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Copper(I) π-Complexes with 2-Butyne-1,4-diol. Synthesis and Crystal Structure of (2-AmpH)[$CuCl_2(HOCH_2C{\equiv}CCH_2OH)$] (2-AmpH$^+$ is 2-Aminopyridinium Cation)

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Abstract—Crystals of the π-complex (2-AmpH)[$CuCl_2(HOCH_2C{\equiv}CCH_2OH)$] (2-AmpH$^+$ is the 2-aminopyridinium cation) were obtained by the reaction of 2-butyne-1,4-diol with CuCl in aqueous 2-aminopyridinium chloride solution and studied by X-ray diffraction: space group $P\bar{1}$, $a = 7.172(4)$, $b = 7.796(3)$, $c = 11.60(9)$ Å, $\alpha = 99.75(6)°$, $\beta = 96.53(7)°$, $\gamma = 101.03(3)°$, $Z = 2$. The crystals consist of individual anions [$CuCl_2(HOCH_2C{\equiv}CCH_2OH)$]$^-$ and cations [2-AmpH]$^+$. The π-coordinated Cu(I) atoms of the complex anion have trigonal-planar surrounding of two chlorine atoms and C≡C bond of the 2-butyne-1,4-diol molecule. The alcohol groups form stable hydrogen bonds N–H···O (1.89 Å) and O–H···Cl (2.20 Å).

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In many processes of alkyne transformations catalyzed by copper(I) salts [1, 2], the π-complexes of Cu(I) with disubstituted alkynes are formed as intermediates [3]. The systematic study of their structures is the necessary step of elucidation of the mechanism of cuprocatalytic processes.

The previous study of the π-complex formation of Cu(I) halides with 2-butyne-1,4-diol, $HOCH_2C{\equiv}CCH_2OH$ (**L**), in aqueous CuCl and MCl solutions (M$^+$ is cation of the alkali metals, ammonium, and organic amines) using the formation of the anionic π-complexes K[$CuBr_2$(L)] [4], K[$CuCl_2$(L)] and NH_4[$CuCl_2$(L)] [5], Rb[$CuCl_2$(L)] (modifications A and B) [6], Cs[$CuCl_2$(L)] · H_2O [7], and (ImH)[$CuCl_2$(L)] (**II**) (ImH$^+$ is the imidazolinium cation) [8] as examples, showed that the efficiency of π-bonding Cu(I)–(C≡C) and the formation of the Cu(I) anionic π-complexes with 2-butyne-1,4-diol is predetermined by capability of the outer-sphere M$^+$ cation to realize the target cation–anion interaction.

It was of interest to study the structure-forming function of 2-aminopyridinium chloride in the process of the π-complex formation of CuCl with 2-butyne-1,4-diol. With this aim in view, we obtained and studied by X-ray diffraction the crystals of the anionic π-complex (2-AmpH)[$CuCl_2$(L)] (**I**) in the system (2-AmpH)Cl-CuCl-L-H_2O (2-AmpH$^+$ is the cation of 2-aminopyridinium ($C_5N_2H_7^+$)).

EXPERIMENTAL

Synthesis. Crystals of the π-complex I were obtained by interaction of Cu(I) chloride with 2-butyne-1,4-diol in aqueous 2-aminopyridinium chloride solution. The saturated aqueous solution of 2-aminopyridinium (0.9 g, 0.01 mol) titrated with HCl to pH ~3 was prepared and then, CuCl (1.0 g, 0.01 mol) and $HOCH_2C{\equiv}CCH_2OH$ (0.9 g, 0.01 mol) were added at ~90°C. On slow cooling to room temperature, colorless crystals of complex I were formed.

X-ray diffraction analysis of the crystals, preliminarily studied by the photomethod, was performed on a DARCh single-crystal automated diffractometer (MoK_α radiation, $\theta/2\theta$ scan mode). The crystal parameters, the summary of data collection and crystallographic characteristics of complex I are listed in Table 1.

The structure of the complex was solved by the direct methods with the CSD program package [9]; After localization and refinement of all non-hydrogen atoms by the least-squares method in isotropic approximation, the absorption correction was applied with the DIFABS program. The hydrogen atoms were located geometrically. For non-hydrogen atoms, the final structure refinement was performed in anisotropic variant. The positional parameters of the H atoms were not refined, the temperature factor was refined as a group parameter. The atomic coordinates and their thermal parameters are given in Table 2.

Table 1. The crystallographic parameters and summary of data collection for single crystal of $(C_5NH_5NH_2)[CuCl_2(C_4H_6O_2)]$

Parameter	Value
M	315.66
T, K	293
Space group	$P\bar{1}$
Unit cell parameters:	
a, Å	7.172(4)
b, Å	7.796(3)
c, Å	11.60(9)
α, deg	99.75(6)
β, deg	96.53(7)
γ, deg	101.03(3)
V, Å^3	620(6)
$\mu(MoK_\alpha)$, cm^{-1}	22.39
ρ(exp), g/cm^3	1.65(2)
ρ(calcd.), g/cm^3	1.67(2)
Z	2
Crystal size, mm	0.2 × 0.3 × 0.4
$F(000)$	313.0
$2\theta_{max}$, deg	57.00
Number of independent reflections	2536
Number of independent reflections with $\|F \geq 4\sigma(F)\|$*	2027
Weighting scheme (w)	$[\sigma(F_o)^2 + 0.0037\sigma(F_o)^2]^{-1}$
R	0.0425
R_w	0.0540

* With correction for Lorentz and polarization factor.

Table 2. The atomic coordinates and thermal parameters in structure I*

Atom	x	y	z	U_{eq}, Å^2
Cu	0.20478(6)	0.41330(5)	0.40879(4)	0.0415(2)
Cl(1)	0.2009(2)	0.52647(1)	0.24239(8)	0.0525(3)
Cl(2)	0.13808(2)	0.11633(1)	0.35554(9)	0.0525(3)
O(1)	0.4241(5)	0.9224(4)	0.6404(3)	0.060(1)
O(2)	0.3478(7)	0.4119(5)	0.7751(3)	0.086(2)
N(1)	0.2277(5)	0.0625(4)	0.0874(3)	0.046(1)
N(2)	0.2970(6)	0.3066(5)	–0.0023(3)	0.058(1)
C(1)	0.3216(6)	0.8054(5)	0.5359(4)	0.048(1)
C(2)	0.2821(5)	0.6163(4)	0.5492(3)	0.039(1)
C(3)	0.2593(5)	0.4779(5)	0.5863(3)	0.039(1)
C(4)	0.2478(6)	0.3409(5)	0.6613(3)	0.047(1)
C(5)	0.2699(5)	0.1297(5)	–0.0088(3)	0.041(1)
C(6)	0.2831(5)	0.0128(5)	–0.1110(3)	0.044(1)
C(7)	0.2528(6)	–0.1646(5)	–0.1123(4)	0.052(1)
C(8)	0.2116(7)	–0.2309(5)	–0.0121(4)	0.059(2)
C(9)	0.2001(6)	–0.1168(5)	0.0864(4)	0.053(1)
H(1)	0.551	0.889	0.660	
H(2)	0.492	0.456	0.768	
H(3)	0.200	0.842	0.517	
H(4)	0.398	0.818	0.470	
H(5)	0.109	0.298	0.670	
H(6)	0.297	0.239	0.623	
H(7)	0.217	0.145	0.162	
H(8)	0.287	0.387	0.073	
H(9)	0.329	0.360	–0.073	
H(10)	0.316	0.060	–0.183	
H(11)	0.260	–0.248	–0.186	
H(12)	0.190	–0.362	–0.013	
H(13)	0.170	–0.162	0.159	

* For non-hydrogen atoms $U_{eq} = 1/3\sum_i\sum_j U_{ij}a_i^*a_j^*(\vec{a}_i\vec{a}_j)$, for H atoms, $U_{iso(total)} = 0.102$ Å^2.

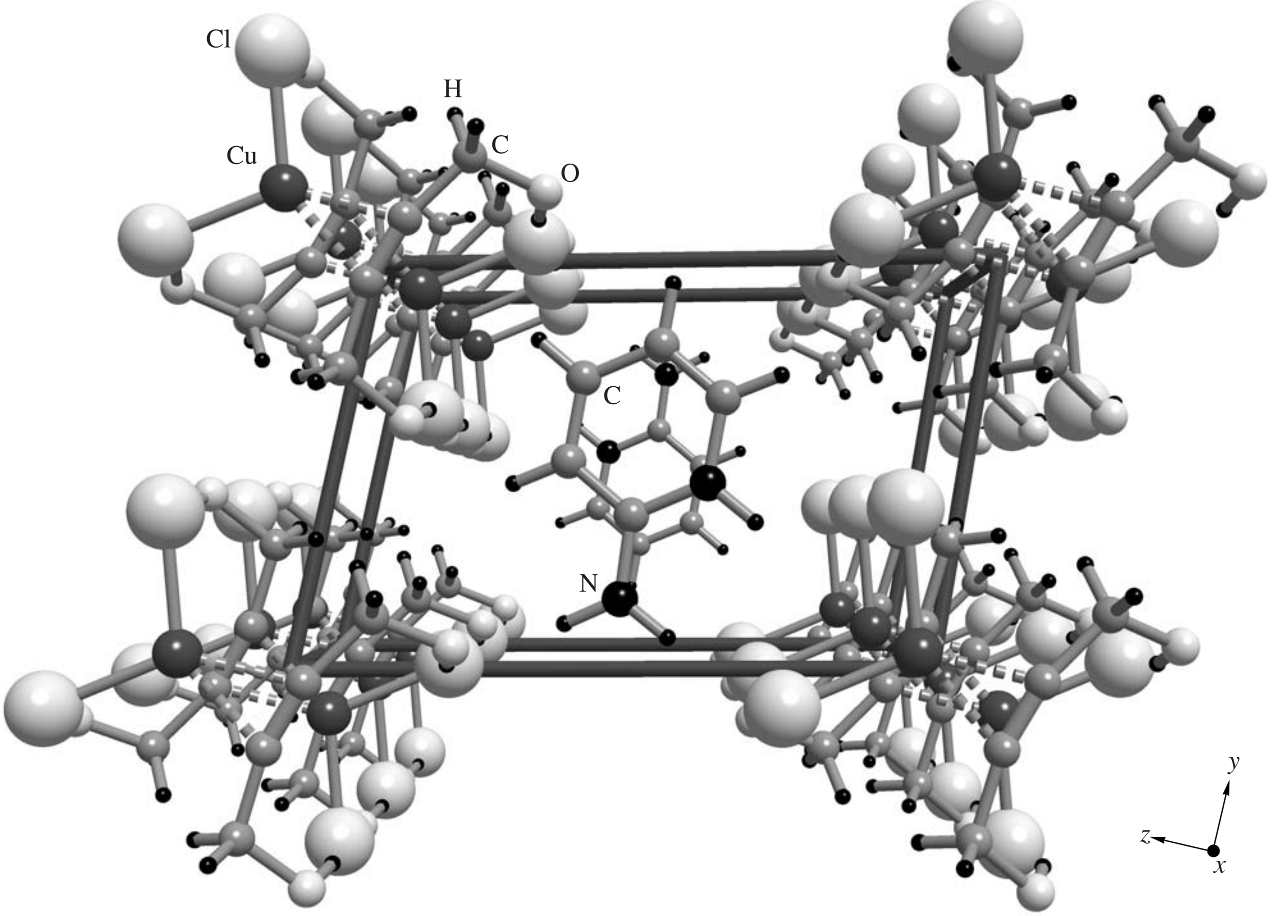

Fig. 1. The structure of π-complex I.

RESULTS AND DISCUSSION

The structure of π-complex I (Fig. 1) is similar to the structure of previously studied complex II consisting of individual complex anions $[CuCl_2(HOCH_2C{\equiv}CCH_2OH)]^-$ and the 2-aminopyridinium cations located in a free space between the anions. Despite the presence of three functional groups (the C≡C bonds and two alcohol groups at the opposite sides of a molecule) in 2-butyne-1,4-diol, the Cu(I) atom in the complex anion is coordinated with a ligand molecule particularly at the C≡C bond. In addition to the ethynyl group, the metal atom is bonded also with two Cl atoms thus completing its coordination number to three (Fig. 2).

As a result of the π-bonding Cu–(C≡C) in complex I, the geometry of the $HOCH_2C{\equiv}CCH_2OH$ molecule is slightly changed as compared to a free molecule of 2-butyne-1,4-diol [10] and the chekered arrangement of the methoxyl groups $–CH_2OH$ about triple bond changes to "eclipsed" arrangement. In this case, the bond angles C(1)–C(2)≡C(3) and C(4)–C(3)≡C(2) decrease to 165.6(4)° and 165.3(5)°, respectively (as compared to a straight angle typical of noncoordinated molecule of 2-butyne-1,4-diol), whereas the C(2)≡C(3) bond π-coordinated at the metal center is elongated to 1.22(2) Å (Table 3) (in a free molecule L [10], the C≡C bond length is 1.200(2) Å). Note that in structure II [8], the C≡C bond is not almost elongated (1.208(7) Å), while in cuprobromide compound with the alkali metal cations in the outer sphere $(K[CuBr_2(HOCH_2C{\equiv}CCH_2OH)]$ [1]), the C≡C bond is significantly elongated to 1.24(1) Å.

In complex I, two "halves" of the 2-butyne-1,4-diol molecules have almost identical conformation about the midpoint of the C≡C bond; each fragment ≡C–C–O–H has a synclinal configuration with respect to the bonds C(1)–O(1) and C(4)–O(2) (the corresponding torsion angles C(2)C(1)O(1)H(1) and C(3)C(4)O(2)H(2) being 60.1° and –61.7°). The above conformation peculiarities of the 2-butyne-1,4-diol molecule are explained by involvement of the H atoms of two opposite alcohol groups in the hydrogen bonds (Fig. 3) with the Cl atoms (H(2)···Cl(1) 2.20 Å [11], which strongly link the fragment of two complex anions into centrosymmetric dimers $\{[CuCl_2(HOCH_2C{\equiv}CCH_2OH)]^-\}_2$. However, unlike $Rb[CuCl_2(HOCH_2C{\equiv}CCH_2OH)]$ (modification B) [6], where the analogous dimers lie at right angle to one

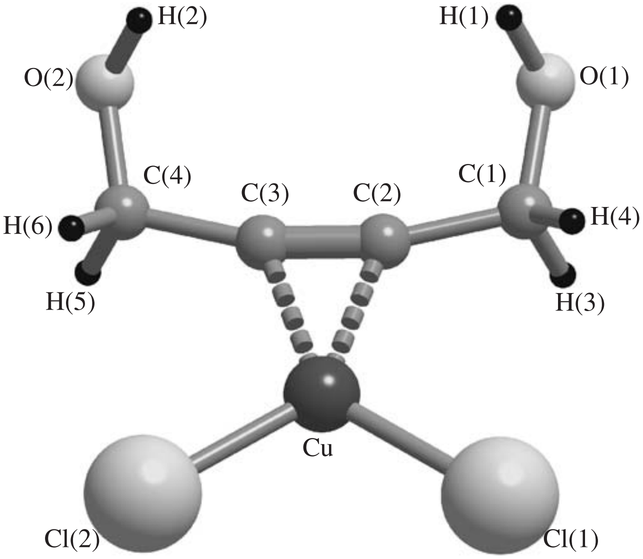

Fig. 2. The structure of the $[CuCl_2(HOCH_2C{\equiv}CCH_2OH)]^-$ anion in structure I.

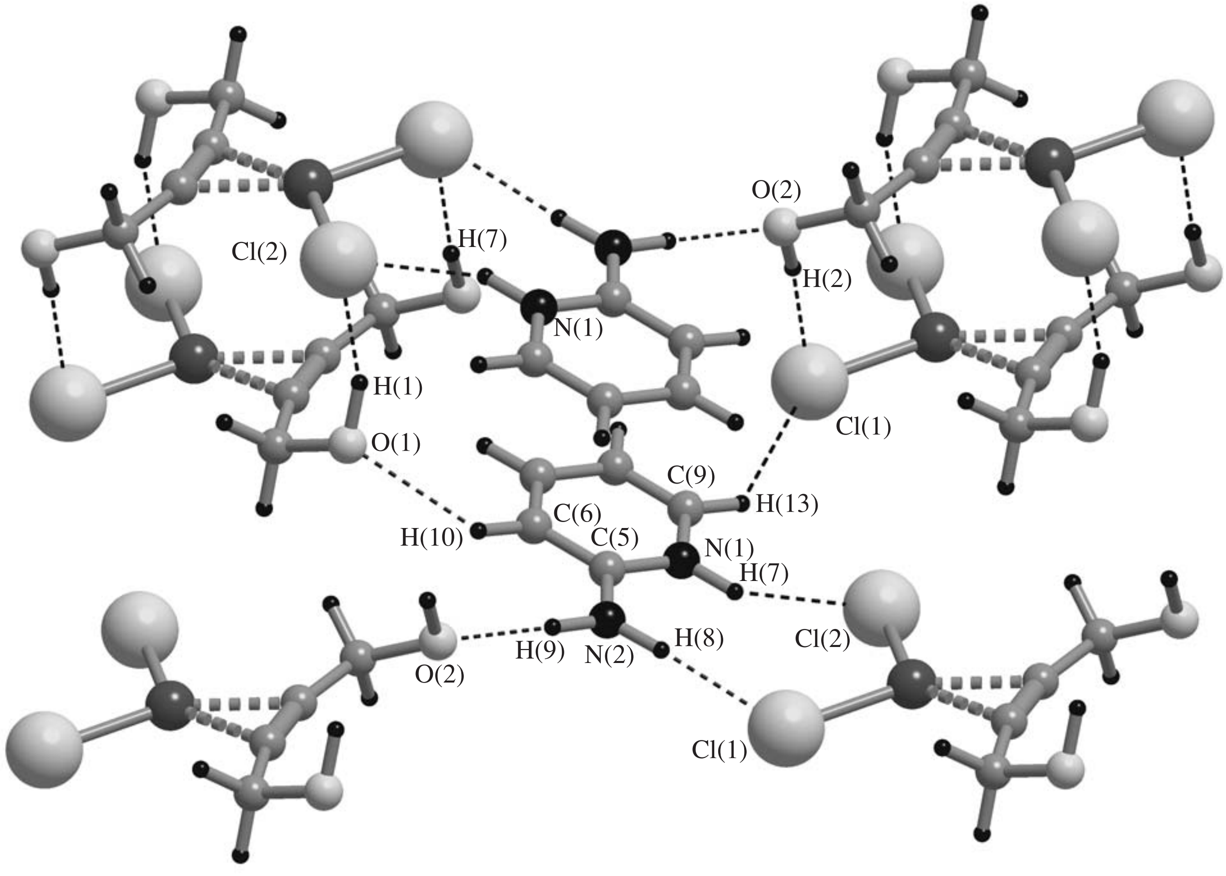

Fig. 3. Hydrogen bonds in structure I.

Table 3. The bond lengths (*d*) and bond angles (ω) in structure I

Bond	*d*, Å	Angle	ω, deg
Cu–Cl(1)	2.25(5)	Cl(1)CuCl(2)	107.8(1)
Cu–Cl(2)	2.24(4)	Cl(1)Cu*m*	126.2(4)
Cu–C(2)	2.01(8)	Cl(2)Cu*m*	125.9(2)
Cu–C(3)	2.01(4)	C(2)CuC(3)	35.2(3)
Cu–*m**	1.92(7)		
C(2)≡C(3)	1.22(2)	O(1)C(1)C(2)	112.5(4)
C(1)–C(2)	1.49(1)	C(1)C(2)C(3)	165.6(4)
C(3)–C(4)	1.48(4)	C(2)C(3)C(4)	165.3(5)
C(1)–O(1)	1.42(7)	C(3)C(4)O(2)	111.3(6)
C(4)–O(2)	1.40(6)	C(1)O(1)H(1)	108.9(4)
N(1)–C(5)	1.35(3)	C(4)O(2)H(2)	108.0(5)
N(1)–C(9)	1.372(8)		
N(2)–C(5)	1.343(9)	N(1)C(5)N(2)	118.8(4)
C(5)–C(6)	1.39(5)	N(2)C(5)C(6)	118.7(6)
C(6)–C(7)	1.355(9)	N(1)C(5)C(6)	119.7(4)
C(7)–C(8)	1.39(3)	C(6)C(7)C(8)	120.7(4)
C(8)–C(9)	1.35(5)	C(8)C(9)N(1)	120.3(4)
H(1)···Cl(2)	2.27	O(1)–H(1)···Cl(2)	154.9
H(2)···Cl(1)	2.20	O(2)–H(2)···Cl(1)	164.1
H(8)···Cl(1)	2.29	N(2)–H(8)···Cl(1)	167.1
H(9)···O(2)	1.89	N(2)–H(9)···O(2)	166.6
H(7)···Cl(2)	2.42	N(1)–H(7)···Cl(2)	136.4
H(13)···Cl(1)	2.80	C(9)–H(13)···Cl(1)	134.3
H(10)···O(1)	2.43	C(6)–H(10)···O(1)	131.0
		H(1)O(1)C(1)C(2)	60.1
		O(1)C(1)C(2)C(3)	17(3)
		C(1)C(2)C(3)C(4)	–3(4)
		C(2)C(3)C(4)O(2)	–16(3)
		C(3)C(4)O(2)H(2)	–61.7

* *m* is the midpoint of the C≡C bond.

another, the dimers $\{[CuCl_2(HOCH_2C{\equiv}CCH_2OH]^-\}_2$ in I are arranged in stacks along the direction [100] (Fig. 1).

The electrostatic cation–anion interaction in structure I has a pronounced direction due to the active participation of a six-membered cyclic 2-aminopyridinium cation in the formation of a strong hydrogen bonding system N–H···O and N–H···Cl (H(9)···O(2) 1.89, H(8)···Cl(1) 2.29 Å), which cross links the dimeric anions to give peculiar framework.

Thus, as compared to spherical alkali metal cations or highly symmetric ammonium cation, the planar 2-aminopyridinium cations with asymmetric distribution of the positive charge in the pyridine ring are incapable of radical changing of the packing type of the complex anions, but affect the parameters of the copper π-coordination core as compared to the previously stided compounds $M[CuCl_2(HOCH_2C{\equiv}CCH_2OH)]$ ($M = NH_4^+$, K^+, Rb^+), space groups *Ibam* [5, 6] and $(ImH)[CuCl_2(HOCH_2C{\equiv}CCH_2OH)]$ [8].

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