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Crystal Structure of the Polymer Copper(II) Complex with 1-Phenyl-3-Methyl-4-Formyl-5-Hydroxypyrazole Hetarylhydrazone

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Abstract—A new coordination polymer of Cu(II) based on 1-phenyl-3-methyl-4-formyl-5-hydroxypyrazole 4,6-dimethylpyrimidylhydrazone is synthesized. The polymer is studied by X-ray diffraction analysis (CIF file CCDC no. 1565772). It is shown that the polymer is formed due to the coordination of the nitrogen atom of the pyrazolone fragment to the copper(II) ion of the adjacent monomeric fragment.

Keywords: coordination compounds, coordination polymers, X-ray diffraction analysis

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INTRODUCTION

The study of supramolecular and polymer compounds based on transition metal complexes with polydentate ligand systems is one of the tasks of the modern coordination chemistry, since these compounds are significant for the production of magnetically active, optic, and catalytic materials [1–5]. However, the process of self-assembling and structures of coordination polymers depend on many factors, first of all, on the nature of complexing metal and structural features of the ligand system. To obtain polymer complexes, the ligand should have a wide set of donor atoms, an appropriate arrangement of functional groups, and the capability of changing denticity depending on the reaction conditions. Among these compounds are acylhydrazones of 4-acylpyrazolone derivatives, and their structures and coordination modes in complexes are studied in rather detail [6–13]. Various supramolecular complexes were obtained on the basis of these ligand systems, and the dimensionality (1D, 2D, or 3D) of their polymer chain is determined by the nature of O–H···O and N–H···O intermolecular hydrogen bonds [7, 10, 11, 13]. Unlike supramolecular compounds, the copper(II) coordination polymers based on hydrazones of 4-acylpyrazolone in which the monomeric moieties are linked due to the coordination of one of the donor atoms of the ligand system to the metal ion of the adjacent fragment are met rarely [14–16]. For the further study of the influence of the structural features of the pyrazolone derivatives on the structures of the coordination compounds, we synthesized new hetarylhydrazone (H_2L), which is the condensation product of 1-phenyl-3-methyl-4-formyl-5-hydroxypyrazole and 2-hydrazino-4,6-pyrimidine, and the related polymer copper(II) complex (**I**). The X-ray diffraction data on the structure of this coordination polymer are reported.

EXPERIMENTAL

1-Phenyl-3-methyl-4-formyl-5-hydroxypyrazole was synthesized according to a described procedure [17]. 2-Hydrazino-4,6-dimethylpyrimidine was obtained using a known procedure [18].

Synthesis of hetarylhydrazone H_2L. A solution of 1-phenyl-3-methyl-4-formyl-5-hydroxypyrazole (1 mmol) in isopropanol (5 mL) was added to a hot solution of 2-hydrazino-4,6-dimethylpyrimidine (1 mmol) in isopropanol (5 mL) to form a yellow solution. A yellow precipitate was formed in 15 min. The reaction mixture was heated with a reflux condenser for 3 h and left to stay overnight. The precipitate was filtered off and recrystallized from an ethanol–dimethylformamide (3 : 1) mixture. The yield of the yellow amorphous precipitate was 49%; mp = 130°C.

For $C_{17}H_{18}N_6O$

Anal. calcd., %	C, 63.34	H, 5.63	N, 26.07
Found, %	C, 63.1	H, 5.7	N, 26.2

IR (ν, cm^{-1}): 3337, 3163 ν(NH), 1663 (C=O), 1572, 1538 ν(C=N).

Table 1. Crystallographic data and experimental and refinement characteristics for compound **I**

Parameter	Value
FW	516.40
Crystal size, mm	0.31 × 0.30 × 0.29
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	12.0180(5)
b, Å	11.5298(5)
c, Å	15.1489(6)
β, deg	91.879(3)
V, Å^3	2097.99(14)
Z	2
ρ_{calc}, g/cm^3	1.632
μ, mm^{-1}	1.218
F(000)	1056
Scan range over θ, deg	1.67–26.15
Number of measured reflections	8459
Number of independent reflections	4123
Number of reflections with $I > 2\sigma(I)$	3252
Ranges of reflection indices	$-14 \le h \le 14$, $-11 \le k \le 14$, $-18 \le l \le 18$
Number of refined parameters	289
R_1 ($I > 2\sigma(I)$)	0.0414
wR_2 (all reflections)	0.0567
GOOF (all reflections)	1.025
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.538/–0.496

^{1}H NMR (DMSO-d_6), δ, ppm: 2.2 (s, 6H, 2CH_3), 2.3 (s, 3H, CH_3), 6.5 (s, 1$H_{pyrimid}$), 7.2–8.0 (m, 5H_{ap}), 8.10 (s, 1H, =CH–N), 10.0 (s, 1H, NH), 15.0 (s, 1H, NH).

Synthesis of complex I. A hot solution of copper(II) perchlorate (1 mmol) in methanol (10 mL) was added to a hot solution of ligand H_2L (1 mmol) in methanol (10 mL). The obtained solution was refluxed for 4 h and left overnighed. The precipitate was filtered off and recrystallized from methanol. The yield of dark brown crystals was 57%; mp > 250°C.

IR (ν, cm^{-1}): 3406 ν(CH_3OH), 3249 ν(NH), 1623, 1606, 1571 ν(C=N), 1235 ν(C–O), 1112 ν(ClO_4).

For $C_{18}H_{21}N_6O_6ClCu$

Anal. calcd., %	C, 41.87	H, 4.10	Cu, 12.31	N, 16.27
Found, %	C, 41.6	H, 4.5	Cu, 12.1	N, 16.5

IR spectra were recorded on a Varian Scimitar 1000 FT-IR instrument in a range of 400–4000 cm^{-1} for samples prepared as a suspension in Nujol. Elemental analysis was carried out on a PerkinElmer 240C instrument at the Laboratory of Microanalysis of the Southern Federal University.

X-ray diffraction analysis of complex **I** was carried out at 150.0(1) K on an Xcalibur Eos type automated diffractometer (MoK_α radiation, graphite monochromator). The structure was solved by a direct method and refined by full-matrix least squares in the anisotropic approximation for nonhydrogen atoms for F^2_{hkl}. The structure was decoded and refined using the SHELXTL program [19]. The experimental characteristics and crystallographic data are presented in Table 1. Selected interatomic distances and bond angles are given in Table 2.

The description of the experiment, coordinates of atoms, and temperature factors were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1565772; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Table 2. Selected interatomic distances (Å) and bond angles (ω) in the coordination polyhedra of the copper atoms in a molecule of compound **I**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(1)	1.927(2)	Cu(1)–N(2*A*)	2.058(2)
Cu(1)–O(2)	2.158(2)	O1(2)–C(7)	1.280(4)
Cu(1)–N(3)	2.001(2)	C(8)–C(11)	1.417(4)
Cu(1)–N(6)	2.012(2)	N(3)–C(11)	1.929(3)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)Cu(1)N(6)	173.34(9)	N(6)Cu(1)N(3)	80.83(9)
O(1)Cu(1)N(3)	93.42(9)	N(6)Cu(1)N(2*A*)	95.85(9)
O(1)Cu(1)N(2*A*)	90.29(9)	N(6)Cu(1)O(2)	93.94(9)
O(1)Cu(1)O(2)	86.33(8)	C(18)O(2)Cu(1)	125.45(19)
O(2)Cu(1)N(3)	122.65(9)	N(3)Cu(1)N(2*A*)	127.24(9)

RESULTS AND DISCUSSION

The reaction of 1-phenyl-3-methyl-4-formyl-5-hydroxypyrazole 4,6-dimethylpyrimidylhydrazone with copper(II) perchlorate in methanol afforded polymer complex **I** with the monomeric fragment [Cu(HL)(CH$_3$OH)]ClO$_4$, where HL is the monodeprotonated tridentate form of the ligand.

The structure and enumeration of atoms of the independent moiety of the polymer complex are shown in Fig. 1 along with the atoms of the adjacent molecules involved in the formation of the polymer structure: Cu(1*A*) and N(2*A*) ($1/2 - x$, $-1/2 + y$, $1/2 - z$).

The initial unit of the structure of compound **I** is the mononuclear cationic copper(II) complex [Cu(HL)(CH$_3$OH)]$^+$. The coordination polyhedron of the copper atom is close to a trigonal bipyramid, which is indicated by the value of Addison's τ descriptor [20] equal to 0.77 and the values of angles between the coordination bonds (see Table 2). The N(3) atom of hydrazone fragment HL, the N(2*A*) atom of the pyrazolone cycle of the adjacent molecule, and the O(2) atom of the coordinated methanol molecule are arranged in the equatorial positions. The O(1) atom of the pyrazolone fragment and N(6) of the pyrimidine fragment of the organic ligand occupy the axial vertices of the bipyramid (the O(1)Cu(1)N(6) angle is 173.3°).

The polymer structure of the compound is formed due to the coordination of the N(2) atom of the pyrazolone cycle of the cationic complex to the equatorial position of the copper(II) ion of the adjacent molecule. This becomes possible because of the turn of the N-phenyl substituent of the pyrazolone fragment relative to the plane of the pyrazole cycle by 68.13(16)°. The length of the corresponding Cu(1)–N(2*A*) coordination bond is 2.058(2) Å. The formation of infinite chains is shown in Fig. 2.

The structural translational unit in the polymer chain is the angular dimeric fragment due to which infinite zigzag stacks of molecules parallel to the crystallographic axis *b* are formed. In turn, the stacks of molecules are linked by intermolecular hydrogen bonds involving the perchlorate anions to form infinite extended layers oriented along the vector [1, 0, 1] (Fig. 3). The infinite chains and ClO$_4^-$ anions are arranged in the unit cell in such a way that the O(5) atom of each chain forms two hydrogen bonds O(5)···H(4)–N(4) with the hydrazone fragment of the complex and the O(5)···H(1)$^{\text{i}}$–O(2)$^{\text{i}}$ bond with the coordinated methanol molecule (i: $1 - x$, $2 - y$, $1 - z$). The oxygen atom of the perchlorate anion O(5)$^{\text{i}}$ in the adjacent crystallographic position form equivalent bonds O(5)$^{\text{i}}$···H(4)$^{\text{i}}$–N(4)$^{\text{i}}$ with the complex in the position (i) and O(5)$^{\text{i}}$···H(1)–O(2) with the methanol molecule in the starting position. Thus, the centrosymmetric cycles formed by hydrogen bonds and including two complexes and two perchlorate anions are formed. The geometric characteristics of the hydrogen bonds are presented in Table 3.

The hydrogen bonds between the adjacent stacks of the complexes are formed via the same mechanism at both sides from each stack alternating at one monomeric unit in the chain of the coordination polymer.

It should be mentioned that the hydrazone and Schiff derivatives of 4-acylpyrazolone rather rarely participate in the coordination of the copper atoms by the nitrogen atom of the pyrazole cycle in spite of a significant number of structurally characterized complexes with ligands of this type. Presently, the Cambridge Structural Database (CSD) [21] contains only seven structures with a similar coordination mode of which five structures are coordination polymers and two compounds are molecular structures [14–16, 22]. In the majority of cases, the nitrogen atom of the pyrazole cycle is coordinated in the equatorial plane of

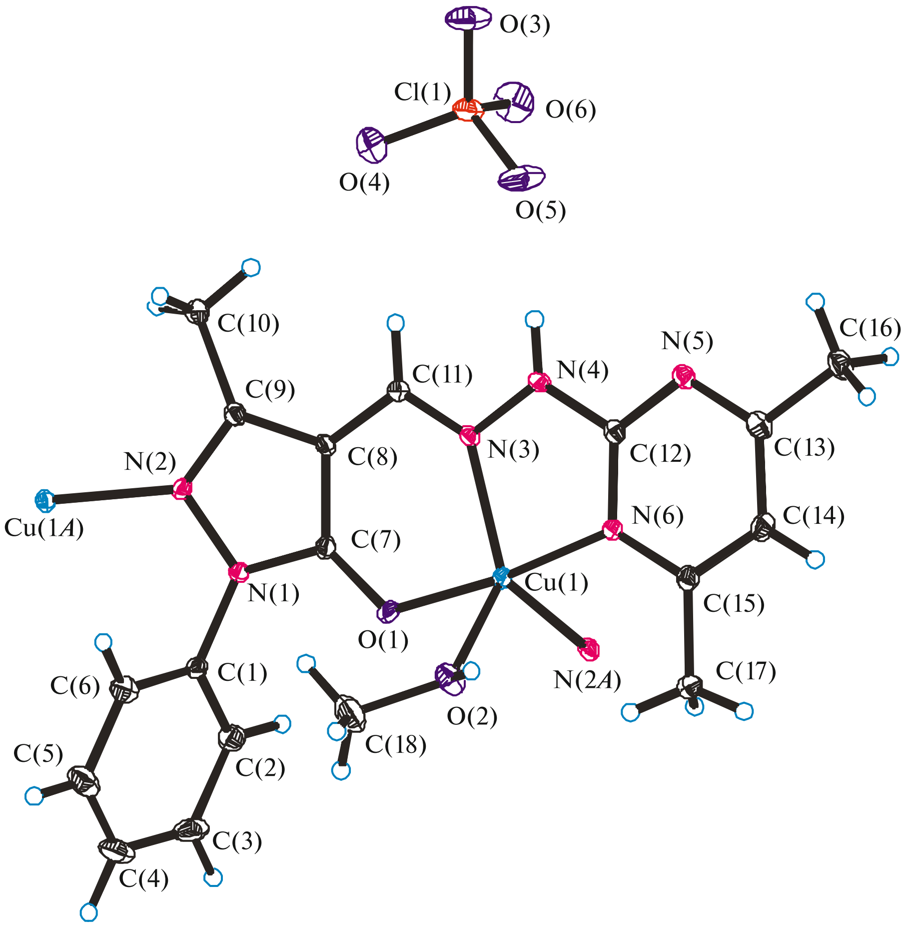

Fig. 1. Structure of the monomeric moiety of complex **I**; the Cu(1*A*) and N(2*A*) atoms (symmetry transform: 1/2 – *x*, –1/2 + *y*, 1/2 – *z*) involved in the formation of the polymer structure are shown.

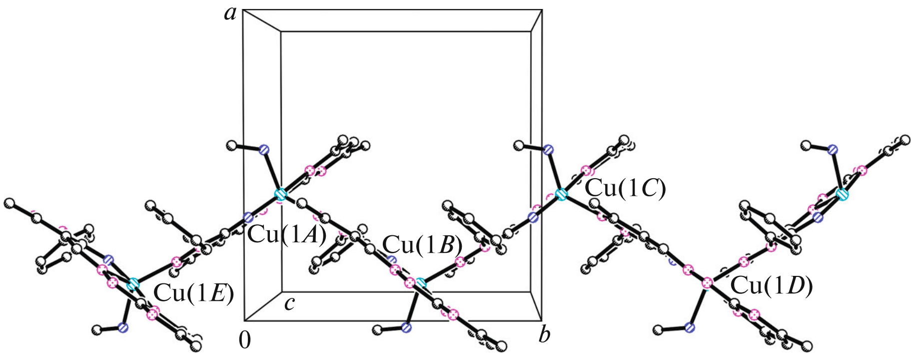

Fig. 2. Polymer structure in the crystal of compound **I**.

the square or square bipyramidal coordination polyhedron of the copper(II) ion. The polymer Cu(II) complexes with 1-phenyl-3-methyl-4-formylpyrazolone-5 quinolylhydrazone [Cu(HL^1)(EtOH)]NO_3 (CSD code ZAXLAO) and 1-phenyl-3-methyl-4-formylpyrazolone-5 2-benzthiazolylhydrazone [Cu(HL^2)(MeOH)-]ClO_4 (ZAXKUH) described earlier [14] are close in structure to complex **I**. The square bipyramidal coordination of the Cu(II) atom also takes place in the case of these compounds. Compound **I** is distinguished by

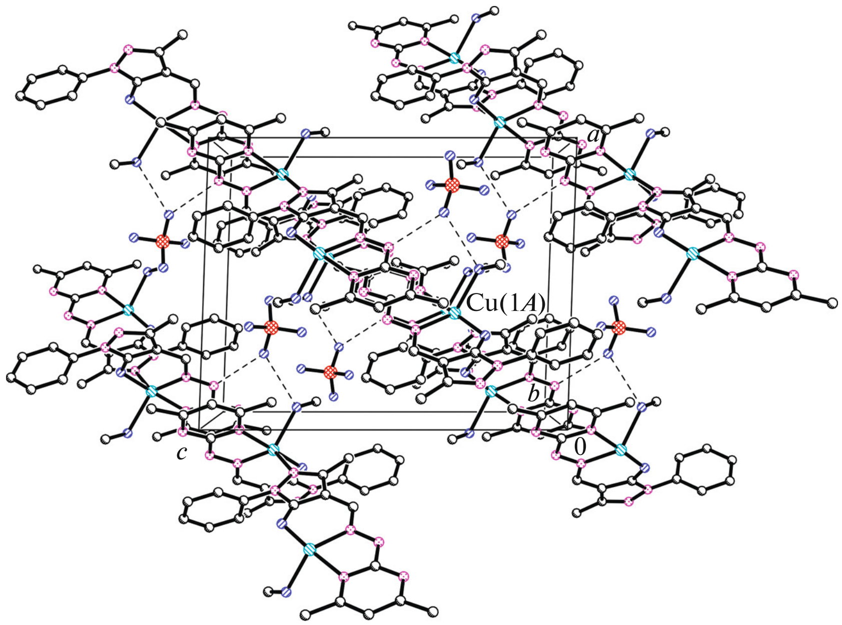

Fig. 3. Fragment of the projection of the crystal structure of complex **I** along the crystallographic axis b (axis c is horizontal); hydrogen bonds involving perchlorate anions are shown by dashed lines.

Table 3. Geometric parameters of hydrogen bonds in the crystal structure of compound **I***

D···H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
O(2)–H(1)···O(5)^{i} O(5)···H(1)^{i}–O(2)^{i}	0.96	1.84	2.772(3)	165
O(5)···H(4)^{i}–N(4)^{i} N(4)–H(4)···O(5)^{i}	0.86	2.03	2.850(3)	159

* Crystallographic position: ^{i} $1 - x, 2 - y, 1 - z$.

the shortest coordination bond (2.058(2) Å) between the monomers compared to distances of 2.101 and 2.093 Å for ZAXLAO and ZAXKUH, respectively.

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