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Reactions of $PhenCuX_2$ ($X = OOCMe, O_3SCF_3$) with 3,5-Dimethylpyrazole: Effect of the Anion Nature on the Composition and Structure of the Complexes

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Abstract—The reaction of aqueous copper(II) acetate with phenanthroline (Phen) gave the complex $PhenCu(OOCMe)_2 \cdot 2MeCN$ (**I**), which was converted to the single crystals of the monomer $PhenCu(OOCMe)_2 \cdot 1.5CH_2Cl_2$ (**II**) upon recrystallization of dichloromethane. Recrystallization of **I** from wet benzene gave the single crystals of $PhenCu(OOCMe)_2(OH_2) \cdot 0.5\ C_6H_6 \cdot 0.5MeCN$ (**III**) containing a coordinated water molecule. The reaction of **I** with 3.5 dimethylpyrazole (HDmpz) (1 : 2) resulted in the synthesis of $PhenCu(OOCMe)_2HDmpz \cdot 0.5H_2O \cdot 0.5CH_2Cl_2$ (**IV**) in which the pyrazole molecule occupied the same coordination site as the water molecule in **III.** The reaction of **I** with trifluoromethanesulfonic acid yielded $PhenCu(OH_2)(NCMe)(Otf)_2$ (**V**), which was also prepared by the reaction of copper acetate with HOtf followed by the addition of 1 mole of $Phen \cdot H_2O$. Monomer **V** reacted with 2 moles of HDmpz to be converted to $PhenCu(HDmpz)_2(Otf)_2$ (**VI**). Compounds **I**–**VI** were characterized by elemental analysis data, IR spectra, and X-ray diffraction (CCDC nos. 1948544 (**I**), 1948541 (**II**), 1987813 (**III**), 1948542 (**IV**), 1948540 (**V**), 1948543 (**VI**)). The geometry of complexes and the effect of solvent used for the reactions and crystallization on the molecular packing in the crystals were considered on the basis of X-ray diffraction data.

Key words: copper acetate, copper triflate, phenanthroline, 3,5-dimethylpyrazole, synthesis, X-ray diffraction

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INTRODUCTION

The nature of the anion in transition metal complexes largely determines their composition, structure, and geometry. For example, depending on the donor ability of the substituent R, carboxylate anions can act as terminal ligands or as bi-, tri-, tetra-, and penta-bridging ligands, forming the corresponding complexes and clusters [1–3]. The anions of strong trifluoromethanesulfonic acid are, most often, displaced to the outer sphere even by weak donor solvents such as acetonitrile, thus giving formally a metal cation in a very labile ligand shell, which is used to attach various donor molecules to the metal [3]. Since the modes of coordination of transition metals are rather diverse, for example, in the degradation of clusters to smaller species, including monomers [2, 3] or in catalysis [4–8], they are often deliberately restricted by blocking some orbitals via attachment of bidentate four-electron donors such as bipyridine or phenanthroline, which remain in the molecule almost in all cases, irrespective of the performed reactions. Finally, only a limited number of orbitals of the complex can be used for attachment of the donor molecule [3].

Meanwhile, heterocyclic pyrazoles containing pyridine nitrogen atom and pyrrole NH group capable of being deprotonated are convenient compounds for the preparation of binuclear transition metal complexes. These compounds can be considered as structural analogues of the active part of natural metalloenzymes with MN_2O_2 coordination units such as copper-containing blue oxidases [3, 9–14].

Here we report the preparation and structure of phenanthroline copper(II) acetate and triflate and the structures of products formed in their reactions with heterocyclic 3,5-dimethylpyrazole (HDmpz).

EXPERIMENTAL

Unless otherwise indicated, all operations on the synthesis and isolation of complexes were carried out under pure argon in anhydrous solvents.

Synthesis of $PhenCu(OOCMe)_2 \cdot 2MeCN$ (I). Phenanthroline (0.2 g, 1 mmol) was added to an aqueous solution of copper acetate (0.2 g, 0.5 mmol) in acetonitrile (10 mL) and the mixture was refluxed for 30 min. The resulting blue solution was left at room temperature for 4 h. The light blue crystals thus formed were separated from the mother liquor by decantation, washed successively with benzene (5 mL) and hexane (5 mL), and dried in an argon flow. The yield was 0.3 g (68%).

For $C_{20}H_{20}N_4O_4Cu$

Anal. calcd., %	C, 54.11	H, 4.54	N, 12.62
Found (powder), %	C, 53.22	H, 3.98	N, 9.54

IR (ν, cm^{-1}): 3070 w.br, 1560 s, 1518 s, 1492 w, 1428 s, 1382 s, 1331 m, 1253 w, 1223 w, 1107 w, 1143 w, 1020 w, 872 w, 846 s, 778 w, 738 w, 721 s, 674 m, 659 m, 622 m, 515 w, 429 w.

Synthesis of PhenCu(OOCMe)$_2$ · 1.5CH$_2$Cl$_2$ (II) was performed by recrystallization of complex **I** from dichloromethane. A weighed portion of PhenCu(OOCMe)$_2$ · 2MeCN (0.04 g, 0.1 mmol) was dissolved in dichloromethane (10 mL) and stirred with heating for 30 min. The resulting blue solution was kept at room temperature for 2 h. The precipitated blue crystals were separated from the mother liquor by decantation, washed with hexane (5 mL), and dried in an argon flow.

The yield of the single crystalline product, unstable at room temperature, was 0.13 g (30%).

For $C_{35}H_{34}N_4O_8Cl_6Cu_2$

Anal. calcd., %	C, 42.96	H, 3.50	N, 5.73
Found (powder), %	C, 51.74	H, 3.74	N, 6.66

IR (ν, cm^{-1}): 3060 w, 1558 s, 1516 s, 1493 w, 1427 s, 1383 s, 1334 s, 1253 w, 1223 w, 1107 w, 1013 w, 873 m, 846 s, 738 m, 778 w, 721 s, 675 m, 519 w, 452 w, 429 m.

Synthesis of PhenCu(OOCMe)$_2$(OH$_2$) · 0.5C$_6$H$_6$ · 0.5MeCN (III) was performed by recrystallization of PhenCu(OOCMe)$_2$ · 2MeCN from benzene containing 2–3% of water. A weighed portion of PhenCu(OOCMe)$_2$ · 2MeCN (0.04 g, 0.1 mmol) was dissolved in acetonitrile (5 mL). Wet benzene (5 mL) was added to the obtained blue solution and the mixture was stirred at reflux for 30 min. The resulting green solution was concentrated (to ~5 mL) by heating in an oil bath with evaporation of the boiling solvent in an argon flow and cooled down to room temperature in this flow. The green crystals thus formed were separated from the mother liquor by decantation, washed successively with cold benzene (5 mL) and hexane (5 mL), and dried in an argon flow.

For $C_{20}H_{20.5}N_{2.5}O_5Cu$

Anal. calcd., %	C, 54.66	H, 4.70	N, 7.97
Found, %	C, 54.25	H, 4.53	N, 7.48

IR (ν, cm^{-1}): 3207 m.br, 3061 w, 2245 w, 1573 s, 1515 s, 1493 w, 1480 w, 1424 s, 1388 s, 1337 m, 1330 s, 1243 w, 1107 w, 1047 m, 1015 w, 908 w, 872 m, 846 s, 772 m, 721 s, 702 s, 620 s, 560 m, 508 m, 490 w, 429 m.

Synthesis of PhenCu(OOCMe)$_2$HDmpz · 0.5H$_2$O · 0.5CH$_2$Cl$_2$ (IV). HDmpz (0.05 g, 0.55 mmol) was added to a blue-colored solution of PhenCu(OOCMe)$_2$ · 1.5CH$_2$Cl$_2$ (0.13 g, 0.27 mmol) in dichloromethane (10 mL) and the mixture was stirred for 20 min at room temperature. Hexane (5 mL) was added to the solution and the mixture was kept for 24 h at 5°C. The precipitated blue crystals were separated from the mother liquor by decantation, and dried in an argon flow. The yield was 0.09 g (67%).

For $C_{21.5}H_{24}N_4O_{4.5}ClCu$

Anal. calcd., %	C, 51.91	H, 4.88	N, 11.31
Found, %	C, 55.05	H, 4.13	N, 11.44

IR (ν, cm^{-1}): 3434 s, 2924 w, 1582 s, 1518 m, 1427 w, 1401 w, 1385 w, 1332 w, 1225 w, 1147 w, 1107 w, 1050 w, 1011 w, 919 w, 871 w, 780 w, 850 m, 723 m, 648 w, 674 w, 621 w, 427 w.

Synthesis of PhenCu(OH$_2$)(NCMe)(Otf)$_2$ (V). Method 1. Trifluoromethanesulfonic acid (0.16 mL, 0.8 mmol) was added to a blue-colored solution of PhenCu(OOCMe)$_2$ · 2MeCN (0.18 g, 0.4 mmol) in acetonitrile (15 mL). The blue-green solution obtained on stirring was concentrated to 5 mL and kept for 24 h at 5°C. The precipiatated blue crystals were separated from the mother liquor by decantation. The yield was 0.25 g (81%).

For $C_{16}H_{13}N_3O_7S_2F_6Cu$

Anal. calcd., %	C, 31.98	H, 2.18	N, 6.99
Found, %	C, 31.57	H, 2.31	N, 6.21

Method 2. Trifluoromethanesulfonic acid (0.17 mL, 2 mmol) and Phen (0.2 g, 1 mmol) were added to an aqueous solution of copper acetate (0.2 g, 1 mmol) in acetonitrile (15 mL). The blue-green solution formed on stirring was concentrated to 5 mL and kept for 24 h at 5°C. The precipitated blue crystals were separated from the mother liquor by decantation, washed successively with dichloromethane (5 mL) and hexane (5 mL), and dried in an argon flow. The yield was 0.59 g (93%).

For $C_{16}H_{13}N_3O_7S_2F_6Cu$

Anal. calcd., %	C, 31.98	H, 2.18	N, 6.99
Found, %	C, 31.42	H, 2.39	N, 6.58

IR (ν, cm^{-1}): 3445 m.br, 3050 w, 1628 w, 1607 w, 1587 w, 1513 s, 1496 w, 1424 m, 1349 m, 1259 s, 1178 s, 1147 m, 1107 m, 1033 s, 870 w, 851 m.

Synthesis PhenCu(HDmpz)$_2$(Otf)$_2$ (VI). HDmpz (0.1 g, 1 mmol) was added to a suspension of PhenCu(OH$_2$)(NCMe)(Otf)$_2$ (0.3 g, 0.5 mmol) in dichloromethane (15 mL). Hexane (5 mL) was added to the blue solution thus formed and the mixture was allowed to evaporate at room temperature. The precipitated blue crystals were separated from the mother liquor by decantation and dried in an argon flow. The yield was 0.3 g (84%).

For $C_{24}H_{24}N_6O_6S_2F_6Cu$

Anal. calcd., %	C, 39.56	H, 3.29	N, 11.54
Found, %	C, 40.12	H, 3.11	N, 11.34

IR (ν, cm^{-1}): 3201 w.br, 3141 w, 2880 w, 1610 m, 1584 w, 1523 w, 1497 m, 1430 w, 1343 w, 1279 s, 1234 s, 1160 w, 1112 w, 1053 m, 1022 s, 874 w, 851 m, 758 m, 722 s, 573 s, 515 s, 431 w.

The ATR IR spectra of crystalline samples were measured in the 4000–550 cm^{-1} range on an NEXUS NICOLET FT IR spectrometer with a MIRacle attachment (PIKE Technologies) equipped with a diamond crystal.

X-ray diffraction studies of I–VI were performed by a standard procedure on a Bruker SMART ApexII automated diffractometer equipped with a CCD array detector (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator, ω-scan mode). The crystals of complex **III** slowly decomposed during the X-ray diffraction study. The structures were refined using the SHELXT LPLUS software package (PC version) [15–18]. The crystal data and X-ray experiment details are summarized in Table 1.

Full tables of atomic coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1948544 (**I**), 1948541 (**II**), 1987813 (**III**), 1948542 (**IV**), 1948540 (**V**), 1948543 (**VI**)); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Aqueous copper(II) acetate reacts with phenanthroline containing a water molecule in polar coordinating acetonitrile with refluxing for 30 min to give blue mononuclear complex **I** (68% yield). According to X-ray diffraction data, complex **I** contains a coordinated Phen molecule and two acetonitrile solvate molecules. The metal ion in **I** occurs in a square–planar environment of two acetate oxygen atoms (Cu–O, 1.953(3), 1.964(3) Å) located in *trans*-positions relative to the PhenCu plane (Cu–N, 2.015(3), 2.017(3) Å) (Table 1, Fig. 1a). The distances to oxygen atoms of the anion not bonded to copper are 2.578(6) and 2.614(6) Å. In the crystals, the molecules are stacked, with Cu···Cu distances in the neighboring monomers being 8.321(3) Å, which may be ditated by the stacking contacts of the Phen ligands (C···C, 3.387–3.503 Å; the PhenCu/ PhenCu angle in the stack is 2.1°). The distance between the copper atoms of neighboring stacks is 7.782(3) Å, and the phenanthrolines of the neighboring stacks are inclined at an angle of 78.1°, the acetonitrile solvate molecules reside between the stacks, and their nitrogen atoms form no significant contacts (Fig. 1b).

Recrystallization of **I** from dichloromethane gives complex $PhenCu(OOCMe)_2 \cdot 1.5CH_2Cl_2$ (**II**) of a similar structure (Cu–O, 1.9225(14), 1.9554(14); Cu–N, 2.0041(16), 2.0178(15); Cu···O, 2.5776(14), 2.7603(16) Å), but containing CH_2Cl_2 solvate molecules (Table 1, Fig. 2a). The introduction of a more sterically congested solvent into the crystal induces changes in the molecule packing. Like in **I**, stacks are also formed in **II**; however, in **II**, the molecules are formally dimerized via π–π stacking contacts (PhenCu/PhenCu, 0.0°; C···C, 3.378(4)–4.038(6) Å) in which metal atoms are arranged at 6.920(3) Å distances (Fig. 2b). The nearest analogous dimer is located in the stack at a Cu···Cu distance of 5.485(3) Å, while the distance to the copper atom of the neighboring stack is 9.7183(4) Å. Note that all PhenCu groups in the crystal are parallel. Apart from steric factors, the different type of packing in **II** compared with **I** may be caused by hydrogen bonds between the solvent and the oxygen atoms of the anion, as opposed to acetonitrile containing a lone pair (C···O, 3.126–3.266 Å).

Complexes **I** and **II**, unlike the well-known green complexes of copper with phenathroline or bipyridine and their derivatives, contain no coordinated water, which would give rise to a pentahedral environment of copper, depending on the reaction and crystallization conditions [19, 20].

A green complex containing a coordinated water molecule is actually formed upon dissolution of **I** or **II** in acetonitrile and subsequent recrystallization with the addition of wet benzene (2–3% H_2O). According to X-ray diffraction data, in complex $PhenCu(OOCMe)_2(OH_2) \cdot 0.5C_6H_6 \cdot 0.5MeCN$ (**III**), the metal atom of each of two independent molecules has a tetragonal pyramidal environment composed of two phenanthroline nitrogen atoms (Cu–N, 2.021(7), 2.024(7) and 2.024(7), 2.024(7) Å), two acetate oxygen atoms (Cu–O, 1.923(5), 1.926(5) and 1.920(6), 1.937(5) Å), and the oxygen atom of water (Cu–O, 2.307(6) and 2.319(6) Å) (Table 1, Fig. 3a). Note that the oxygen atom of water that occupies the fifth site of complex **III** barely affects the bond lengths between copper and phenanthroline nitrogen and between copper and anionic oxygen with respect to those in **I** or **II**. The anions are located in the *trans*-positions relative to the phenanthroline plane, like those in **I** and **II**.

Table 1. Crystallographic data and structure refinement details for structures **I–VI**

Parameter	Value					
	I	**II**	**III**	**IV**	**V**	**VI**
CCDC	1948544	1948541	1987813	1948542	1948540	1948543
Molecular formula	$C_{16}H_{14}N_2O_4Cu \cdot 2(C_2H_3N)$	$C_{16}H_{14}N_2O_4Cu \cdot 1.5(CH_2Cl_2)$	$C_{16}H_{16}N_2O_5Cu \cdot 0.5(C_6H_6 \cdot C_2H_3N)$	$C_{21}H_{22}N_4O_4Cu \cdot 0.5(CH_2Cl_2 \cdot H_2O)$	$C_{16}H_{13}N_3O_7S_2F_6Cu$	$C_{24}H_{24}N_6O_6S_2F_6Cu$
M	443.95	489.23	439.43	509.44	600.96	734.16
Color	Blue	Blue	Green	Blue	Blue	Blue
T, K	150(2)	150(2)	296(2)	150(2)	150(2)	150(2)
System	Orthorhombic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$Pbca$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	10.5563(5)	9.3242(7)	7.5791(13)	12.280(5)	7.6851(10)	7.4558(14)
b, Å	15.5580(8)	9.7181(7)	24.501(5)	14.052(6)	9.9725(13)	21.583(4)
c, Å	24.9004(14)	11.4778(8)	21.558(4)	15.046(7)	14.4581(19)	19.515(4)
α, deg	90	99.071(1)	90	70.271(7)	82.240(2)	90
β, deg	90	97.039(1)	95.914(5)	88.171(7)	85.597(2)	93.168(3)
γ, deg	90	97.467(1)	90	76.326(7)	77.545(2)	90
V, Å^3	4089.5(4)	1007.40(13)	3982.0(12)	2371.4(18)	1070.8(2)	3135.5(10)
Z	8	2	8	2	2	4
ρ(calcd.), mg/m^3	1.442	1.613	1.466	1.427	1.864	1.555
μ, mm^{-1}	1.102	1.508	1.132	1.070	1.313	0.913
F(000)	1832	496	1816	1052	602	1492
Crystal size, mm	0.24 × 0.22 × 0.20	0.24 × 0.22 × 0.20	0.24 × 0.22 × 0.20	0.14 × 0.12 × 0.10	0.24 × 0.22 × 0.20	0.14 × 0.12 × 0.10
Scanning region of θ, deg	3.09–7.00	2.09–30.00	2.52–5.00	2.18–29.00	2.45–30.01	2.32–29.99
Ranges of reflection indices	$-13 \le h \le 13$, $-19 \le k \le 19$, $-31 \le l \le 31$	$-13 \le h \le 13$, $-13 \le k \le 13$, $-16 \le l \le 16$	$-9 \le h \le 8$, $-29 \le k \le 29$, $-25 \le l \le 25$	$-16 \le h \le 16$, $-19 \le k \le 19$, $-20 \le l \le 20$	$-10 \le h \le 10$, $-14 \le k \le 14$, $-20 \le l \le 20$	$-10 \le h \le 10$, $-30 \le k \le 30$, $-27 \le l \le 27$
Number of measured reflections	63717	12276	6992	26174	12527	35885
Number of unique reflections (R_{int})	4434 (0.0639)	6145 (0.0150)	6992 (0.1590)	12526 (0.0792)	6184 (0.0268)	9143 (0.1122)
GOOF	1.106	0.962	1.098	1.000	1.003	1.008
R ($I > 2\sigma(I)$)	$R_1 = 0.0629$, $wR_2 = 0.1516$	$R_1 = 0.0374$, $wR_2 = 0.0920$	$R_1 = 0.1046$, $wR_2 = 0.2524$	$R_1 = 0.0769$, $wR_2 = 0.1716$	$R_1 = 0.0343$, $wR_2 = 0.0922$	$R_1 = 0.0662$, $wR_2 = 0.1569$
R (for all reflections)	$R_1 = 00.0684$, wR_2 0.1550	$R_1 = 0.0528$ $wR_2 = 0.0978$	$R_1 = 0.1566$ $wR_2 = 0.2872$	$R_1 = 0.1857$ $wR_2 = 0.2176$	$R_1 = 0.0420$, $wR_2 = 0.0967$	$R_1 = 0.1472$, $wR_2 = 0.1930$
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	2.495/–0.844	0.966/–0.686	0.579/–1.047	1.154/–0.615	0.641/–0.592	0.443/–0.881

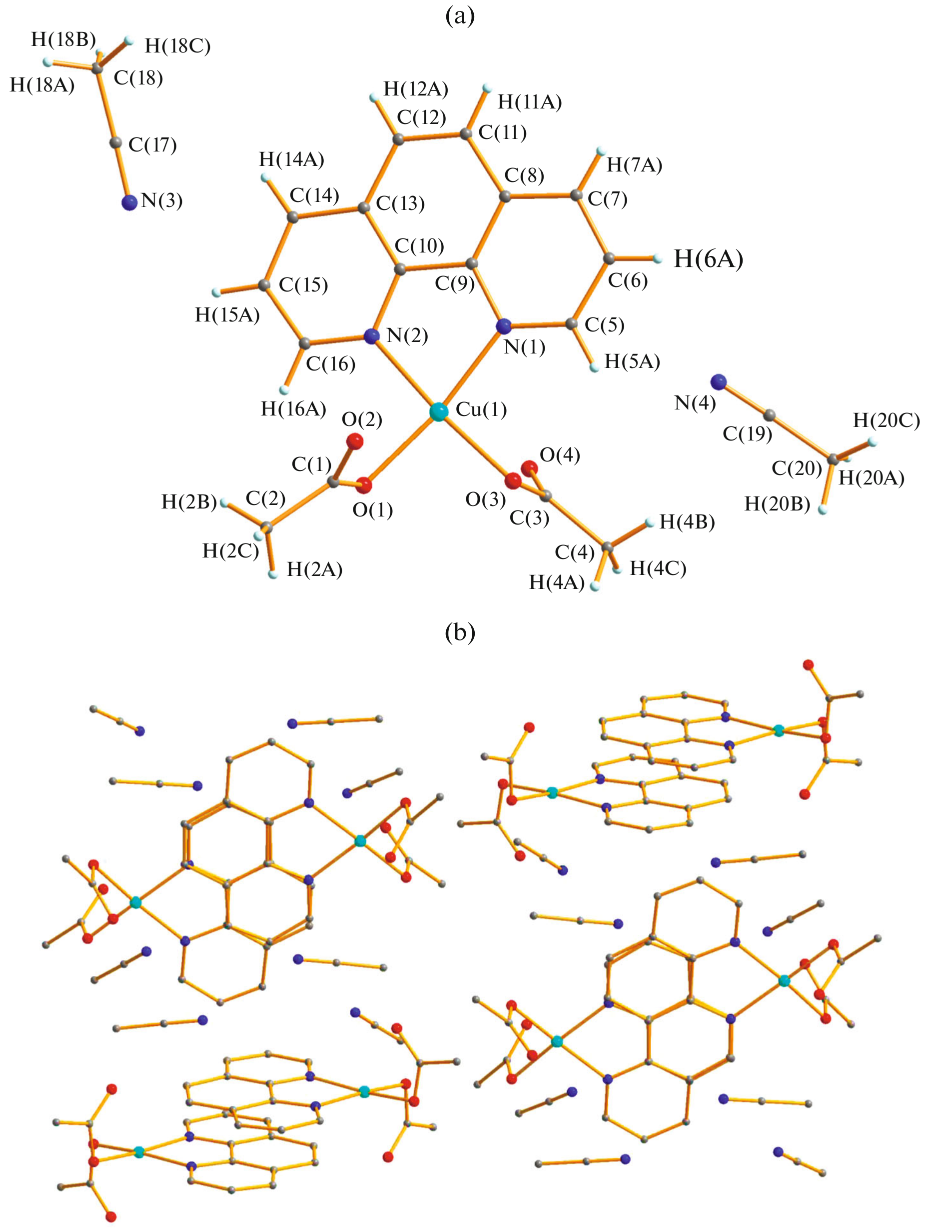

Fig. 1. (a) Structure of complex **I** and (b) fragment of molecular packing in the crystal of **I**; color of atoms: Cu is light blue, N is blue, O is red.

One hydrogen atom of the coordinated water molecule forms an intramolecular hydrogen bonds with the acetate anion (O(5)···O(4), 2.726; O(10)···O(9), 2.689Å), while the other one is bound to the acetate anion belonging to an adjacent copper atom (O(5)···O(2*A*), 2.751Å; O(10)···O(7*A*), 2.757 Å). Finally, intermolecular hydrogen bonds give rise to two 1D polymer chains, Cu(1)(**Cu1**) for one complex and Cu(2)(**Cu2**) for the other complex (Cu(1)···Cu(2), 6.356(1) Å; PhenCu/PhenCu, 6.3°). In the crystal, the **Cu1** and **Cu2** chains are interpenetrated into each other due to the π–π stacking interactions between the coordinated Phen molecules (C···C, 3.578–4.017 Å), with the solvent molecules being located between them (Fig. 3b).

It is also noteworthy that the angles between the $CuPhen/Cu(OOCMe)_2$ and Cu(OOCMe)/Cu(OOCMe) planes in **I**–**III** are 88.1°, 92.7°, 91.7°; 85.0°, 97.6°, 93.5°; 90.4°, and 98.4°, respectively, which is determined by the molecular packing in crystals.

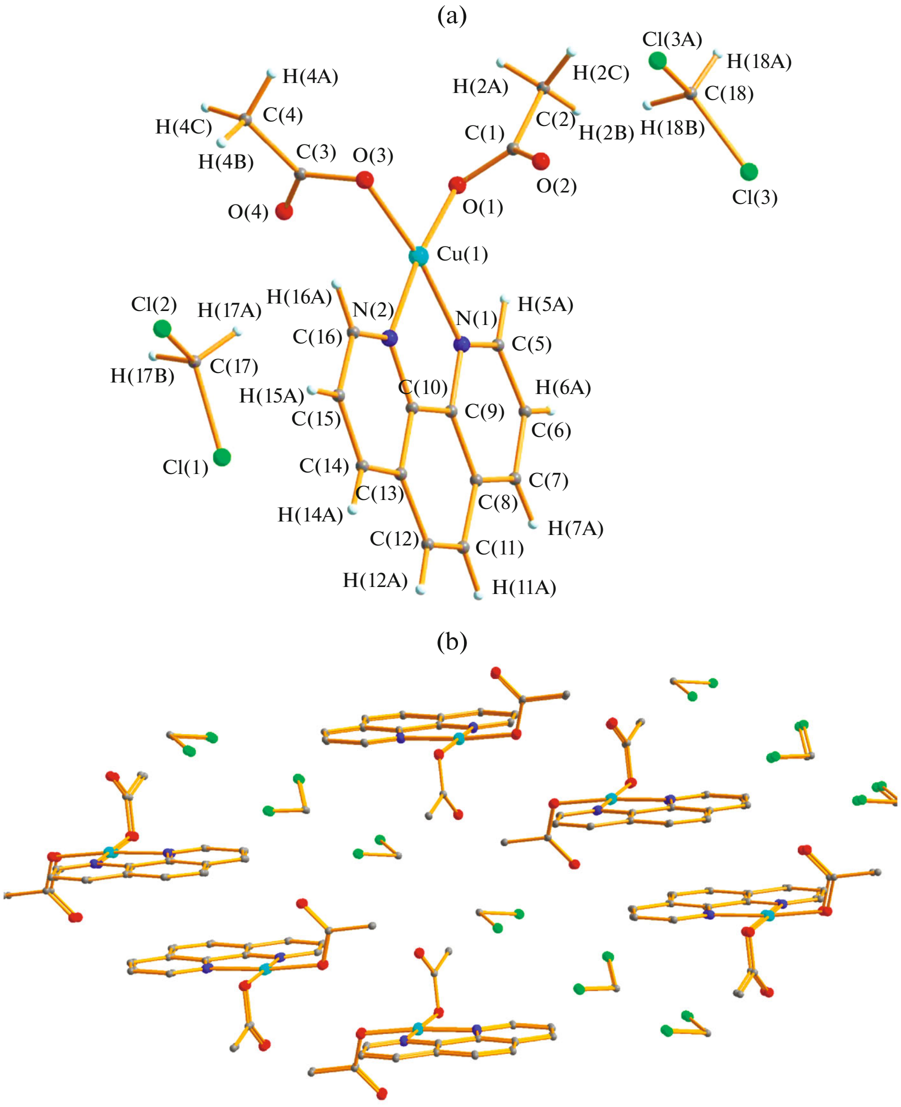

Fig. 2. (a) Structure of complex **II** and (b) fragment of molecular packing in the crystal of **II**; color of atoms: Cu is light blue, N is blue, O is red, Cl is green.

Blue anhydrous complexes of copper acetate with bipyridine and its analogues are known, but they are also formed in polar solvents [21–25].

The reaction of **II** with 2 moles of HDmpz at room temperature in dichloromethane affords blue complex PhenCu(OOCMe)$_2$HDmpz · 0.5H$_2$O · 0.5CH$_2$Cl$_2$ (IV) in 67% yield. According to X-ray diffraction data, a nitrogen atom of the molecule of the heterocycle in **IV** (Table 1, Fig. 4a) occupies the fifth site at the copper atom, like the water oxygen atom in complex **III**; as a result, copper has a distorted tetragonal pyramidal environment composed of two oxygen atoms of *trans*-arranged anions (Cu–O, 1.938(3), 2.208(4) and 1.948(4), 2.226(4) Å in two independent molecules) and three nitrogen atoms, two of which belong to Phen (Cu–N, 2.038(4), 2.067(4) and 2.027(4), 2.039(5) Å), while the thitd one is a part of coordinated pyrasol molecule (Cu–N, 1.999(4), 1.972(5) Å). The H atoms of the NH groups of heterocycles in two independent molecules form intramolecular hydrogen bonds with one of the acetate oxygen atoms (O···N, 2.618(5), 2.672(6)). The slight differences between the geometries of two independent molecules of **IV** are due to the asymmetric arrangement of the solvate molecules of water and dichloromethane (Fig. 4b). Like in **I**–**III**, the molecules are arranged in the crystal cell in pairs due to the π–π stacking contacts (Cu···Cu, 8.4056(9); C···C, 3.635–4.167 Å). These dimers are related by stacking contacts and alternate as Cu(1)–Cu(2)···Cu(2)–

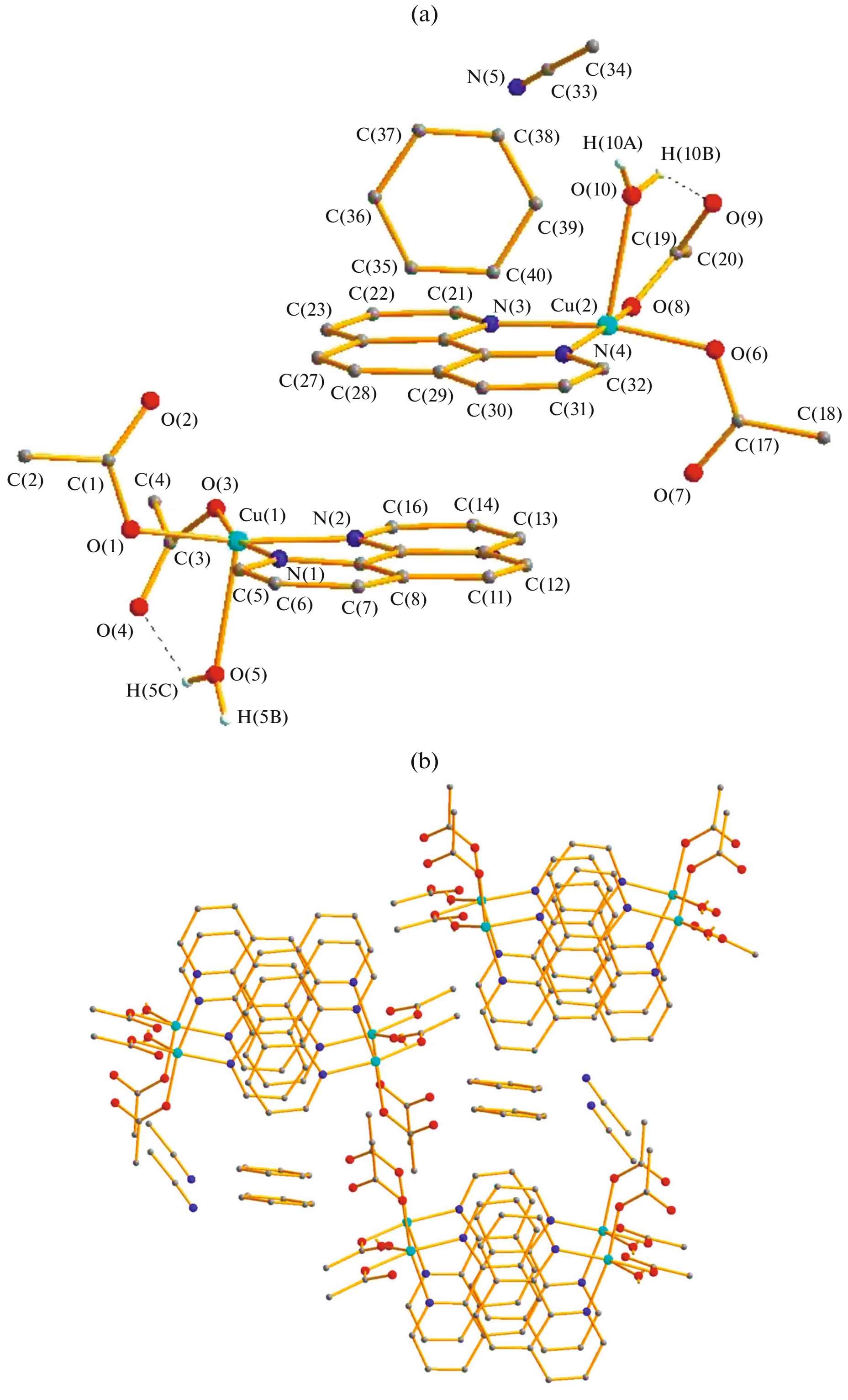

Fig. 3. (a) Structure of complex **III** and (b) fragment of molecular packing in the crystal of **III**; color of atoms: Cu is light blue, N is blue, O is red.

Cu(1)···Cu(1)–Cu(2) and so on, with the following distances between the copper atoms: Cu(1)···Cu(1), 8.3802(9); Cu(2)···Cu(2), 8.2811(9) Å. The shortest distance between the stack metal atoms is 9.352(1) Å.

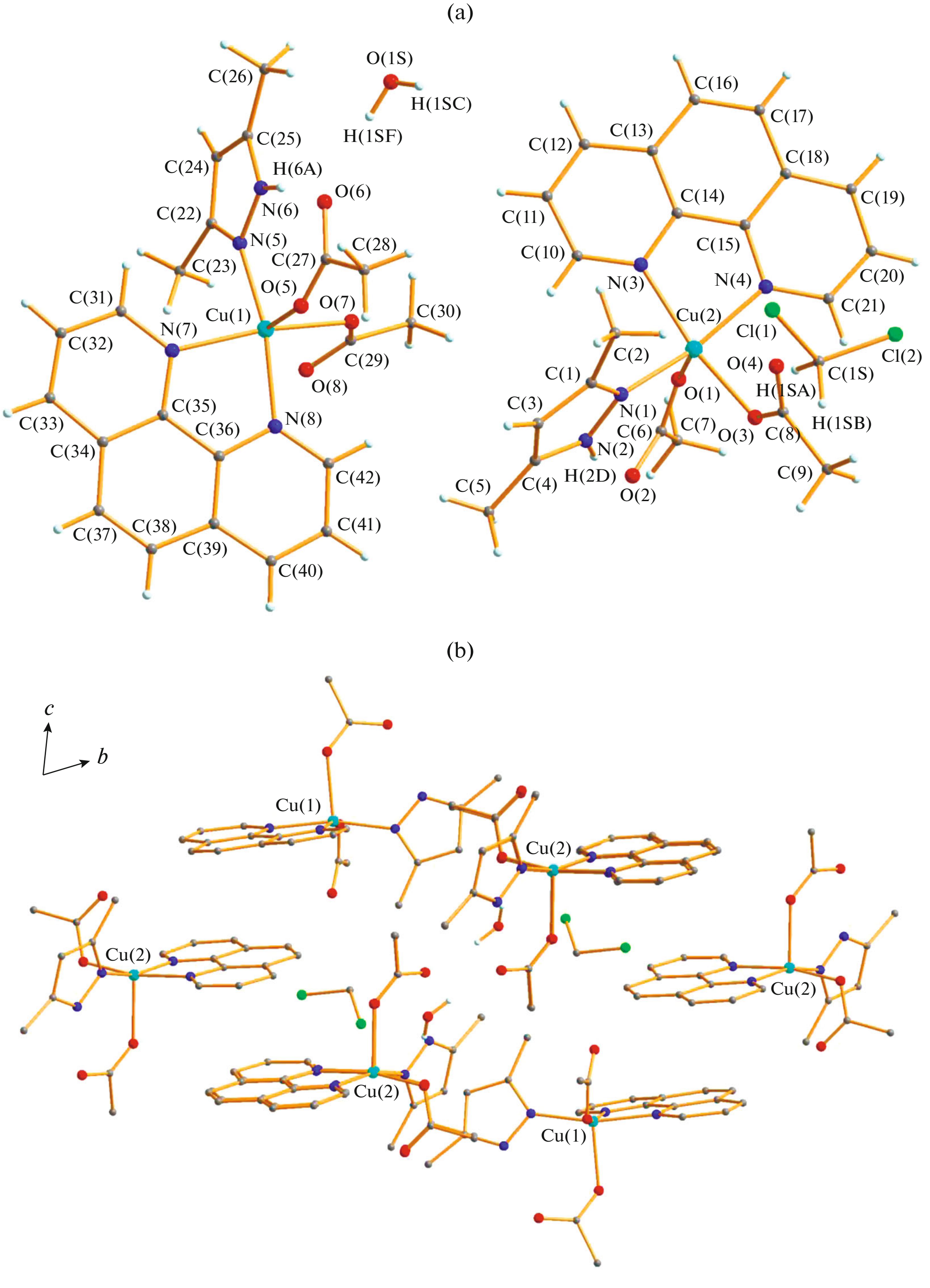

Fig. 4. (a) Structure of complex **IV** (two independent molecules) and (b) fragment of molecular packing in the crystal of **IV** along the *a* direction; color of atoms: Cl is green, N is blue, O is red, C is gray.

The hydrogen atoms of the solvation water molecule form bonds only with the anions that belong to Cu(2) copper atom (O(1S)···O(6), 2.826; O(1S)···O(7), 3.012 Å) and with a hydrogen atom of dichloromethane molecule (O(1S)···C(1S) 3.417 Å), the second hydrogen atom of which is bound to the Cu(1) atom anion (C(1S)···O(4), 3.276 Å) (Fig. 5).

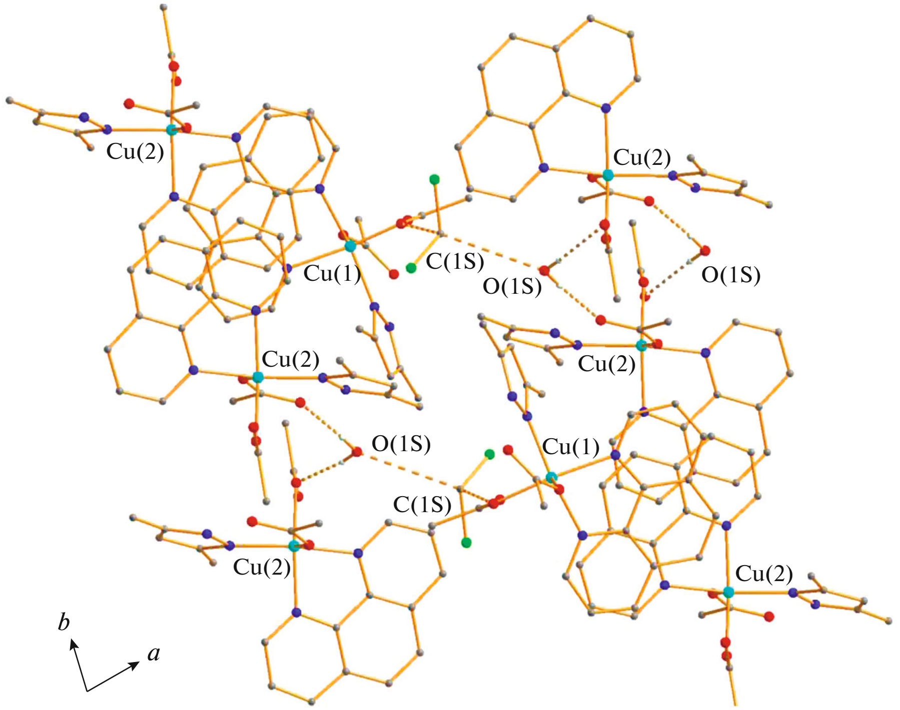

Fig. 5. Arrangement of molecules in the crystal of compound **IV** along the *c* direction. Intermolecular hydrogen bonds are shown by dashed lines; color of atoms: Cl is green, N is blue, O is red, C is gray.

The reaction of **I** with one mole of trifluoromethanesulfonic acid and the reaction of aqueous copper(II) acetate with two moles of HOtf followed by addition of Phen · H_2O in acetonitrile at room temperature give complex $PhenCu(OH_2)(NCMe)(Otf)_2$ (**V**) (81 and 93%, respectively). In complex **V**, the metal atom is surrounded by two nitrogen atoms of coordinated Phen (Cu–N, 1.9941(15), 1.9986(16) Å), acetonitrile nitrogen atom (Cu–N, 1.9730(16) Å), and water oxygen atom (Cu–O, 1.9713(13) Å). Oxygen of one of the triflate anions located most closely to copper is separated by a distance of 2.3826(15) Å; oxygen of the other triflate anion is at a distance of 2.6696(16) Å (Table 1, Fig. 6a).

Like in **I**–**IV**, the presence of Phen gives rise to stacking contacts, so that molecules in the crystal are packed in stacks (C···C, 3.341–4.025 Å). The H atoms of the water molecule are hydrogen-bonded to the Otf oxygen atoms (O(1)···O(5), 3.092; O(1)···O(6), 2.710; O(1)···O(7), 2.723 Å), thus forming the crystal (Fig. 6b).

There are known mononuclear phenanthroline and bipyridine complexes with copper(II) triflate, which were prepared in non-coordinating solvents and contained a water molecule; the geometry of the complexes virtually does not differ from that found for complex **V** [26, 27].

The reaction of **V** with HDmpz in dichloromethane at room temperature furnishes blue single crystals of complex $PhenCu(HDmpz)_2(Otf)_2$ (**VI**) in a virtually quantitative yield. According to X-ray diffraction, complex **VI** retains the square environment of the central copper(II) atom (Cu–N(HDmpz), 1.988(4), 2.008(3)Å; Cu–N(Phen), 2.019(3), 2.044(3) Å) with long contacts to the oxygen atoms of triflate anions (Cu(1)···O(1), 2.590(5); Cu(1)···O(4), 2.580(5) Å) (Table 1, Fig. 7a). These contacts are markedly elongated with respect to those in **V**, first of all, due to the steric interaction of the outer-sphere anions with the methyl groups of coordinated HDmpz molecules. Only one oxygen atom of the Otf anion forms hydrogen bonds with the heterocycle NH group (O(2)···N(4), 2.816; O(6)···N(2), 2.857 Å). Although all coordinated Phen ligands are parallel, no stacking contacts are present in the crystal (Fig. 7b).

Thus, it was shown that the nature of anion present in the coordination compounds plays a significant role in the interaction with donor molecules, in particular, with heterocyclic 3,5-dimethylpyrazole; the anions of strong acids are displaced into the outer sphere during the reactions, thus leaving free coordination sites, while the anions of weaker acids remain bound to the metal atoms, so that donor molecules are coordinated

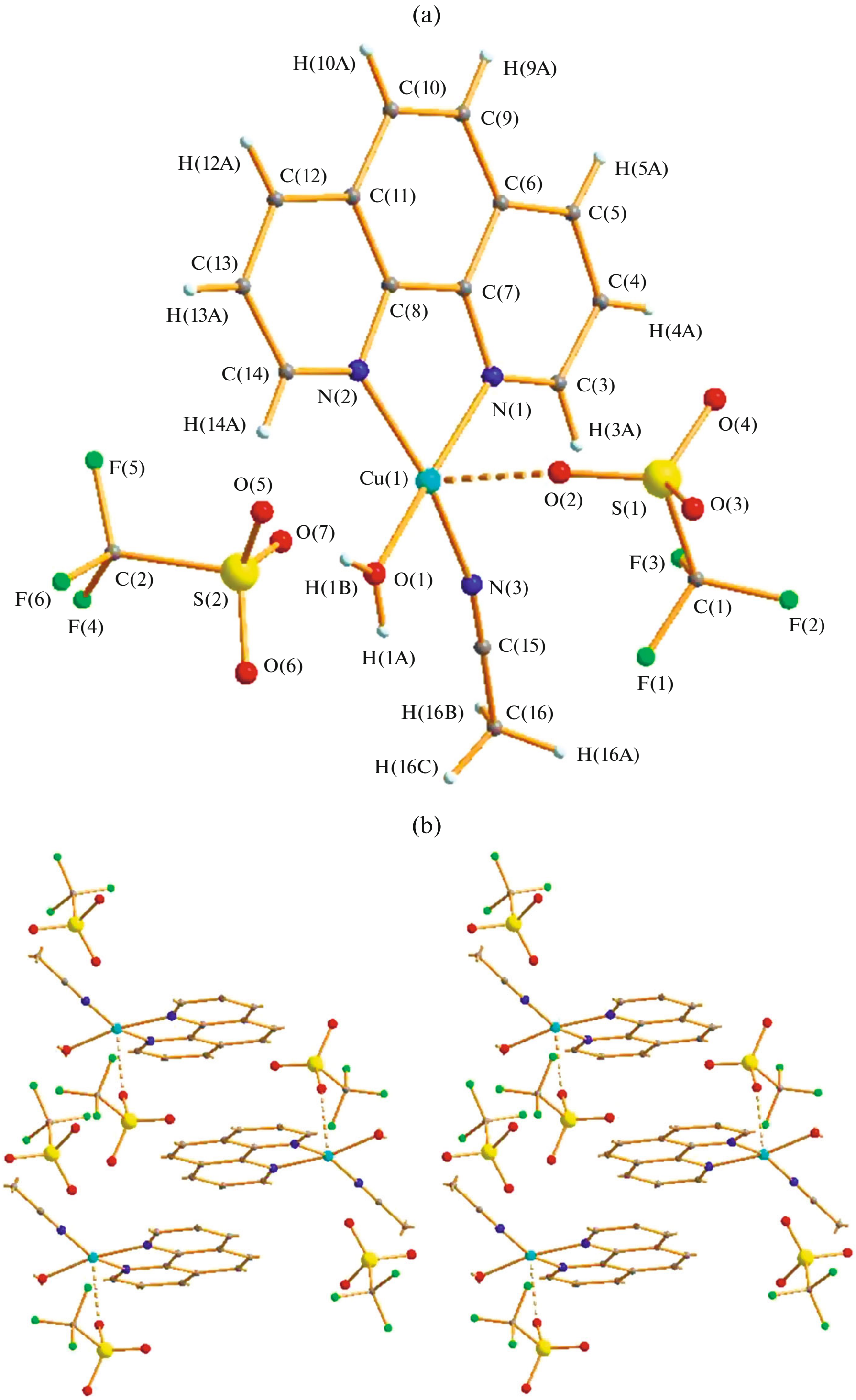

Fig. 6. (a) Structure of complex **V** and (b) molecular packing in the crystal of **V**; color of atoms: Cu is light blue, N is blue, O is red, C is gray.

at the free orbitals. The nature of the solvent (polarity, the presence of donor atoms, the possibility of hydrogen bonding) used to conduct the reactions and grow single crystals is also an important factor, which considerably affects not only the packing of molecules in the crystal cell of complex compounds, but also the geometry of the complex, which is important for understanding their physicochemical properties.

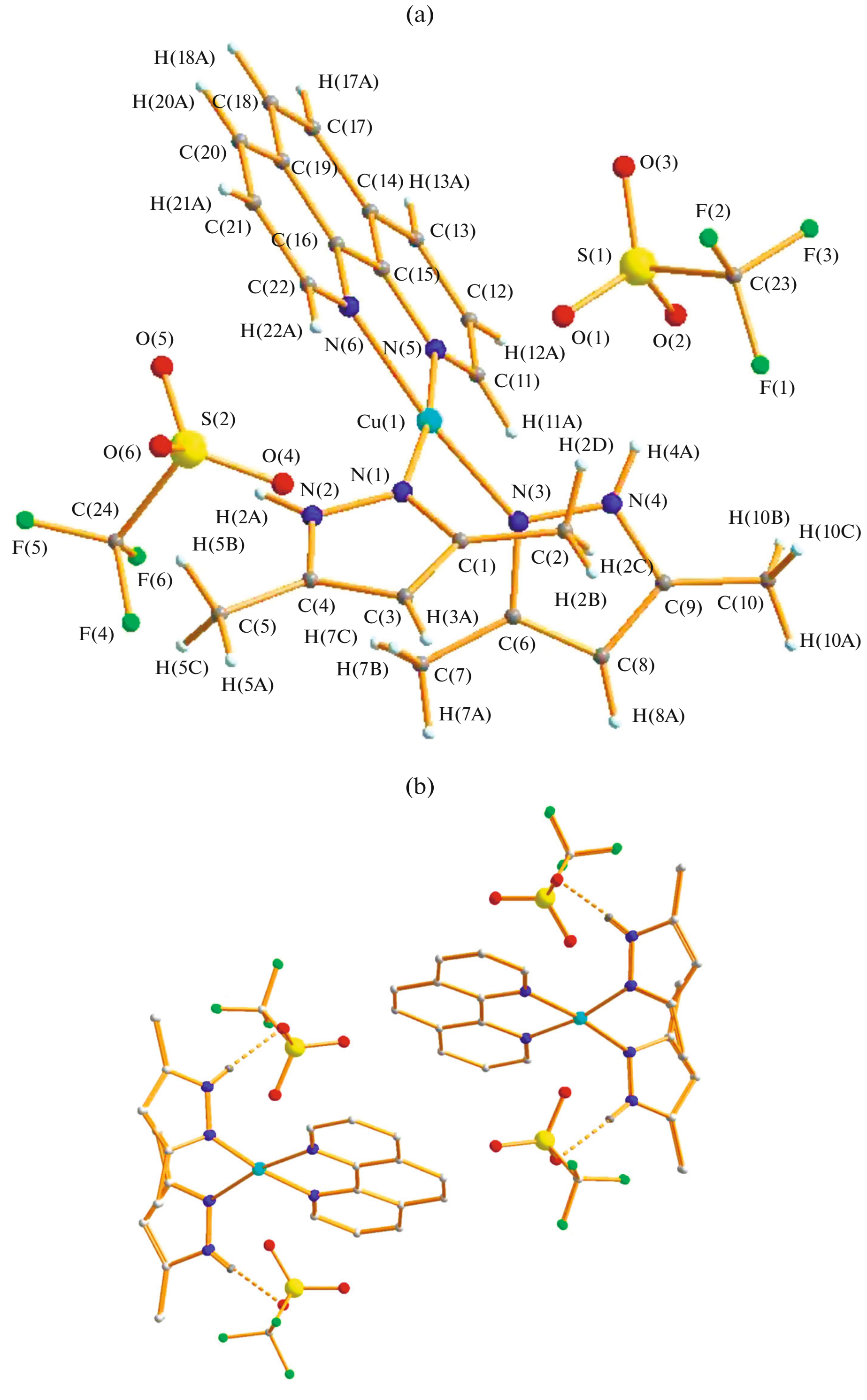

Fig. 7. (a) Structure of complex **VI** and (b) fragment of molecular packing in the crystal of **VI**.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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