

Uncommon Behavior of Copper(I) Tetrafluoroborate and Perchlorate in $[\text{Cu}(\text{DAF})(\text{H}_2\text{O})]\text{BF}_4$ and $[\text{Cu}(\text{DAF})(\text{ClO}_4)]$ π -Complexes (DAF—Diallyl Formamide)

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Received November 9, 2000

Abstract—Crystals of $[\text{Cu}(\text{DAF})(\text{H}_2\text{O})]\text{BF}_4$ (**I**) and $[\text{Cu}(\text{DAF})(\text{ClO}_4)]$ (**II**) (DAF is diallyl formamide) were synthesized by an alternate-current electrochemical method, and their structures were determined ($\text{MoK}\alpha$ radiation, 1247 and 859 independent reflections with $I \geq 2\sigma(I)$, $R = 0.043$ and 0.032 for **I** and **II**, respectively). The complexes crystallize in space group $P2_1/n$, $Z = 4$. For **I**, $a = 10.782(3)$ Å, $b = 12.096(5)$ Å, $c = 9.185(3)$ Å, $\gamma = 103.62(3)^\circ$, and $V = 1164.2(7)$ Å³; for **II**, $a = 10.064(3)$ Å, $b = 10.753(6)$ Å, $c = 10.002(3)$ Å, $\gamma = 87.52(4)^\circ$, and $V = 1081.4(8)$ Å³. The copper atom in structures **I** and **II** coordinates both C=C bonds in one DAF molecule and oxygen atom of the amide group of another DAF molecule, as well as an oxygen atom of H_2O (in **I**) or ClO_4 (in **II**) in the axial position. The uncommon behavior of the anions in structures **I** and **II** is explained by their different values of Pierson hardness.

Acidoligand nature is one of the key factors in the formation of copper(I) π -complexes. Unlike Cl^- or Br^- anions that can form involved cuprohalide fragments, tetrafluoroborate and perchlorate anions are most liable to coordinate with copper(I) in the peripheral axial position [1]. In this case, the cationic nature of Cu(I) favors π -interaction of the copper atom with two C=C bonds. Indeed, in the structurally studied π -complexes of copper(I) tetrafluoroborate and perchlorate with diallyl amine (DAA), diallyl cyanamide (DACA), and diallyl sulfide (DAS), the metal atom is in the π, π -chelate cycle, while the monodentate acidoligand is in the axial position.

Complexes with diallyl amine $[\text{Cu}(\text{DAA})(\text{BF}_4)]$ (Cu–F 2.49(1) Å) [2], $[\text{Cu}(\text{DAA})(\text{ClO}_4)]$ (Cu–O 2.47(1) Å) [3], and diallyl cyanamide $[\text{Cu}(\text{DACA})(\text{BF}_4)]$ (Cu–F 2.69(2) Å) [4], $[\text{Cu}(\text{DACA})(\text{ClO}_4)]$ (Cu–O 2.71(2) Å) [5] are isostructural. For the π -complex with diallyl sulfide $[\text{Cu}(\text{DAS})(\text{BF}_4)]$ (Cu–F 2.598(3) Å) [6], only one analogous compound with silver perchlorate $[\text{Ag}(\text{DAS})(\text{ClO}_4)]$ (Ag–O 2.77(1) Å) is known [7]. Although silver(I) and copper(I) π -complexes are non-isostructural, they are similar in both inorganic anion behavior and the π, π -chelate function of the ligands, as, for example, in the case with $[\text{Ag}(\text{DAA})(\text{ClO}_4)]$ (Ag–O 2.754(7) Å) [8]. Thus, BF_4^- and ClO_4^- anions act as peripheral ligands in the Cu(I) and Ag(I) π -complexes.

This paper presents, for the first time, the results of the synthesis and X-ray diffraction analysis of copper(I) tetrafluoroborate and perchlorate π -complexes

with diallyl formamide (DAF) that exhibit uncommon BF_4^- and ClO_4^- anion behavior.

EXPERIMENTAL

Diallyl formamide was prepared from equimolar amounts of diallyl amine and 90% formic acid via azeotropic evaporation of water with toluene and subsequent fractional distillation [9].

Complex **I** was obtained as irregular colorless crystals using alternate-current electrochemical synthesis on copper electrodes ($U = 0.40$ V, $I = 0.24$ mA) from 6 ml of a $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ solution (2 mmol) in butanol-2 and 0.5 ml of DAF (4 mmol). Crystals **I** were grown for 2 days. They are sufficiently stable in air, but readily decompose in a dry atmosphere (over $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$). The density of **I** was determined by flotation from the chloroform/bromoform mixture and is equal to 1.68 g/cm³.

Complex **II** was obtained as faced plates using alternate-current electrochemical reduction of Cu(II) to Cu(I) on the copper electrodes ($U = 0.40$ V, $I = 0.24$ mA) from a 6 ml $\text{Cu}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ solution (2 mmol) in butanol-2 and 0.5 ml of DAF (4 mmol). Crystals **II** are sufficiently stable in both air and dry atmosphere. They were grown over a week. Crystals suitable for X-ray diffraction analysis could be chosen only after they were stored in a mother liquor for a long period of time (9 months).

Table 1. Crystallographic data and details of the X-ray experiment and structure refinement for complexes **I** and **II**

Parameter	I	II
<i>M</i> , au	293.53	288.16
<i>F</i> (000)	592	584
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	10.782(3)	10.064(3)
<i>b</i> , Å	12.096(5)	10.753(6)
<i>c</i> , Å	9.185(3)	10.002(3)
γ, deg	103.62(3)	87.52(4)
<i>V</i> , Å ³	1164.2(7)	1081.4(8)
<i>Z</i>	4	4
ρ(calcd), g/cm ³	1.675	1.770
μ _{Mo} , mm ⁻¹	1.912	2.266
Crystal size, mm	0.5 × 0.2 × 0.2	0.3 × 0.2 × 0.1
2θ _{max} , deg	60	54
	0 ≤ <i>h</i> ≤ 13	-12 ≤ <i>h</i> ≤ 12
Range of indices <i>hkl</i>	-16 ≤ <i>k</i> ≤ 15	0 ≤ <i>k</i> ≤ 12
	0 ≤ <i>l</i> ≤ 11	-12 ≤ <i>l</i> ≤ 12
Number of reflections:		
measured	1330	1506
independent	1255	865
independent with <i>I</i> ≥ 2σ(<i>I</i>)	1247	859
Number of parameters	152	136
<i>R</i> (<i>F</i>), <i>I</i> ≥ 2σ(<i>I</i>)	0.0425	0.0316
w <i>R</i> (<i>F</i> ²) for all reflections	0.1170	0.0820
Weighed scheme*: A, B	0.0820, 1.214	0.0541, 0.1002
GOOF (<i>F</i> ²)	1.082	1.069
(Δσ) _{max}	0.001	0.001
Δρ _{max} /Δρ _{min} , e/Å ³	0.65/-0.36	0.47/-0.27

$$* w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}, P = [F_o^2 + 2F_c^2]/3.$$

After preliminary studies by a photomethod, the diffraction arrays obtained on a single-crystal DARCH-1 diffractometer were used for solving the structures (MoK_α radiation, Zr filter, θ/2θ scan mode). The intensities of reflections were corrected for the Lorentz and polarization effects. Structures **I** and **II** were solved by direct methods, light atoms were located from Fourier syntheses. Absorption correction was performed using the DIFABS program. A CSD program package was used to solve the structures and account for the absorption [10]. Full-matrix anisotropic refinement of all non-hydrogen atoms for *F*² was performed using the SHELXL97 program [11]. Hydrogen atoms found geometrically were refined from a rider model with isotropic thermal parameters equal to 1.2*U*_{eq} for the neighboring non-hydrogen atom. Hydrogen atoms of the

Table 2. Atomic coordinates and thermal parameters* in structures **I** and **II**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} , Å ²
I				
Cu	-0.25905(7)	0.01440(5)	0.34217(8)	0.0457(3)
B	-0.082(1)	0.1312(7)	0.835(1)	0.070(2)
F(1)	0.0383(6)	0.1052(5)	0.8535(6)	0.113(2)
F(2)	-0.0953(5)	0.2019(4)	0.9423(6)	0.110(2)
F(3)	-0.1662(7)	0.0297(5)	0.8477(8)	0.153(3)
F(4)	-0.0859(7)	0.1734(6)	0.7023(7)	0.142(2)
O(1)	-0.1125(4)	0.1475(3)	0.3274(5)	0.056(1)
O(2)	-0.3303(5)	0.1075(5)	0.5318(6)	0.064(2)
N	0.0805(4)	0.2493(3)	0.2572(5)	0.044(1)
C(1)	0.3243(6)	0.4140(5)	0.0164(8)	0.055(2)
C(2)	0.2089(5)	0.3498(4)	0.0530(6)	0.042(1)
C(3)	0.1912(5)	0.2566(4)	0.1624(7)	0.052(2)
C(4)	0.0822(6)	0.3405(4)	0.3604(6)	0.050(2)
C(5)	0.0720(6)	0.4490(5)	0.2900(7)	0.048(1)
C(6)	0.1364(7)	0.5525(5)	0.3382(8)	0.062(2)
C(7)	-0.0162(6)	0.1592(4)	0.2503(7)	0.045(1)
H(w1)**	-0.277(8)	0.127(7)	0.597(9)	0.08(2)
H(w2)**	-0.344(8)	0.153(7)	0.50(1)	0.08(2)
II				
Cu	0.93797(8)	0.24022(7)	0.78236(8)	0.0399(3)
Cl	0.6600(2)	0.0342(2)	0.795(2)	0.0456(5)
O(1)	0.8095(4)	0.3827(4)	0.7955(5)	0.044(1)
O(2)	0.7656(5)	0.0805(5)	0.8728(5)	0.068(2)
O(3)	0.5529(7)	0.1280(6)	0.7938(8)	0.105(2)
O(4)	0.6983(7)	0.0127(7)	0.6625(6)	0.098(2)
O(5)	0.6097(6)	-0.0745(6)	0.8510(6)	0.087(2)
N	0.7281(5)	0.5724(4)	0.7313(5)	0.034(1)
C(1)	0.5118(7)	0.7746(7)	0.5221(6)	0.047(2)
C(2)	0.5773(6)	0.6703(6)	0.5662(6)	0.040(2)
C(3)	0.7119(6)	0.6649(6)	0.6255(7)	0.040(2)
C(4)	0.6654(6)	0.6020(6)	0.8596(6)	0.030(2)
C(5)	0.5166(6)	0.6029(5)	0.8555(6)	0.031(2)
C(6)	0.4368(6)	0.6862(6)	0.9202(6)	0.041(2)
C(7)	0.7957(6)	0.4657(6)	0.7106(7)	0.037(2)

* For non-hydrogen atoms $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (a_i a_j)$.

** The coordinates and *U*_H are only given for H atoms found by the unbiased method.

water molecule were found from Fourier syntheses and refined independently, using a common thermal parameter. No extinction correction was introduced. The peaks of residual electronic density are concentrated around the BF₄⁻ and ClO₄⁻ anions subject to libration.

Table 3. Bond lengths and angles (ω) and selected torsion angles (ϕ) in structures **I** and **II**

Bond	$d, \text{\AA}$		Angle	ω, deg	
	I	II		I	II
Cu–O(1)	1.977(4)	1.966(4)	$m(12)Cum(56)^*$	123.96(4)	125.41(4)
Cu– $m(12)$	2.033(5)	2.045(6)	O(1)Cum(12)	116.7(1)	109.9(2)
Cu– $m(56)$	2.037(6)	2.019(6)	O(1)Cum(56)	116.3(1)	124.0(2)
Cu–C(1)	2.117(6)	2.130(6)	C(1)CuC(2)	36.6(2)	36.5(2)
Cu–C(2)	2.164(5)	2.176(6)	$m(12)CuO(2)$	95.0(1)	90.3(1)
Cu–C(5)	2.177(6)	2.147(6)	C(5)CuC(6)	36.8(2)	36.8(2)
Cu–C(6)	2.115(6)	2.108(6)	$m(56)CuO(2)$	104.7(2)	94.3(1)
Cu–O(2)	2.302(6)	2.652(5)	O(1)CuO(2)	87.0(2)	93.2(2)
Cu...O(5)		3.006(8)	O(2)CuO(5)		172.5(2)
X–Y(1)**	1.422(5)	1.413(11)	Y(1)XY(2)	107.2(8)	107.9(4)
X–Y(2)	1.444(6)	1.337(9)	Y(1)XY(3)	104.1(7)	111.7(4)
X–Y(3)	1.401(6)	1.35(1)	Y(1)XY(4)	108.3(8)	112.1(4)
X–Y(4)	1.408(6)	1.32(1)	Y(2)XY(3)	111.4(8)	107.2(5)
			Y(2)XY(4)	114.4(7)	107.4(4)
			Y(3)XY(4)	110.8(8)	110.1(4)
C(1)–C(2)	1.345(7)	1.349(9)	C(1)C(2)C(3)	122.8(6)	125.3(7)
C(2)–C(3)	1.488(8)	1.478(9)	C(2)C(3)N	113.9(5)	113.2(6)
C(3)–N	1.464(7)	1.457(8)	C(3)NC(4)	118.6(4)	117.1(5)
N–C(4)	1.451(7)	1.459(8)	NC(4)C(5)	113.3(5)	113.6(5)
C(4)–C(5)	1.491(8)	1.497(8)	C(4)C(5)C(6)	122.9(6)	124.1(6)
C(5)–C(6)	1.354(8)	1.343(8)	C(3)NC(7)	119.7(5)	121.1(6)
N–C(7)	1.321(6)	1.325(7)	C(4)NC(7)	121.7(5)	121.8(5)
C(7)–O(1)	1.237(7)	1.235(7)	NC(7)O(1)	123.0(6)	123.8(6)
			C(7)O(1)Cu	128.3(4)	124.5(5)
Angle	ϕ, deg		Angle	ϕ, deg	
	I	II		I	II
CuC(1)C(2)C(3)	–102.7(5)	–98.4(6)	C(1)C(2)C(3)N	140.7(6)	144.8(7)
CuC(6)C(5)C(4)	100.2(6)	102.5(5)	C(6)C(5)C(4)N	–142.7(6)	–140.5(6)
CuO(1)C(7)N	–174.9(4)	–166.6(4)			

* $m(12)$ and $m(56)$ are midpoints of C(1)–C(2) and C(5)–C(6) bonds, respectively.

** X and Y(1–4) correspond to atoms B and F(1–4) in structure **I** and to Cl and O(2–5) atoms in structure **II**.

The crystallographic data, and the details of the X-ray diffraction experiment and of the refinement of structures **I** and **II** are given in Table 1. Atomic coordinates and thermal parameters are listed in Table 2. Selected interatomic distances and bond and torsion angles are presented in Table 3.

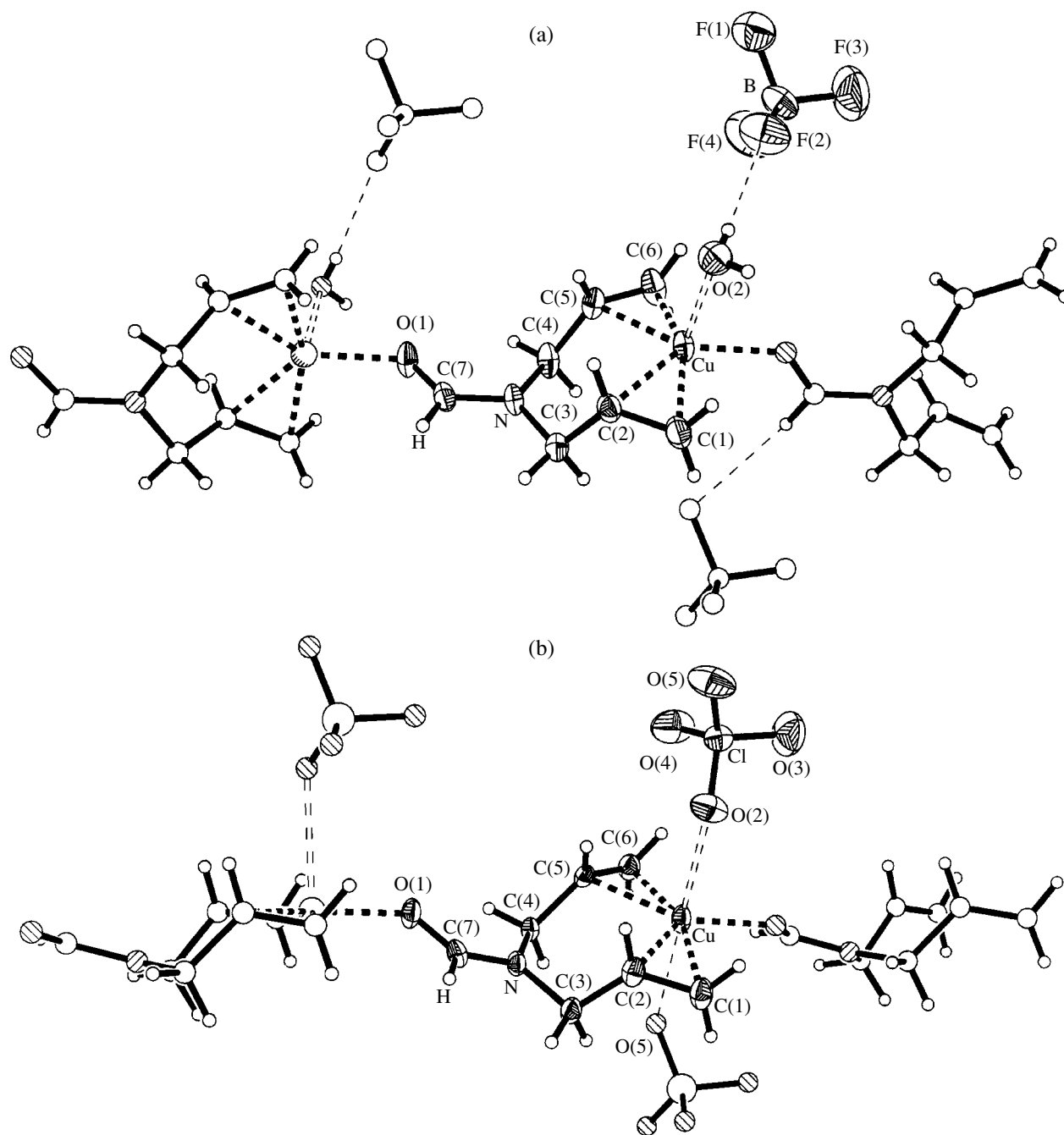
RESULTS AND DISCUSSION

In structures **I** and **II**, the copper atom coordinates both C=C bonds of one DAF molecule and an oxygen atom of the amide group of another DAF molecule, as well as an oxygen atom of H₂O (in **I**) or ClO₄ (in **II**) in the axial position.

Due to the chelate-bridging function of the DAF molecule, structures **I** and **II** consist of polymer chains, in which the neighboring copper atoms are joined by a n symmetry plane (see figure).

The displacement of the metal atom from the plane of equatorial ligands correlates with the extent of axial deformation of the Cu(I) coordination polyhedron and equals 0.206 Å (Cu–O(2) 2.302(6) Å and 0.093 Å (Cu–O(2) 2.652(5) Å) for **I** and **II**, respectively.

The elongation of the bond between the apical ligand and the central copper atom in **II** is attended by the appearance of a contact Cu...O(5) 3.006(8) Å on the opposite side of the equatorial plane (angle



Fragments of polymer chains along $[110]$ and $[1\bar{1}0]$ in (a) structure **I** and (b) structure **II**. For asymmetric units, ellipsoids of 30% probability and numbering schemes are shown.

$O(2)CuO(5)$ $172.5(2)^\circ$); the trigonal-bipyramidal surrounding of the copper atom is thus formed. The formation of this intermediate coordination, which is not typical of Cu(I), is one of the stages of the ligand substitution and racemization of the complexes that takes place in the solutions [1].

Two C=C bonds in the environment of copper(I) make the Cu–(C=C) distances somewhat longer (2.033(5) and 2.037(6) Å in **I**, 2.045(6) and 2.019(6) Å

in **II**). The coordinated C=C bonds in the DAF molecule are coplanar within 0.009(4) and 0.022(4) Å in **I** and **II**, respectively, the angles between them and the plane of the equatorial ligands being 4.6° and 3.3° in **I** and 7.0° and 10.3° in **II** for C(1)=C(2) and C(5)=C(6), respectively. Such stereospecific π,π -chelating is caused by electronic factors [12], as well as by the formation of an energetically advantageous chair conformation of the six-membered chelate cycle similar to

Table 4. Geometric parameters of hydrogen bonds in structures **I** and **II**

D–H...A	H...A, Å	D...A, Å	D–H, Å	Angle DHA, deg
I				
C(3)–H(3A)...F(3)	2.59	3.411(8)	0.97	143
C(3)–H(3B)...F(1)	2.59	3.476(9)	0.97	153
C(4)–H(4B)...O(1)	2.36	2.764(7)	0.97	105
C(5)–H(5)...O(2)	2.57	3.470(8)	0.93	163
C(7)–H(7)...F(1)	2.48	3.292(8)	0.93	146
O(2)–H(w1)...F(4)	2.23(8)	3.007(9)	0.82(8)	158(8)
O(2)–H(w2)...F(2)	2.09(8)	2.740(7)	0.65(8)	172(11)
II				
C(3)–H(3A)...O(5)	2.45	3.399(9)	0.97	165
C(4)–H(4B)...O(1)	2.39	2.789(8)	0.97	104
C(6)–H(6B)...O(4)	2.51	3.211(9)	0.93	133

those previously discovered in complexes with DAA, DACA, and DAS [2–8, 12].

An identical chelate cycle was discovered in the copper(I) sulfamate π -complex with DAF [Cu(DAF)NH₂SO₃(H₂O)] (**III**) [13]. In structure **III**, the nitrogen atom of the sulfamate anion is coordinated by a copper atom in equatorial position, while the apical position is occupied by a water molecule (Cu–O 2.313(3) Å). Although the amide oxygen atom of DAF only participates in the formation of hydrogen bonds, it is capable of effective interaction with the metal atom, as follows from quantum-chemical calculations of the charges on the atoms in structure **III** [13]. This situation occurs in **I** and **II**: Cu–O(1) bonds are among the shortest in copper(I) complexes (1.977(4) Å in **I** and 1.966(4) Å in **II**). In this case, the effective transfer of the electronic density from the nitrogen atom in the course of the amide group coordination makes this atom extend from its plane only by 0.015(6) and 0.006(6) Å in **I** and **II**, respectively (0.057 Å in **III**). The O(1) atom is coordinated by a copper atom through a sp^2 -hybrid electron pair (the torsion CuO(1)C(7)N angle being close to 180°; the C(7)O(1)Cu angle is almost 120°; see Table 3). The mutual orientation of asymmetrical units in **I** and **II** is different: the dihedral angle between the planes of the equatorial ligands and the adjacent amide group is equal to 88.9(4)° and 40.6(4)°, respectively.

A branched system of hydrogen bonds of the O–H...F and C–H...O(F) type (see Table 4) unites the organometallic chains into three-dimensional structures **I** and **II**. The participation of F and O atoms in the formation of hydrogen bonds (and in the interaction of Cu in **II**) results in imaginary elongation of B–F and Cl–O bonds. In fact, the anion atoms that have weaker bonds are more liable to imaginary reduction of the respective bonds (Table 3 gives their lengths without libration corrections). Indeed, the anisotropic thermal

parameters of the anions are satisfactorily described by the TLS model [14]: for the BF₄[–] anion, the standard deviation of anisotropic parameters U_{calcd} , calculated from TLS matrices, from U_{init} is only 0.013 Å² (see Table 2).

Finally, the revealed difference in the structures of the complexes is, most likely, due to a higher tendency of the tetrafluoroborate anion to formation of strong hydrogen bonds (see Table 4), especially with the participation of a water molecule, while the perchlorate anion displays a tendency to interact with a mild acid Cu(I). This is confirmed by the fact that no coordination was observed between the metal atom and rigid SiF₆^{2–} and PF₆[–] anions in the studied copper(I) and silver(I) π -complexes [1].

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