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Copper(II) Complexes with Bis(4-Iodo-3,5-Dimethylpyrazol-1-yl)methane: Synthesis, Spectroscopic Study, and Crystal Structure

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Abstract—New complexes of copper(II) nitrate, chloride, tetrafluoroborate, perchlorate, and perrhenate with bis(4-iodo-3,5-dimethylpyrazol-1-yl)methane (L) were obtained. The molecular and crystal structures of $[CuL(H_2O)(NO_3)_2] \cdot (CH_3)_2CO$, $[CuL_2(H_2O)][CuL_2Cl][CuCl_4]$, $[CuL_2](BF_4)_2 \cdot (CH_3)_2CO$, and $[CuL_2(H_2O)](ClO_4)_2 \cdot (CH_3)_2CO$ were determined by X-ray diffraction analysis. In all the complexes, L was found to serve as a chelating bidentate ligand through the N^2 and $N^{2'}$ atoms of its pyrazole rings to form a six-membered chelate ring.

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Bis(pyrazol-1-yl)alkanes [1] are widely used in coordination and bioinorganic chemistry. The synthesis of complexes with these ligands promotes the development of biomimetic coordination chemistry. For instance, copper complexes with bis(pyrazol-1-yl)methane derivatives exhibit pronounced antioxidant activity. Like copper-containing superoxide dismutase, they catalyze the decomposition of toxic superoxide radical ($O_2^{\cdot-}$) to molecular oxygen and hydrogen peroxide [2]. Copper-containing enzymes catalyze the decomposition of $O_2^{\cdot-}$ through the reduction and oxidation of the active sites of copper:

$$\text{E–Cu(II)} + O_2^{\cdot-} + H^+ \rightleftharpoons \text{E'–Cu(I)} + O_2,$$

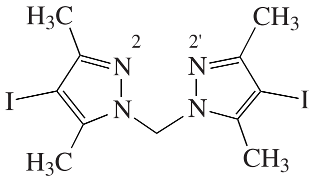
$$\text{E'–Cu(I)} + O_2^{\cdot-} \rightleftharpoons \text{E–Cu(II)} + H_2O_2.$$

Transition metal complexes are structural and spectroscopic models of the oxygenate forms of proteins responsible for oxygen transportation, binuclear centers of metal proteins containing oxygen bridges, active sites of "blue" or type 1 cupredoxins [3–7].

In addition, bis(pyrazol-1-yl)alkanes derived from chiral pyrazoles are active as chiral catalysts [8].

The physicochemical studies (including X-ray diffraction analysis) of metal complexes with bis(pyrazol-1-yl)alkanes revealed that the ligand is mainly coordinated in a chelating bidentate fashion to form a six-membered chelate ring [9–13].

Earlier, we have synthesized and studied complexes of cobalt(II) iodide with bis(3,5-dimethylpyrazol-1-yl)methane [14] and a number of complexes of copper(II) with bis(pyrazol-1-yl)methane, bis(4-bromo-3,5-dimethylpyrazol-1-yl)methane, and bis(4-iodo-3,5-dimethylpyrazol-1-yl)methane [15]. Proceeding further in our investigations, here we obtained and studied (using X-ray diffraction analysis) complexes of various copper(II) salts with bis(4-iodo-3,5-dimethylpyrazol-1-yl)methane (**L**):



(L)

EXPERIMENTAL

Complexes were synthesized from $Cu(NO_3)_2 \cdot 3H_2O$, $CuCl_2 \cdot 2H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, $Cu(BF_4)_2 \cdot 6H_2O$, and $NaReO_4$ (all high-purity grade). Bis(4-iodo-3,5-dimethylpyrazol-1-yl)methane was prepared by iodination of

Table 1. Compositions and elemental analysis data for complexes **III**–**V**

Complex	Content (found/calculated), %			
	C	H	N	M
$[CuL_2](BF_4)_2 \cdot (CH_3)_2CO$ (**III**)	25.0/24.9	2.8/2.8	9.3/9.3	5.4/5.3
$[CuL_2(H_2O)](ClO_4)_2 \cdot (CH_3)_2CO$ (**IV**)	24.4/24.0	3.0/2.9	8.9/9.0	5.1/5.1
$[CuL_2(H_2O)](ReO_4)_2 \cdot (CH_3)_2CO$ (**V**)	17.2/17.7	2.0/2.0	7.1/7.5	4.1/4.2

bis(3,5-dimethylpyrazol-1-yl)methane with a mixture of iodine and iodic acid as described in [16], T_m = 184–185.5°C (cf. [16]: T_m = 183–184°C).

Synthesis of $[CuL(H_2O)(NO_3)_2] \cdot (CH_3)_2CO$ (I). Cupric nitrate trihydrate (0.48 g, 2 mmol) was dissolved in acetone (7 ml) and added to the ligand (0.23 g, 0.5 mmol) in acetone (12 ml) while stirring the mixture with a magnetic stirring bar. The bright green solution was left in air at room temperature. Slow crystallization gave green single crystals of complex **I** suitable for X-ray diffraction analysis. The composition of the polycrystalline phase obtained in this reaction corresponds to $Cu(L)(NO_3)_2$ structurally characterized in [15].

Synthesis of $[CuL_2(H_2O)][CuL_2Cl][CuCl_4]$ (II). Cupric chloride dihydrate (0.10 g, 0.6 mmol) was dissolved in acetone (5 ml) and added to the ligand (0.14 g, 0.3 mmol) in acetone (10 ml) while stirring the mixture with a magnetic stirring bar. The resulting red-brown solution was left at room temperature for a week. Slow crystallization gave green single crystals of complex **II** suitable for X-ray diffraction analysis. Attempted isolation of the individual polycrystalline complex from the solutions gave a mixture of phases (X-ray diffraction data).

Synthesis of $[CuL_2](BF_4)_2 \cdot (CH_3)_2CO$ (III). Cupric tetrafluoroborate hexahydrate (0.35 g, 1 mmol) was dissolved in ethanol (5 ml) and added to a stirred solution of the ligand (0.23 g, 0.5 mmol) in acetone (12 ml). The resulting mixture was left for a week. Slow crystallization gave a crystalline precipitate of complex **III**, which was filtered off, washed with acetone and ethanol, and dried in air. A similar treatment was applied to all the precipitates obtained in our experiments. The crystals of complex **III** were suitable for X-ray diffraction analysis. The yield was 0.24 g (76%).

Synthesis of $[CuL_2(H_2O)](ClO_4)_2 \cdot (CH_3)_2CO$ (IV).[1] Cupric perchlorate hexahydrate (0.37 g, 1 mmol) was dissolved in ethanol (6 ml) and added to a stirred solution of the ligand (0.23 g, 0.5 mmol) in acetone (12 ml). The resulting mixture was left for a week. Slow crystallization gave single crystals of complex **IV** suitable for X-ray diffraction analysis. The yield was 0.19 g (60%).

Synthesis of $[CuL_2(H_2O)](ReO_4)_2 \cdot (CH_3)_2CO$ (V). A hot solution of $NaReO_4$ (0.83 g, 3 mmol) in ethanol–water (1 : 1, 15 ml) was added to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.24 g, 1 mmol) in ethanol (6 ml). The solution was concentrated on a water bath to one third of the initial volume and added to a solution of the ligand (0.23 g, 0.5 mmol) in acetone (12 ml). The light green precipitate that formed was filtered off. The yield was 0.35 g (94%).

The metal content of complexes **III**–**V** was determined by complexometric titration of samples decomposed by heating in a mixture of concentrated H_2SO_4 and $HClO_4$ (1 : 2). The C, H, and N contents were determined at the Laboratory of Microanalysis of the Novosibirsk Institute of Organic Chemistry (Siberian Division, Russian Academy of Sciences) on a Carlo Erba analyzer according to a standard procedure. The compositions and elemental analysis data for complexes **III**–**V** are given in Table 1. The number of acetone molecules of crystallization was determined by TGA. TG curves were recorded in air in quartz crucibles on a Paulik–Paulik–Erdey derivatograph (heating rate 2.5 K/min, Al_2O_3 as a standard, sample weights 50 mg).

X-ray diffraction analysis of complexes I–IV was performed according to a standard procedure on a Bruker-Nonius X8Apex CCD automated four-circle diffractometer at room temperature (MoK_αradiation, λ = 0.71073 Å, graphite monochromator). Crystallographic parameters and a summary of data collection are given in Table 2. The reflection intensities were measured in the φ- and ω scan modes (scan step 0.5°, 2θ = 50°). Absorption correction was applied empirically with the SADABS program [17]. Structures **I**–**IV**

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[1] Be very careful while using perchlorate as an anion!

Table 2. Crystallographic parameters and a summary of data collection for structures **I–IV**

Parameter	Value			
	I	**II**	**III**	**IV**
Empirical formula	$C_{14}H_{22}CuI_2N_6O_8$	$C_{44}H_{58}Cl_5Cu_3I_8N_{16}O$	$C_{25}H_{34}B_2CuF_8I_4N_8O$	$C_{25}H_{36}Cl_2CuI_4N_8O_{10}$
M	719.72	993.04	1207.36	1250.66
T, K	150.0(2)	293(2)	296(2)	150.0(2)
Crystal system	Triclinic	Hexagonal	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$P6_522$	$Pnma$	$Cmc2_1$
a, Å	10.1154(4)	16.7947(3)	24.0346(13)	16.4299(14)
b, Å	11.2639(6)	16.7947	16.0407(8)	13.7036(10)
c, Å	11.3527(6)	44.4962(15)	9.6926(5)	16.7987(16)
α, deg	69.5240(10)	90	90	90
β, deg	74.6990(10)	90	90	90
γ, deg	83.560(2)	120	90	90
V, Å^3	1168.55(10)	10869.2(5)	3736.8(3)	3782.2(6)
Z	2	6	4	4
ρ(calcd), g/cm^3	2.045	2.026	2.146	2.196
μ, mm^{-1}	3.627	4.508	3.963	4.045
F(000)	694	6228	2284	2388
Crystal size, mm	$0.14 \times 0.10 \times 0.07$	$0.10 \times 0.10 \times 0.02$	$0.06 \times 0.06 \times 0.05$	$0.20 \times 0.18 \times 0.03$
θ scan range, deg	1.93–27.50	1.47–25.00	1.69–26.37	1.94–26.37
Ranges of h, k, and l indices	$-8 \le h \le 13$	$-15 \le h \le 19$	$-28 \le h \le 30$	$-20 \le h \le 19$
	$-14 \le k \le 14$	$-19 \le k \le 19$	$-19 \le k \le 20$	$-17 \le k \le 11$
	$-14 \le l \le 14$	$-51 \le l \le 52$	$-9 \le l \le 12$	$-21 \le l \le 21$
Number of measured reflections	8984	56721	24972	13296
Number of independent reflections	5279 ($R_{int} = 0.0184$)	6372 ($R_{int} = 0.0789$)	3953 ($R_{int} = 0.0361$)	4001 ($R_{int} = 0.0201$)
Number of reflections with $I \ge 2\sigma(I)$	4447	4294	3272	3836
Number of parameters refined	294	357	238	272
GOOF	1.066	0.967	1.082	1.032
R_1 ($I > 2\sigma(I)$)	0.0536	0.0743	0.0376	0.0166
wR_2 (for all reflections)	0.1821	0.2207	0.0949	0.0413
Residual electron density (min/max), e Å^{-3}	–1.878/0.236	–1.617/0.752	–1.117/0.133	–0.395/0.072
Flack parameter		0.02(7)		0.000(17)

were solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms with the SHELX-97 program package [18]. The hydrogen atoms of the organic ligands in all structures were located geometrically, except for the H atoms of coordinated water molecules in structures **I** and **IV**. They were found from the difference electron-density map and refined with fixed thermal parameters. In structure **II**, the Cl atom and the water O atom both coordinated to copper share the same position with a 50% probability. Since the positions of these atoms were not separated, they were refined with shared coordinates and thermal parameters. The hydrogen atoms of the water molecule were not located.

Atomic coordinates and thermal parameters for structures **I–IV** have been deposited with the Cambridge Crystallographic Data Collection (nos. 687544–687547, respectively). Selected bond lengths and angles in structures **I–IV** are given in Tables 3–6. The

Table 3. Selected bond lengths and angles in structure **I**

Bond	d, Å	Bond	d, Å	Angle	ω, deg
Cu(1)–O(1l)	2.144(5)	C(3)–C(4)	1.407(8)	N(1)Cu(1)O(1l)	100.9(2)
Cu(1)–N(1)	2.055(5)	C(3)–I(2)	1.959(6)	N(4)Cu(1)O(1l)	92.3(2)
Cu(1)–N(4)	2.006(5)	C(4)–C(41)	1.478(8)	N(4)Cu(1)N(1)	88.98(19)
Cu(1)–O(1n)	1.956(5)	C(5)–C(6)	1.419(8)	N(4)Cu(1)O(4n)	90.58(19)
Cu(1)–O(4n)	2.026(4)	C(5)–C(51)	1.491(8)	O(1n)Cu(1)O(1l)	85.8(2)
N(1)–N(2)	1.368(6)	C(6)–C(7)	1.383(8)	O(1n)Cu(1)N(1)	92.0(2)
N(1)–C(5)	1.340(7)	C(6)–I(1)	1.950(5)	O(1n)Cu(1)N(4)	178.0(2)
N(2)–C(1)	1.437(7)	C(7)–C(71)	1.491(8)	O(1n)Cu(1)O(4n)	89.20(19)
N(2)–C(7)	1.350(7)	N(1n)–O(1n)	1.309(8)	O(4n)Cu(1)O(1l)	101.69(18)
N(3)–N(4)	1.371(6)	N(1n)–O(2n)	1.213(8)	O(4n)Cu(1)N(1)	157.44(19)
N(3)–C(1)	1.451(7)	N(1n)–O(3n)	1.237(8)	N(2)C(1)N(3)	110.4(5)
N(3)–C(2)	1.349(7)	N(2n)–O(4n)	1.298(7)		
N(4)–C(4)	1.341(8)	N(2n)–O(5n)	1.243(7)		
C(2)–C(3)	1.387(8)	N(2n)–O(6n)	1.229(7)		
C(2)–C(21)	1.483(8)				

geometrical parameters of the hydrogen bonds in structures **I** and **IV** are listed in Table 7.

X-Ray powder diffraction analysis was carried out on a PHILIPS-PW1700 diffractometer (CuK_α radiation, graphite monochromator, scintillation detector, scan step 0.02°, $5° < 2\theta < 70°$) at room temperature with powdered silicon ($a = 5.4309$ Å) as an external standard.

IR spectra of complexes **III**–**V** were recorded on Scimitar FTS 2000 and Vertex 80 spectrometers in the 4000–400 cm^{-1} range. Samples were prepared as suspensions in Vaseline and fluorinated oils and in PE. The frequencies of selected vibrations are given in Table 8.

EPR spectra of complexes **III**–**V** were recorded on a Varian E-109 radio spectrometer fitted with a signal digitizer and an original software designed for accumulation and primary processing of spectra. Measurements were carried out in the Q range at room temperature. To calibrate the operating frequency of the spectrometer, the spectra of complexes **III**–**V** were recorded together with powdered MgO containing an impurity of Mn^{2+} ions as a standard ($g = 2.003$, $a = 86.8$ Gs).

The EPR spectra were interpreted to find their parameters, which were refined by modeling the theoretical spectra with the Simfonia program (Bruker). The parameters of the modeling are given in Table 9.

RESULTS AND DISCUSSION

Copper salts reacted with ligand L in acetone to give complexes **I** and **II**; their single crystals were grown by slow crystallization. Complexes **III**–**V** were obtained by reactions of the corresponding copper salts in ethanol with a solution of ligand L in acetone as shown below:

$$\mathrm{Cu}^{2+} + 2\mathrm{L} + n\mathrm{H_2O} + (\mathrm{CH_3})_2\mathrm{CO} + 2\mathrm{A} \longrightarrow [\mathrm{CuL_2(H_2O)}_n]\mathrm{A_2}\cdot(\mathrm{CH_3})_2\mathrm{CO},$$

$$\mathrm{A} = \mathrm{BF_4^-}\ (n = 0);\ \mathrm{A} = \mathrm{ClO_4^-},\ \mathrm{ReO_4^-}\ (n = 1).$$

The polycrystalline phases of complexes **III**–**V** were isolated.

In the synthesis of the complexes, the molar metal-to-ligand ratio was 2 : 1. Because the ligand is poorly soluble in an acetone–ethanol mixture, we used an excess of copper salts to prevent the precipitation of the unreacted ligand from the reaction mixture. Thorough washing of complexes **III**–**V** with acetone, in which the ligand is soluble, substantially lowered their yields because of appreciable dissolution of the phases themselves.

The complexes obtained are poorly soluble in acetone, are insoluble in ethanol, propan-2-ol, and chloroform, and are unstable in aqueous solutions.

Table 4. Selected bond lengths and angles in structure **II**

Bond	d, Å	Bond	d, Å	Angle	ω, deg
Cu(1)–N(11)	1.985(13)	C(12)–C(13)	1.44(3)	N(11)Cu(1)N(21)	171.4(8)
Cu(1)–N(21)	2.024(17)	C(13)–C(14)	1.40(2)	N(11)Cu(1)N(24)	89.8(5)
Cu(1)–N(24)	2.176(15)	C(13)–I(1)	2.019(17)	N(21)Cu(1)N(24)	86.4(7)
Cu(1)–N(14)	2.187(13)	C(14)–C(15)	1.46(3)	N(11)Cu(1)N(14)	89.4(5)
Cu(1)–Cl(1)/O(1)	2.214(5)	C(16)–C(17)	1.45(3)	N(21)Cu(1)N(14)	98.6(7)
N(11)–C(14)	1.32(2)	C(17)–C(18)	1.37(2)	N(24)Cu(1)N(14)	94.4(5)
N(11)–N(12)	1.394(19)	C(18)–C(19)	1.40(2)	N(11)Cu(1)Cl(1)	87.8(4)
N(12)–C(12)	1.36(2)	C(18)–I(2)	2.062(14)	N(21)Cu(1)Cl(1)	90.3(5)
N(12)–C(1)	1.42(2)	C(19)–C(20)	1.53(2)	N(24)Cu(1)Cl(1)	140.8(5)
N(13)–N(14)	1.385(19)	C(21)–C(22)	1.44(3)	N(14)Cu(1)Cl(1)	124.6(4)
N(13)–C(17)	1.39(2)	C(22)–C(23)	1.34(3)		
N(13)–C(1)	1.455(18)	C(23)–C(24)	1.46(2)	Cl(3)*Cu(2)Cl(3)	106.5(4)
N(14)–C(19)	1.314(19)	C(23)–I(3)	2.044(17)	Cl(3)*Cu(2)Cl(2)	100.6(3)
N(21)–C(29)	1.39(4)	C(24)–C(25)	1.48(3)	Cl(3)Cu(2)Cl(2)	122.8(4)
N(21)–N(22)	1.43(3)	C(26)–C(27)	1.50(4)	Cl(2)Cu(2)Cl(2)*	105.3(6)
N(22)–C(2)	1.33(3)	C(27)–C(28)	1.33(5)		
N(22)–C(27)	1.38(4)	C(28)–C(29)	1.55(5)	N(12)C(1)N(13)	112.1(13)
N(23)–C(22)	1.34(3)	C(28)–I(4)	2.14(2)	N(22)C(2)N(23)	109.5(15)
N(23)–N(24)	1.39(2)	C(29)–C(30)	1.36(5)		
N(23)–C(2)	1.45(3)				
N(24)–C(24)	1.32(2)	Cu(2)–Cl(2)	2.165(7)		
C(11)–C(12)	1.47(3)	Cu(2)–Cl(3)	2.239(5)		

* The symmetry operation code is $-x + 2, -x + y + 1, -z + 4/3$.

According to X-ray diffraction data, complexes **I–IV** have island structures; in complex **II**, the cations $[CuL_2(H_2O)]^{2+}$ and $[CuL_2Cl]^{+}$ form a solid solution in the ratio 1 : 1. In all the complexes, the ligand L is coordinated to the copper atom in a chelating bidentate fashion through the N^2 and $N^{2'}$ atoms of the pyrazole rings to form the six-membered chelate ring CuN_4C.

The coordination polyhedron of the copper ion in structure **I** is built from two N atoms of the ligand L, the O atom of the coordinated water molecule, and two O atoms of two nitrate groups coordinated in a monodentate manner (Fig. 1a). In addition, structure I shows two longer Cu···O contacts (2.78 and 2.84 Å) involving the O atoms of the coordinated nitrate groups. Without regard to these contacts, the coordination polyhedron of the Cu atom is a distorted tetragonal pyramid.

In the crystals, a centrosymmetric pair of the complexes $[CuL(H_2O)(NO_3)_2]$ and two acetone molecules are united through hydrogen bonds into associates (Fig. 1b). The molecules of the complex form the intermolecular contacts $O(H_2O)$–H···$O(NO_3)$ (2.823(6) and 3.160(7) Å). In addition, the O atom of the solvated acetone molecule is bound to the coordinated water molecule by the hydrogen bond O···H–O (O···O 2.736(8) Å) (Table 7). In the crystal structure, the associates are linked by the shortened non-valence contacts I···I (3.98 Å).

Structure **II** contains copper atoms in two oxidation states: Cu^{2+} ions are in the complex cations $[CuL_2(H_2O)]^{2+}$ and $[CuL_2Cl]^{+}$, which form a solid solution, and the Cu^{+} ion is in the anion $[CuCl_4]^{3-}$. Apparently, Cu^{2+} ions are reduced to Cu^{+} ones by the ligand L.

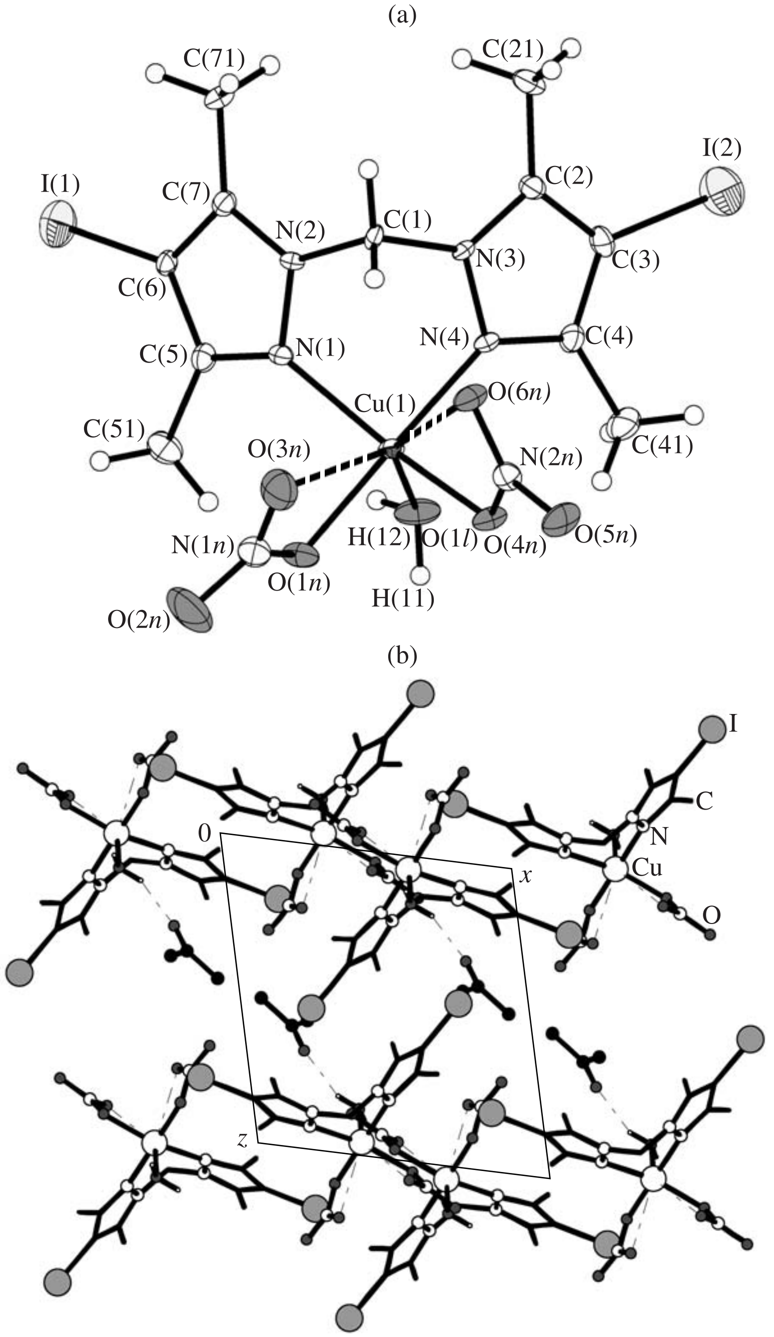


Fig. 1. Structure **I**: (a) neutral complex with atomic thermal displacement ellipsoids (50% probability) and (b) crystal packing. The hydrogen atoms, except for the H atoms of coordinated water, are omitted for clarity. Hydrogen bonds and extra contacts of the nitrate groups are indicated with dashed lines.

The complex cations $[CuL_2(H_2O)]^{2+}$ and $[CuL_2Cl]^{+}$ are randomly disordered (Fig. 2a). Each copper(II) ion coordinates two ligand molecules making an angle of ~30°. Another coordination site is occupied with equal probability by the Cl atom or the O atom of the coordination water molecule. The coordination polyhedron of the copper atom is a distorted trigonal bipyramid with the Cl/O atom in the equatorial plane. The observed scatter in bond lengths, the low accuracy of their determination, and the high value of the *R* factor for complex **II** are probably due to the low quality of its single crystal (Table 4).

Table 5. Selected bond lengths and angles in structure **III**

Bond	*d*, Å	Bond	*d*, Å	Angle	ω, deg
Cu(1)–N(1)	2.010(4)	C(11)–C(12)	1.486(8)	N(1b)Cu(1)N(1)	87.1(3)
Cu(1)–N(3)	2.014(4)	C(12)–C(13)	1.371(8)	N(1b)Cu(1)N(3)	179.23(18)
Cu(1)–F(22)	2.668(6)	C(13)–C(14)	1.407(8)	N(1)Cu(1)N(3)	92.09(18)
Cu(1)–F(13a)*	2.698(5)	C(14)–C(15)	1.494(8)	N(1)Cu(1)N(3b)	179.23(18)
I(1)–C(23)	2.078(5)	C(21)–C(22)	1.488(7)	N(3)Cu(1)N(3b)	88.7(2)
I(2)–C(13)	2.071(5)	C(22)–C(23)	1.379(8)	N(2b)C(1)N(2)	108.1(6)
N(1)–N(2)	1.374(6)	C(23)–C(24)	1.400(7)	N(4)C(2)N(4b)	109.4(6)
N(1)–C(14)	1.326(7)	C(24)–C(25)	1.476(7)	N(1)Cu(1)F(22)	82.63(16)
N(2)–C(1)	1.450(6)	B(1)–F(11)	1.328(13)	N(3)Cu(1)F(22)	97.36(16)
N(2)–C(12)	1.353(6)	B(1)–F(12)	1.350(8)	N(1b)Cu(1)F(13a)	96.09(15)
N(3)–N(4)	1.365(6)	B(1)–F(13)	1.430(12)	N(3)Cu(1)F(13a)	83.90(15)
N(3)–C(24)	1.344(7)	B(2)–F(21)	1.366(9)	F(22)Cu(1)F(13a)	178.23(17)
N(4)–C(2)	1.441(6)	B(2)–F(22)	1.411(14)		
N(4)–C(22)	1.360(7)	B(2)–F(23)	1.367(15)		

* The symmetry operation codes are (a) x, y, $z + 1$ and (b) x, $-y + 3/2$, z.

Table 6. Selected bond lengths and angles in structure **IV**

Bond	*d*, Å	Bond	*d*, Å	Angle	ω, deg
Cu(1)–N(1)	2.037(2)	C(12)–C(13)	1.374(4)	N(1)Cu(1)N(1b)	87.69(13)
Cu(1)–N(3)	2.039(2)	C(13)–N(2)	1.351(4)	N(1)Cu(1)N(3)	174.49(11)
Cu(1)–O(1)	2.296(3)	C(13)–C(131)	1.497(4)	N(1b)Cu(1)N(3)	93.05(8)
Cu(1)–O(13a)	3.033(4)	C(21)–C(22)	1.406(4)	N(3)Cu(1)N(3b)	85.69(13)
I(1)–C(22)	2.073(3)	C(21)–C(211)	1.482(4)	N(1)Cu(1)O(1)	86.25(9)
I(2)–C(12)	2.070(3)	C(22)–C(23)	1.375(4)	N(3)Cu(1)O(1)	99.25(9)
N(1)–C(11)	1.342(4)	C(23)–N(4)	1.352(4)	N(2)C(1)N(2b)	109.5(3)
N(1)–N(2)	1.375(3)	C(23)–C(231)	1.496(4)	N(4)C(2)N(4b)	108.5(3)
N(3)–C(21)	1.349(4)	Cl(1)–O(12)	1.435(4)	N(1)Cu(1)O(13a)	94.41(9)
N(3)–N(4)	1.378(3)	Cl(1)–O(11)	1.435(3)	N(3)Cu(1)O(13a)	80.09(9)
C(1)–N(2)	1.439(3)	Cl(1)–O(13)	1.436(4)	O(1)Cu(1)O(13a)	179.08(11)
C(2)–N(4)	1.454(4)	Cl(2)–O(23)	1.405(4)	N(4)Cu(1)O(13a)	93.33(8)
C(11)–C(12)	1.401(4)	Cl(2)–O(21)	1.405(4)	N(2)Cu(1)O(13a)	82.68(8)
C(11)–C(111)	1.490(4)	Cl(2)–O(22)	1.408(5)		

The symmetry operation codes are (a) $-x + 1$, $-y + 1$, $z + 1/2$ and (b) $-x + 1$, y, z.

Table 7. Geometrical parameters of the hydrogen bonds in structures **I** and **IV**

Contact D–H···A	Distance, Å			Angle DHA, deg	Coordinates of the atom A
	D–H	H···A	D···A		
			I		
O(1*l*)–H(11)···O(4*n*)	0.89(2)	1.99(4)	2.823(6)	156(9)	$-x + 1, -y + 1, -z + 2$
O(1*l*)–H(11)···O(5*n*)	0.89(2)	2.42(6)	3.160(7)	141(8)	$-x + 1, y + 1, -z + 2$
O(1*l*)–H(11)···N(2*n*)	0.89(2)	2.58(3)	3.435(7)	163(8)	$-x + 1, -y + 1, -z + 2$
O(1*l*)–H(12)···O(1*s*)	0.88(2)	1.93(4)	2.736(8)	152(7)	x, y, z
			IV		
O(1)–H(1)···O(21)	0.96(2)	2.145(19)	2.999(6)	147.4(1.3)	x, y, z
O(1)–H(2)···O(11)	0.99(2)	2.260(18)	3.146(4)	149(7)	x, y, z
O(1)–H(2)···Cl(1)	0.99(2)	2.65(2)	3.608(3)	164(5)	x, y, z
O(1)–H(1)···Cl(2)	0.96(2)	2.62(2)	3.576(3)	179(5)	x, y, z

Table 8. Selected vibrational frequencies (cm^{-1}) in the IR spectra of the ligand L and complexes **III–V**

Assignment	Compound			
	L	**III**	**IV**	**V**
$\nu(H_2O)$			3464, 3408	3451, 3358
$\nu(CO)$		1701	1700	1698
$\delta(H_2O)$			1657	1652
ν_{ring}	1536	1532	1533	1534
$\nu_3(A^-)$		1066	1081	915, 891
$\nu_4(A^-)$		523, 516	620	

Table 9. Parameters of the EPR spectra of complexes **III–V**

Complex	$g_{\|}$	$g_{\perp}$	$A_{\|}$	$W_{\|}$	$W_{\perp}$
III	2.243	2.060	110	120	60
IV	2.28	2.0645		200	30
V	2.275	2.069	100	120	25/100

The complex cations $[CuL_2Cl]^+$ and $[CuL_2(H_2O)]^{2+}$ are chiral and have the point symmetry C_1. Because the synthesis of complex **II** is not stereoselective, its crystal could be expected to contain a racemic mixture of enantiomers. However, complex II crystallizes into the polar chiral space group $P6_522$. Thus, the enantiomers are spontaneously separated by crystallization to form dextrorotatory and levorotatory crystals, as with Pasteur's famous example of potassium tartrate.

In crystal structure **II**, the cationic complexes are united into helical chains through the contacts I···I (3.95 Å) (Fig. 2b). The anions $[CuCl_4]^{3-}$ are in the cavities formed by the packing of these chains.

In structure **III**, the copper ion is on the plane *m* in the square environment. The F atoms of two BF_4^- anions form two additional contacts Cu···F (2.668(6) and 2.698(5) Å), which are longer than a coordination bond (Fig. 3a, Table 5). These contacts extend the coordination polyhedron of the copper ion to an elongated square bipyramid (4 + 2).

Crystal structure **III** contains no short intermolecular contacts, except for the I···I interactions (3.98 and 4.30 Å). Solvated acetone molecules are in the cavities between the complexes (Fig. 3b).

The coordination polyhedron of the copper ion in structure **IV** is a square pyramid made up of four N atoms of two molecules of the ligand L and the apical O atom of the coordinated water molecule (Fig. 4a, Table 6). An additional contact Cu···O(ClO_4^-) (3.03 Å) extends the coordination polyhedron of the copper ion to an asymmetrically elongated square bipyramid (4 + 1 + 1). The Cu atoms, the methylene C atoms, and the water O atoms in $[CuL_2(H_2O)]^{2+}$ are on the plane *m*.

In crystal structure **IV**, the H atoms of the coordinated water molecule of each complex cation are bound to the O atoms of two perchlorate anions by weak hydrogen bonds (O···O 2.999(6) and 3.146(4) Å) (Fig. 4b, Table 7). Solvated acetone molecules are in

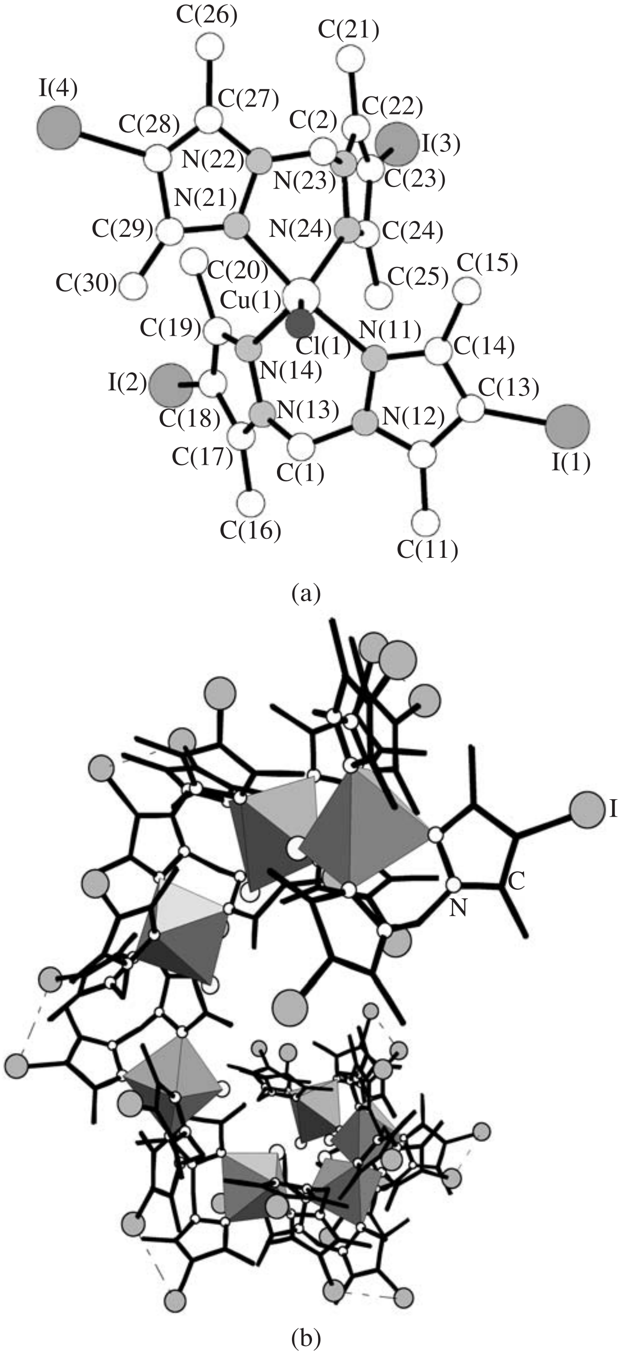


Fig. 2. Structure **II**: (a) the complex cation $[Cu(L)_2Cl]^+$ and (b) a helical chain of the complexes along the helical axis 6_5. The copper atoms are represented as coordination polyhedra; the H atoms are omitted for clarity. The shortened non-valence contacts I···I are indicated with dashed lines.

the cavities between the complexes and do not participate in the hydrogen bonding.

A comparison of the bond lengths in the complexes with the ligand L and in the free ligand L [15] suggests the absence of conjugation in the pyrazole rings and negligible influence of the coordination to the copper atom on the C–C, C–N, N–N, and C–I bond lengths (Table 3). The dihedral angles between the planes of the pyrazole rings are 65.9° in complex **I** and 65.9° and 66.1° for two independent molecules L in structure **II**. The corresponding values for two independent mole-

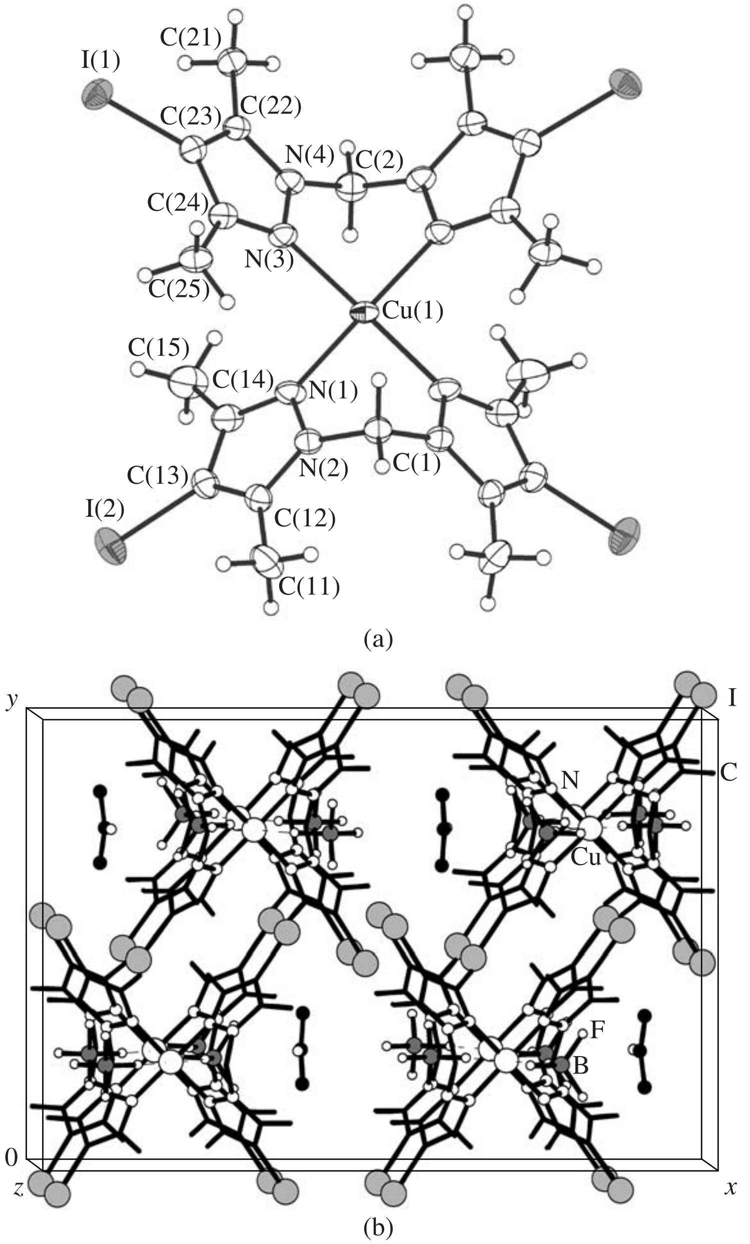
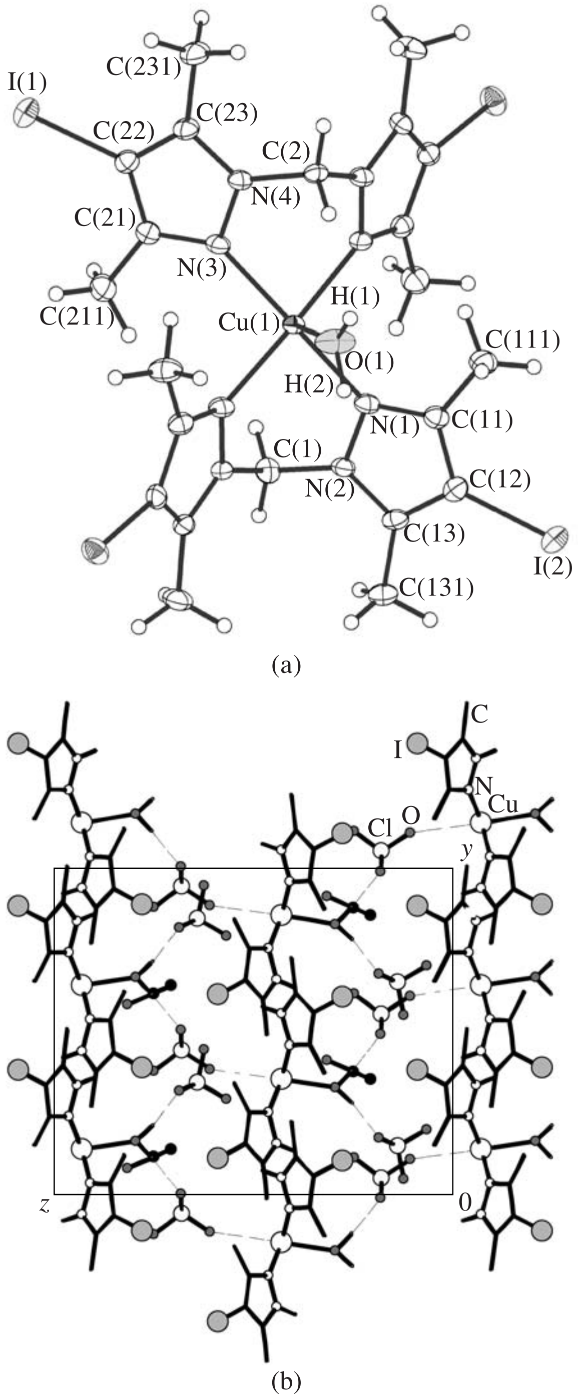


Fig. 3. Structure **III**: (a) the complex with atomic thermal displacement ellipsoids (50% probability) and (b) crystal packing. The hydrogen atoms are omitted for clarity. The weak extra contacts Cu···F(BF_4^-) are indicated with dashed lines.

cules L are 66.6° and 70.8° in complex **III** and 73.5° and 75.6° in complex **IV**. Thus, the dihedral angles between the planes of the pyrazole rings in the ligand L somewhat increases when passing from square pyramidal (**I**) and trigonal bipyramidal complexes (**II**) to square bipyramidal ones (**III**, **IV**).

Experimental powder diffraction patterns for the polycrystalline phases of complexes **III** and **IV** agree with those calculated from single-crystal X-ray diffraction data; this suggests that their polycrystalline phases and single crystals are structurally identical. The polycrystalline phases of complexes **IV** and **V** are not isostructural, despite identical compositions: their diffraction patterns differ in both the reflection width and intensity.

In the high-frequency range, the IR spectra of complexes **IV** and **V** show ν(H_2O) bands at 3464 and 3408 cm^{-1} (**IV**) and at 3451 and 3358 cm^{-1} (**V**) (Table 8). The δ(H_2O) bands appear at 1657 (**IV**) and 1652 cm^{-1} (**V**). The band due to the stretches and bends of the pyrazole ring (1536 cm^{-1} for L) is shifted by 2–4 cm^{-1} to the lower frequencies in the IR spectra of complexes **III**–**V**



(a)

(b)

Fig. 4. Structure **IV**: (a) the complex with atomic thermal displacement ellipsoids (50% probability) and (b) crystal packing. The hydrogen atoms, except for the H atoms of coordinated water, are omitted for clarity. Hydrogen bonds and extra contacts between the copper ions and the perchlorate ions are indicated with dashed lines.

because of the coordination of the ligand by the pyrazole N atoms.

The positions of the bands ν_3 and ν_4 of the BF_4^-, ClO_4^-, and ReO_4^- ions (see Table 8) suggest their location in the outer sphere.

The EPR spectra of complexes **III**–**V** show a typical anisotropic line shape with an axial anisotropy of the *g* factor, the HFS, and the line width (Table 9). The ratio $g_\parallel/g_\perp$ for these complexes is typical of separate ions with the ground-state orbital $d_{x^2-y^2}$. The incomplete averaging of the HFS in complexes **III** and **V** indicates slight exchange interactions between paramagnetic ions. The absence of an HFS for complex **IV** and a very wide line suggest a somewhat stronger exchange interaction and a coaxial (with respect to the axes of symmetry) arrangement of the coordination polyhedra of the copper ions in the crystal structure.

The nearest environment of the copper ion in complex **III** makes up a square. The F atoms of two BF_4^-, anions extend the polyhedron of the Cu atom to a trigonal bipyramid (4 + 2). The Cu···F distances are longer than a coordination bond. In complex **IV**, a similar coordination polyhedron is extended to a square pyramid by the water O atom. Such an additional coordination increases the *g* factors in the EPR spectra, which is consistent with the current concepts and agrees with theoretical calculations. These features of the EPR spectra of complexes **III** and **IV** correlate with the X-ray diffraction data. Crystallographic data for complex **V** are unavailable; however, by comparing the EPR spectra of complexes **III**–**V**, we can state with assurance that the coordination polyhedron of the copper ion is a tetragonal pyramid as in complex **IV**.

To sum up, we obtained new copper(II) complexes with bis(4-iodo-3,5-dimethylpyrazol-1-yl)methane and determined their molecular and crystal structures. We found that the ligand L in all the complexes is coordinated to the metal atom in a chelating bidentate manner through the N^2 and $N^{2'}$ atoms of the pyrazole rings to form the six-membered chelate ring CuN_4C.

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