)	0.0233(7)	0.661(3)
N(21)	0.3093(10)	0.9259(7)	−0.1307(4)	0.0231(15)	0.339(3)
C(1)	0.2611(4)	0.5950(4)	0.0056(2)	0.0284(7)	0.661(3)
C(11)	0.1830(7)	0.6083(7)	0.0349(3)	0.0202(11)	0.339(3)
C(2)	0.3144(5)	0.6941(4)	−0.0670(2)	0.0306(7)	0.661(3)
C(21)	0.1578(6)	0.7415(7)	−0.0317(3)	0.0227(11)	0.339(3)
C(3)	0.2209(4)	0.8711(3)	−0.07497(17)	0.0242(6)	0.661(3)
C(31)	0.3376(6)	0.8020(7)	−0.0589(3)	0.0215(11)	0.339(3)
C(4)	0.1672(4)	1.1232(4)	−0.1740(2)	0.0301(7)	0.661(3)
C(41)	0.1879(7)	1.0758(6)	−0.1150(3)	0.0241(12)	0.339(3)
C(5)	0.2037(3)	1.2597(3)	−0.10632(15)	0.0356(8)	0.661(3)
C(51)	0.2385(6)	1.2365(6)	−0.1621(3)	0.0261(12)	0.339(3)
H(1O)	0.4318	1.3326	−0.1323	0.054	0.661(3)
H(11O)	0.4547	1.3618	−0.1609	0.039	0.339(3)
H(2A)	0.2836	0.6260	−0.1194	0.037	0.661(3)
H(21A)	0.0927	0.8429	−0.0105	0.027	0.339(3)
H(2B)	0.4466	0.7119	−0.0605	0.037	0.661(3)
H(21B)	0.0835	0.6925	−0.0811	0.027	0.339(3)
H(3A)	0.0887	0.8552	−0.0776	0.029	0.661(3)
H(31A)	0.4082	0.8598	−0.0107	0.026	0.339(3)
H(3B)	0.2594	0.9444	−0.0251	0.029	0.661(3)
H(31B)	0.4070	0.6996	−0.0760	0.026	0.339(3)
H(4A)	0.0366	1.0968	−0.1808	0.036	0.661(3)
H(41A)	0.1962	1.1013	−0.0536	0.029	0.339(3)
H(4B)	0.2011	1.1701	−0.2285	0.036	0.661(3)
H(41B)	0.0616	1.0434	−0.1335	0.029	0.339(3)
H(5A)	0.1423	1.3700	−0.1249	0.043	0.661(3)
H(51A)	0.2411	1.2094	−0.2230	0.031	0.339(3)
H(5B)	0.1536	1.2202	−0.0539	0.043	0.661(3)
H(51B)	0.1488	1.3303	−0.1565	0.031	0.339(3)
H(1N)	0.2488	0.8820	−0.1981	0.028	0.661(3)
H(11N)	0.2611	0.8659	−0.1778	0.028	0.339(3)
H(2N)	0.3908	0.9837	−0.1475	0.028	0.661(3)
H(21N)	0.4193	0.9695	−0.1424	0.028	0.339(3)

[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 U_{iso} was set equal to $1.2U_{eq}$(C).

Table 5 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **IV**.

Atom	*x*	*y*	*z*	U_{iso}/U_{eq} [a]	Atom	*x*	*y*	*z*	U_{iso}
Cu	0.52517(18)	0.43239(3)	0.364852(12)	0.01384(6)	H(1N)	0.3039	0.5749	0.2568	0.017
Cl(1)	0.47769(3)	0.72819(5)	0.30685(2)	0.01212(8)	H(1O)	−0.0974	0.4833	0.3304	0.036
Cl(2)	0.73163(3)	0.41169(5)	0.40078(2)	0.01387(8)	H(2A)	0.3081	0.5117	0.1150	0.021
N(1)	0.11676(6)	0.45738(10)	−0.05489(4)	0.0270(3)	H(2B)	0.2607	0.2967	0.1213	0.021
N(2)	0.22811(6)	0.51147(10)	0.27420(4)	0.0136(2)	H(3A)	0.1123	0.6147	0.1640	0.018
O(1)	−0.03711(6)	0.52958(10)	0.30821(4)	0.0243(3)	H(3B)	0.0872	0.3952	0.1859	0.018
C(1)	0.16764(6)	0.44684(10)	0.01764(4)	0.0181(3)	H(4A)	0.1929	0.2507	0.3311	0.017
C(2)	0.23406(6)	0.43026(10)	0.10990(4)	0.0171(3)	H(4B)	0.3015	0.2412	0.2682	0.017
C(3)	0.15211(15)	0.4915(2)	0.18215(10)	0.0153(3)	H(51)	0.3549	0.4424	0.4382	0.016
C(4)	0.26624(15)	0.3183(2)	0.31495(10)	0.0138(3)	H(6A)	0.4534	0.0927	0.3844	0.019
C(5)	0.35867(14)	0.3348(2)	0.39929(10)	0.0130(3)	H(6B)	0.5046	0.2175	0.4763	0.019
C(6)	0.44797(15)	0.2014(2)	0.42238(10)	0.0158(3)	H(7A)	0.2322	0.6759	0.3905	0.020
C(7)	0.16907(11)	0.63981(16)	0.33922(8)	0.0165(3)	H(7B)	0.1420	0.7581	0.3059	0.020
C(8)	0.06107(11)	0.55665(16)	0.37940(8)	0.0184(3)	H(8A)	0.0843	0.4332	0.4093	0.022
					H(8B)	0.0355	0.6440	0.4265	0.022

[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 U_{iso} was set equal to $1.2U_{eq}$(C).

Table 6 Selected bond lengths and angles in the structures of **I**.

Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
Cu(1)−m^a	2.019(8)	Cu(2)−Br(1)−Cu(1)	77.46(3)	Br(3)−Cu(2)	2.4735(10)	N(1)−Cu(2)−Br(1)	126.61(19)
Br(2)−Cu(2)^{ib}	2.6327(10)	Cu(1)−Br(2)−Cu(2)^i	138.55(4)	Cu(2)−N(1)	1.970(7)	N(1)−Cu(2)−Br(3)	123.58(18)
Cu(1)−C(6)^{ii}	2.107(6)	Cu(2)−Br(3)−Cu(1)	73.39(3)	N(1)−C(1)	1.133(9)	Br(1)−Cu(2)−Br(3)	100.94(4)
Cu(1)−C(5)^{ii}	2.150(6)	C(6)^{ii}−Cu(1)−C(5)^{ii}	37.1(2)	N(2)−C(4)	1.510(6)	N(1)−Cu(2)−Br(2)^{iii}	91.33(17)
Br(1)−Cu(1)	2.4583(10)	C(6)^{ii}−Cu(1)−Br(2)	125.56(18)	C(4)−C(5)	1.461(8)	Br(1)−Cu(2)−Br(2)^{iii}	107.71(4)
Br(2)−Cu(1)	2.4508(11)	C(5)^{ii}−Cu(1)−Br(2)	98.80(17)	C(5)=C(6)	1.354(8)	Br(3)−Cu(2)−Br(2)^{iii}	102.25(4)
Br(3)−Cu(1)	2.6500(10)	C(6)^{ii}−Cu(1)−Br(1)	103.75(17)	N(2)−C(3)	1.516(7)	C(4)−N(2)−C(3)	112.9(4)
Br(1)−Cu(2)	2.4401(11)	C(5)^{ii}−Cu(1)−Br(1)	140.69(16)	C(2)−C(3)	1.510(7)	N(1)−C(1)−C(2)	177.5(7)
		Br(2)−Cu(1)−Br(1)	108.62(4)	C(1)−C(2)	1.433(9)	C(1)−C(2)−C(3)	114.8(5)
		C(6)^{ii}−Cu(1)−Br(3)	116.79(19)			C(5)−C(4)−N(2)	112.7(5)
		C(5)^{ii}−Cu(1)−Br(3)	105.54(16)			C(6)−C(5)−C(4)	123.1(6)
		Br(2)−Cu(1)−Br(3)	102.26(3)			N(2)−C(3)−C(2)	112.0(5)
		Br(1)−Cu(1)−Br(3)	95.72(3)				

[a] *m* – middle point of the C(5)=C(6) bond.
[b] Symmetry codes: (*i*) *x*+1, *y*, *z*; (*ii*) *x*+1, *y*, *z*+1; (*iii*) *x*−1, *y*, *z*.

L3(H$^+$) (being disordered) exhibits a monodentate behaviour. It is coordinated to the Cu(I) atom by only the N atom of a CN group, whereas the hydroxyl group stays uncoordinated (Fig. 4). The crystal structure contains infinite inorganic chains $(CuCl_2)_n^{n-}$. In contrast to the structure of **I**, it possesses only one independent copper(I) atom, which has a distorted tetrahedral coordination with one nitrogen and three chlorine atoms. The distance Cu–N is 2.049(4) Å, *d*(Cu–Cl) = 2.2952(8), 2.3949(8) and 2.473(5) Å, the angles Cl–Cu–Cl are in the range 103.1-114.3(4)°, Cl–Cu–N 101.3-125.8° (Table 9). The cations *L3(H$^+$)* are attached to an anionic chain on one side of the plane formed by Cu atoms. One-dimensional coordination polymers are combined into a framework by weak H bonds.

Modification of 3-({2-hydroxyethyl}amino) propanenitrile by adding an allyl group has given one more coordination centre, but in the structure of **IV** 3-({2-hydroxyethyl}allylamino)propanenitrile also behaves as a monodentate ligand, although in this case it is attached to Cu(I) by the C=C bond of an allyl group (not the N atom of a CN group, Fig. 5).The metal atom has trigonal pyramidal coordination formed by one C=C bond and three chlorine atoms. The distance Cu–(C=C) is 1.9505(5) Å, d(Cu–Cl_{ap}) = 2.892(5) Å; the other Cu–Cl contacts are 2.2786(7) and 2.2715(8) Å, the angles Cl–Cu–Cl/Cl–Cu–m are in the range 94.1-126.3° (Table 10). In spite of the differences in the coordination behaviour of *L2(H$^+$)*, *L3(H$^+$)* and *L4(H$^+$)*, the structure of **IV**, as well as **II** and **III,** contains an infinite inorganic anion $(CuCl_2)_n^{n-}$. The structures of the complexes **II** and **IV** are isotopological: one-dimensional structural fragments with branched organic "attachments" are interconnected by hydrogen bonds and weak intermolecular interactions (Fig. 6).

Some similarities and differences can thus be emphasized. In spite of the different coordination behaviour of *L1(H$^+$)* and *L3(H$^+$)* in the crystal structures of compounds **I** and **III**, the nitrile groups of the organic ligands that have only one substituent at the nitrogen atom of the amino-group, are coordinated by copper(I) atoms. In the case of **II** and **IV,** where the organic ligands possess two substituents

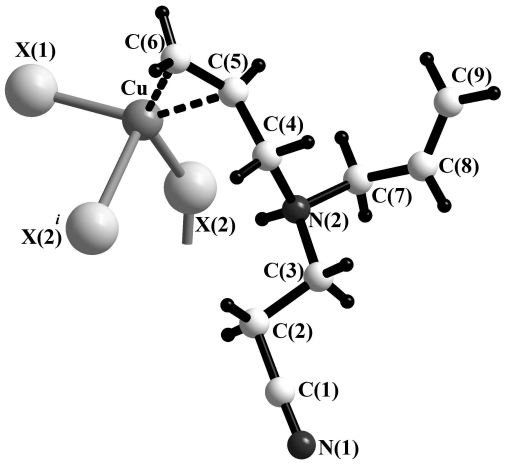

Fig. 2 Fragment of the structure of [{$(C_3H_5)_2$N(H^+)C_2H_4CN}$CuCl_{1.94}Br_{0.06}$] (**II**).

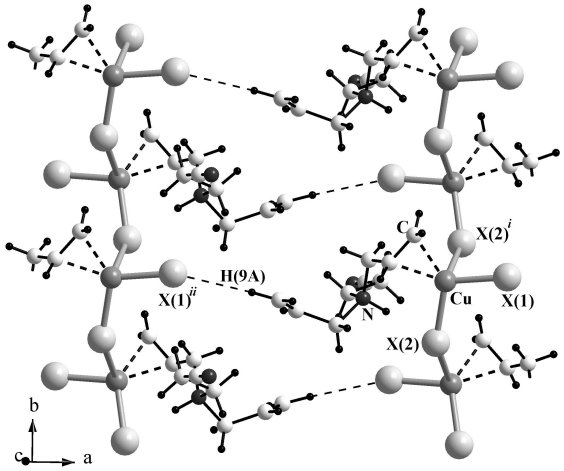

Fig. 3 Projection of the structure of [{$(C_3H_5)_2$N(H^+)C_2H_4CN}$CuCl_{1.94}Br_{0.06}$] (**II**) X – Hal.
Symmetry codes: (*i*) 1 −*x*, 1/2+*y*, 1/2−*z*; (*ii*) −1+*x*, *y*, *z*.

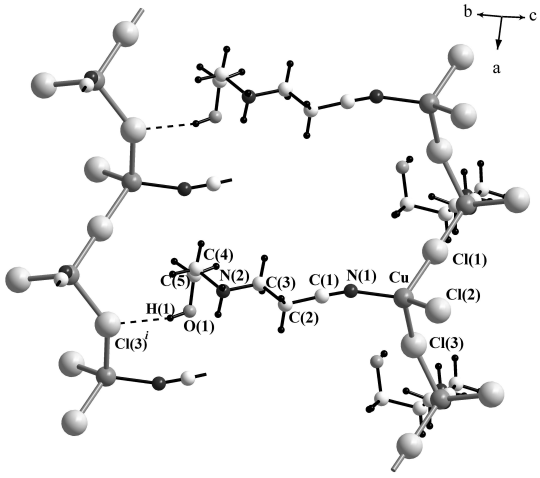

Fig. 4 Fragment of the structure of [$(HOC_2H_5NH(H^+)C_2H_4CN)CuCl_2$] (**III**).
Symmetry code: (*i*) *x*, 2−*y*, −1/2+*z*.

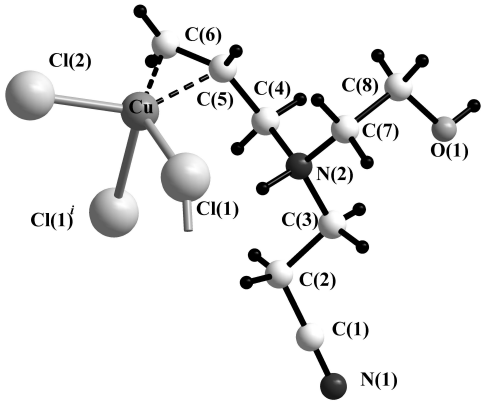

Fig. 5 Fragment of the structure of [{$HOC_2H_4(C_3H_5)N(H^+)C_2H_4CN$}$CuCl_2$] (**IV**).
Symmetry code: (*i*) 1 −*x*, −1/2+*y*, 1/2−*z*

at the nitrogen atom, the copper(I) atom does not coordinate the CN group, which is not typical for nitriles. The anomalous inactivity of the Cu(I) atom to the nitrile group of N-derivatives of propanenitrile disappears in the case of ionic salts of copper(I) [18]. Similarities in the crystal packing of **II** and **IV** show that the character of uncoordinated groups at the N atom has no principal significance in the structure topology, although the presence of the 2-hydroxyethyl substituent leads to the formation of a more complicated system of hydrogen bonds.

Table 7 Geometry of selected H-contacts in the structures of **I-IV**.

No.	Contact *D*–H…*A*	Bond length, Å			Angle *D*–H…*A*, deg	Atom coordinates of *A*
		D–H	H…A	D…A		
I	N(2)–H(1N)···Br(2)	0.90	2.57	3.343(2)	145	2-*x*, –*y*, –*z*
	N(2)–H(2N)···Br(3)	0.90	2.57	3.332(3)	143	2-*x*, –*y*, –*z*
	C(3)–H(3A)···Br(1)	0.97	2.91	3.674(5)	137	1-*x*, 1–*y*, –*z*
II	C(9)–H(9A) ··X(1)[a]	0.99	2.83	3.818(5)	178	*x*–1, *y*, *z*
	C(4)–H(4B)···N(1)	0.95	2.59	3.367(5)	139	*x*, –*y*+1/2, *z*+1/2
	C(5)–H(51)···X(1)[a]	0.93	2.83	3.716(4)	160	–*x*+1, –*y*, –*z*+1
III	N(2)–H(1N)···Cl(1)	0.92	2.60	3.323(4)	136	–*x*, -*y*+1, -*z*
	N(2)–H(2N)···Cl(2)	0.92	2.38	3.263(4)	161	-*x*+1, -*y*+1, -*z*
	C(3)–H(3B)···Cl(2)	0.99	2.70	3.637(3)	159	*x*, *y*+1, *z*
IV	N(2)–H(1N)···Cl(1)	1.01	2.24	3.123(2)	146	*x*, *y*, *z*
	O(1)–H(1O)···Cl(2)	0.84	2.31	3.140(3)	170	*x*-1, *y*, *z*
	C(4)–H(4A)···N(1)	0.99	2.44	3.297(9)	144	*x*, -*y*+1/2, *z*+1/2
	C(5)–H(51)···Cl(2)	0.95	2.84	3.669(8)	146	-*x*+1, -*y*+1, *z*+1
	C(6)–H(6A)···Cl(1)	0.95	2.83	3.760(9)	168	*x*, *y*-1, *z*
	C(2)–H(2B)···Cl(2)	0.99	2.72	3.664(6)	159	-*x*+1, *y*-1/2, -*z*+1/2

[a] X = Cl / Br.

Table 8 Selected bond lengths and angles in the structure of **II**.

Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
Cu−C(6)	2.053(4)	C(6)−Cu−C(5)	38.54(16)	N(2)−C(7)	1.532(5)	C(4)−N(2)−C(7)	112.5(3)
Cu−C(5)	2.070(3)	C(6)−Cu−X(1)	111.06(12)	C(1)−C(2)	1.463(5)	N(1)−C(1)−C(2)	178.4(4)
Cu−*m* [a]	1.945(5)	C(5)−Cu−X(1)	147.68(11)	C(2)−C(3)	1.527(5)	C(1)−C(2)−C(3)	108.5(3)
Cu−X(1) [b]	2.2549(9)	C(6)−Cu−X(2)	139.33(12)	C(4)−C(5)	1.502(5)	N(2)−C(3)−C(2)	111.3(3)
Cu−X(2) [b]	2.2853(10)	C(5)−Cu−X(2)	100.96(11)	C(5)=C(6)	1.361(6)	C(6)−C(5)−C(4)	122.6(4)
Cu−X(2)^{i} [c]	2.8505(10)	X(1)−Cu−X(2)	107.18(4)	C(7)−C(8)	1.492(5)	C(6)−C(5)−Cu	70.1(2)
N(1)−C(1)	1.134(5)	C(6)−Cu−X(2)^{i}	91.62(12)	C(8)=C(9)	1.311(6)	C(4)−C(5)−Cu	111.7(2)
N(2)−C(3)	1.504(5)	C(5)−Cu−X(2)^{i}	98.13(11)			C(5)−C(6)−Cu	71.4(2)
N(2)−C(4)	1.511(5)	X(1)−Cu−X(2)^{i}	92.26(3)			C(8)−C(7)−N(2)	112.1(3)
		X(2)−Cu−X(2)^{i}	100.30(2)			C(9)−C(8)−C(7)	122.3(4)
		C(3)−N(2)−C(4)	111.2(3)			C(5)−C(4)−N(2)	113.6(3)
		C(3)−N(2)−C(7)	110.0(3)				

[a] *m* – middle point of the C(8)=C(9) bond.
[b] X(1) ≡ (0.959(4)Cl+0.041(4)Br); X(2) ≡ (0.979(4)Cl+0.021(4)Br).
[c] Symmetry code: (*i*) −*x*+1, *y*+1/2, −*z*+1/2.

Table 9 Selected bond lengths and angles in the structure of **III**.

Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
Cu–N(1)	2.049(4)	N(1)–Cu–Cl(2)	118.22(16)	C(3)–N(2)	1.488(4)	N(2)–C(4)–C(5)	112.1(3)
Cu–N(11)	1.727(6)	N(11)–Cu–Cl(2)	125.8(3)	N(2)–C(4)	1.491(4)	N(1)–C(1)–C(2)	176.6(4)
Cu–Cl(2)	2.2952(8)	Cl(2)–Cu–Cl(3)^{i}	104.7(2)	C(4)–C(5)	1.503(3)	C(1)–C(2)–C(3)	111.7(3)
Cu–Cl(3)$^{i\,a}$	2.301(5)	N(1)–Cu–Cl(3)^{i}	99.2(3)	C(5)–O(1)	1.4153	N(2)–C(3)–C(2)	108.8(2)
Cu–Cl(1)	2.3949(8)	N(11)–Cu–Cl(3)^{i}	101.3(4)	N(11)–C(11)	1.141(5)	O(1)–C(5)–C(4)	111.46(15)
Cu–Cl(3)	2.473(5)	N(1)–Cu–Cl(1)	117.34(12)	C(11)–C(21)	1.466(5)	C(11)–N(11)–Cu	176.4(8)
Cu–Cl(31)	2.470(11)	N(11)–Cu–Cl(1)	108.2(3)	C(21)–C(31)	1.518(5)	N(11)–C(11)–C(21)	179.2(8)
Cl(3)–Cl(3)^{i}	0.68(3)	Cl(2)–Cu–Cl(1)	103.06(2)	C(31)–N(21)	1.481(5)	C(11)–C(21)–C(31)	111.1(4)
Cl(31)–Cl(3)^{i}	0.444(5)	Cl(3)^{i}–Cu–Cl(1)	114.1(4)	N(21)–C(41)	1.495(5)	N(21)–C(31)–C(21)	110.4(4)
N(1)–C(1)	1.141(4)	N(11)–Cu–Cl(31)	100.6(6)	C(41)–C(51)	1.505(5)	C(31)–N(21)–C(41)	114.0(4)
C(1)–C(2)	1.464(4)	N(1)–Cu–Cl(31)	100.1(5)	C(51)–O(11)	1.417(4)	N(21)–C(41)–C(51)	111.0(4)
C(2)–C(3)	1.521(4)	C(1)–N(1)–Cu	162.2(4)			O(11)–C(51)–C(41)	108.2(4)

[a] Symmetry codes: (*i*) −*x*+1, *y*, −*z*+1/2, (*ii*) −*x*, *y*, −*z*+1/2.

Table 10 Selected bond lengths and angles in the structures of **IV**.

Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
Cu−C(6)	2.0585(16)	C(6)−Cu−C(5)	38.66(6)	N(2)−C(7)	1.5151(13)	C(4)−N(2)−C(7)	113.72(8)
Cu−C(5)	2.0755(16)	C(6)−Cu−Cl(1)	141.55(5)	N(2)−C(3)	1.5019(17)	N(1)−C(1)−C(2)	178.9(4)
Cu−*m*^{a}	1.9505(5)	C(5)−Cu−Cl(1)	102.90(5)	C(8)−O(1)	1.4174(15)	C(1)−C(2)−C(3)	110.33(7)
Cu−Cl(1)	2.2786(7)	C(6)−Cu−Cl(2)	107.84(5)	C(2)−C(3)	1.5353(18)	N(2)−C(3)−C(2)	109.66(11)
Cu−Cl(2)	2.2715(8)	C(5)−Cu−Cl(2)	144.07(4)	C(1)−C(2)	1.459(5)	C(6)=C(5)−C(4)	122.76(14)
C(4)−C(5)	1.503(2)	Cl(1)−Cu−Cl(2)	108.69(18)	N(1)−C(1)	1.140(6)	C(6)=C(5)−Cu	70.00(9)
C(5)=C(6)	1.369(2)	C(5)−C(4)−N(2)	112.29(11)	C(7)−C(8)	1.508(5)	C(4)−C(5)−Cu	110.62(10)
N(2)−C(4)	1.5191(17)	C(3)−N(2)−C(4)	111.42(9)			C(5)=C(6)−Cu	71.34(6)
		C(3)−N(2)−C(7)	112.70(9)			C(8)−C(7)−N(2)	115.86(6)
						O(1)−C(8)−C(7)	109.25(6)

[a] *m* – middle point of the C(5)=C(6) bond.

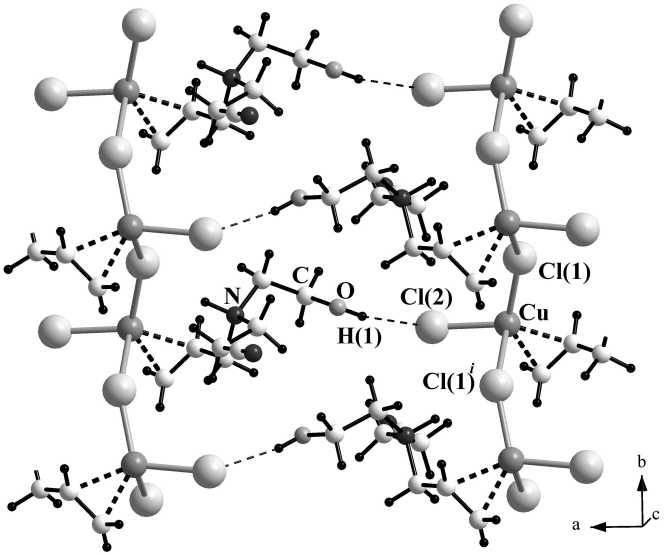

Fig. 6 Projection of the structure of [{$HOC_2H_4(C_3H_5)N(H^+)C_2H_4CN$}$CuCl_2$] (**IV**).
Symmetry code: (*i*) 1 −*x*, −1/2+*y*, 1/2−*z*.

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