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Cu(II) and Cu(I) Complexes with 2-(3,5-Diphenyl-1*H*–pyrazole-1-yl)-4,6-diphenylpyrimidine: Synthesis and Structure. Catalytic Activity of Cu(II) Compounds in Reaction of Ethylene Polymerization

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Abstract—The Cu(II) and Cu(I) complexes with 2-(3,5-diphenyl-1*H*-pyrazole-1-yl)-4,6-diphenylpyrimidine (L) of the composition $CuLX_2$ (X = Cl, Br) and CuL(MeCN)Br are synthesized. According to X-ray diffraction data, the complexes have molecular structures. The molecules L are coordinated to the copper atom in bidentate-cyclic mode, i.e., through the N^2 atom of pyrazole and N^1 atom of pyrimidine rings. The coordination polyhedron of the Cu^{2+} ion in $CuLX_2$ compounds is completed to a distorted tetrahedron with halide ions, that of the Cu^+ ion in CuL(MeCN)Br compounds, with the bromide ion and the nitrogen atom of acetonitrile molecule. The $CuLX_2$ complexes (X = Cl, Br) in combination with cocatalysts (methylaluminoxane and triisobutylaluminium) exhibit catalytic activity in ethylene polymerization.

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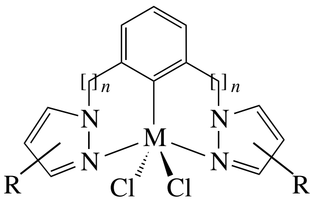
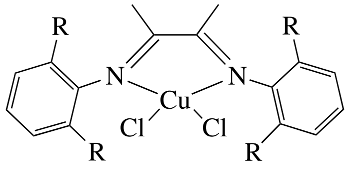
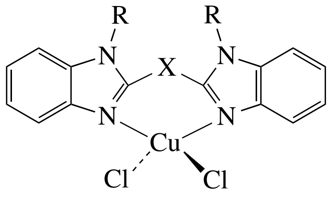
A search for and study of new catalytic systems that can be used in the target synthesis of polymers with the required properties make an urgent task for researchers [1–4]. Recently, a series of new Fe, Co, Ni, and V complexes with the nitrogen-containing organic ligands were used in combination with cocatalysts (methylaluminoxane (**MAO**) or trialkylaluminium compounds) as efficient catalysts in ethylene polymerization [5–10]. Nevertheless, the development of novel complexes of the transition 3*d* metals that can be used as catalysts in olefin polymerization reactions is still of interest today. The authors of [11] reported lately the catalytic activity of the Fe(II) and Co(II) complexes with 2,6-di(pyrazole-1-yl)- and 2,6-di(pyrazole-1-ylmethyl)pyridines in ethylene polymerization in the presence of MAO. Also, the first Cu catalysts of ethylene polymerization were reported (the $CuCl_2$ complexes with bidentate α-diamine [12] and bis(benzimidazole) [13] ligands).



R = H, Me; M = Co, Fe;
n = 0, 1 [11]



R = Ph, *iso*-Pr [12]



R = alkyl; X = C(OMe)Me,
CEt_2, 2,2'-C_6H_4–C_6H_4 [13]

The structural aspects of the Cu(I) and Cu(II) complexes with the nitrogen-containing ligands, which are usually used in the radical atom-transfer polymerization are discussed in [14].

In this connection, the synthesis of new Cu complexes with the nitrogen-containing ligands incorporating heterocycles with several N atoms and the study of their structures and catalytic activity in reactions of olefin polymerization are of unquestionable interest.

The aim of this work was to synthesize the Cu(II) and Cu(I) complexes with a new nitrogen-containing heterocyclic ligand, namely, 2-(3,5-diphenyl-1*H*-pyrazole-1-yl)-4,6-diiphenylpyrimidine (**L**) and to study their structures and catalytic activity of the Cu(II) compounds in the ethylene polymerization reaction.

EXPERIMENTAL

The reagents used in the synthesis were high-purity $CuCl_2 \cdot 2H_2O$ and $CuBr_2$; MAO Witco Gm1H (Berghamen) (a solution in toluene with a total content of Al 1.8 mol/l); triisobutylaluminium (**TIBA**) (a solution in heptane, commercial grade).

Synthesis of L. A mixture of 2-hydrazino-4,6-diphenylpyrimidine (2.6 g, 10 mmol), dibenzoylmethane (2.5 g, 11 mmol), 1 ml of acetic acid, and 30 ml of ethanol was refluxed for 40 h. After cooling to room temperature, the solvent was decanted, and the precipitate formed was washed two times with ethanol. Then, a 50% aqueous solution of ethanol was added to the precipitate and Na_2CO_3 solution for neutralization. The precipitate was filtered off, washed with water to a neutral reaction, and then with a cold ethanol. The yield was 4.2 g (93%); mp = 172–173.5°C. A high-resolution mass spectrum (direct introduction of a sample to the ionic source): found *m/z* 450.1855 $[M]^+$. For $C_{31}H_{22}N_4$ anal. calcd.: *M* = 450.1844. The ^{1}HNMR spectrum (200.13 MHz, $CDCl_3$), δ, ppm: 8.20–8.00, 7.91–7.78, 7.60–7.26 (20 H, 4 × Ph), 7.97 (s, 1 H, $5\text{-H}_{pyrimidine}$), 6.89 (s, 1 H, $4\text{-H}_{pyrazole}$).

Synthesis of $CuLCl_2$ (I) and $CuLBr_2$ (II). A hot solution of L (0.23 g, 0.5 mmol) in 25 ml of ethanol was added dropwise with stirring to a hot solution of 0.5 mmol of the corresponding Cu(II) salt (0.09 g of $CuCl_2 \cdot 2H_2O$ or 0.11 g of $CuBr_2$) in 5–8 ml of ethanol. A red-orange precipitate of complex **I** was formed in 2–3 min after mixing of the solutions, whereas a brown precipitate of complex **II** was formed in the course of addition of the L solution to a solution of $CuBr_2$. The mixtures were stirred for 1.5 h on heating (the final volume of a solution was 5–7 ml). The precipitates were filtered off. Then, 2–3 ml of ethanol was added to a freshly prepared precipitate, and the mixture was stirred for 0.5 h with slight heating. The precipitate was filtered off, washed with a small amount of ethanol, and dried in air. The yield of complex **I** was 0.27 g (92%); the yield of complex **II** was 0.28 g (83%).

For $C_{31}H_{22}N_4Cl_2Cu$ (I)

anal. calcd. (%):	C, 63.6;	H, 3.8;	N, 9.6;	Cu, 10.9.
Found (%):	C, 63.2;	H, 3.8;	N, 9.6;	Cu, 10.9.

For $C_{31}H_{22}N_4Br_2Cu$ (II)

anal. calcd. (%):	C, 55.3;	H, 3.3;	N, 8.3;	Cu, 9.4.
Found (%):	C, 54.9;	H, 3.3;	N, 8.3;	Cu, 9.4.

Single crystals of complexes **I** and **II** for X-ray diffraction analysis were obtained by slow crystallization from their solutions in a mixture of $CHCl_3$–MeCN (2 : 1). Single crystals of **I** (colored red-orange) and of **II** (colored dark brown) were formed over a day.

Synthesis of CuL(MeCN)Br (III). Complex **II** was dissolved in a mixture of $CHCl_3$–MeCN (2 : 1) on heating. The solution was cooled, poured in a weighing bottle, and closed. In several hours, dark brown crystals precipitated from the solution, which were similar in color to crystals **II**. In 2–3 days, the dark brown color of the crystals in the solution changed to red-orange color and the crystals consolidated. They were used in X-ray diffraction analysis and their composition was identified as CuL(MeCN)Br.

The content of Cu in complexes **I** and **II** was determined by complexometric titration after the samples were decomposed in a mixture of concentrate H_2SO_4 and HNO_3; the analysis for C, H, and N was performed on a Carlo Erba analyzer using a standard procedure.

The electronic reflection spectra were recorded on a Unicam 700A spectrophotometer at 340–2300 nm. IR absorption spectra were recorded on a Scimitar FTS 2000 spectophotometer at 375–4000 cm^{-1} and on a BOMEM MB-102 spectrophotometer at 200–400 cm^{-1}; a high-resolution mass spectrum was taken on a Finnigan MAT-8200 spectrometer, electron impact, 70 eV.

X-ray diffraction analysis of **I–III** was performed following a standard procedure on automated four-circle Bruker-Nonius X8Apex diffractometer equipped with two-coordinate CCD detector at room temperature (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The intensities of reflections were measured by the method of φ-scanning of narrow (0.5°) frames to 2θ = 55°. The absorption was corrected empirically with SADABS program [15]. The structures of **I** and **III** were solved by the direct method and refined by a full-matrix least-squares method in anisotropic approximation for non-hydrogen atoms with SHELX97 program package [16]. Compounds **I** and **II** are isostructural and therefore, a model of **I** was used in refinement of structure **II**. The hydrogen atoms were refined in a heavy body approximation.

The crystallographic parameters and details of data collection are given in Table 1; the main bond lengths and selected bond angles for compounds **I–III** are listed in Table 2. The molecular packing of complexes **I–III** was analyzed with the TOPOS program package [17, 18] using the Voronoi–Dirichlet approach.

The coordinates of atoms and their thermal parameters are deposited with the Cambridge Structural Database (CSD) and are available from the authors.

Verification of catalytic activity of the Cu(II) complexes in ethylene polymerization reaction was performed in a temperature-controlled vessel (0.2 l in volume) equipped with a stirrer. MAO and TIBA were used as cocatalysts. The polymerization conditions are given in Table 3. In the course of the reaction (1 h), the

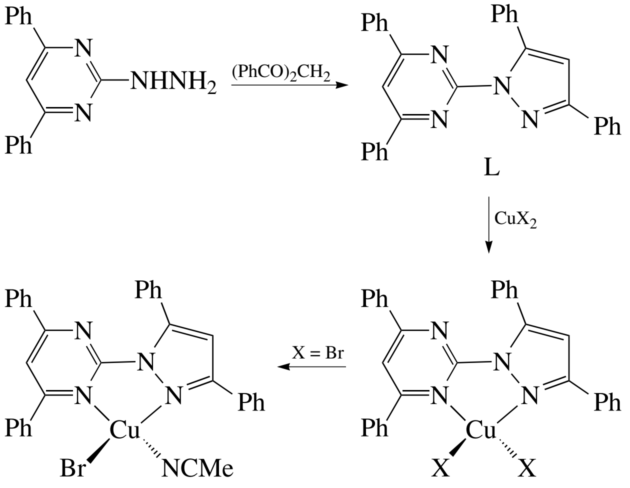
Table 1. Crystallographic parameters and details of data collection for complexes **I–III**

Parameter	Value		
	compound		
	I	**II**	**III**
Formula	$C_{31}H_{22}Cl_2CuN_4$	$C_{31}H_{22}Br_2CuN_4$	$C_{33}H_{25}BrCuN_5$
M	584.97	673.89	635.03
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group, Z	$P2_1/n$; 4	$P2_1/n$; 4	$P2_1/n$; 4
a, Å	12.0295(5)	12.0869(5)	13.6091(6)
b, Å	18.8084(7)	19.1147(8)	13.0721(6)
c, Å	12.4585(5)	12.5963(5)	16.7956(7)
β, deg	106.653(2)	106.555(2)	112.3930(10)
V, Å^3	2700.58(19)	2789.6(2)	2762.6(2)
ρ(calcd.), g/cm^3	1.439	1.605	1.527
μ, mm^{-1}	1.035	3.675	2.269
Crystal size, mm	0.18 × 0.10 × 0.09	0.10 × 0.04 × 0.03	0.60 × 0.25 × 0.10
Number of measured/independent reflections	23558/6193	24206/6355	28342/6248
R_{int}	0.0537	0.1080	0.0304
Number of observed reflections	3709	2559	4634
R_1 for observed reflections	0.0423	0.0479	0.0355
wR_2 for all reflections	0.1103	0.1029	0.0944
GOOF for all reflections	0.989	0.889	1.012

constant temperature and pressure were maintained. The obtained polyethylene (PE) powder was dried in air and weighed.

RESULTS AND DISCUSSION

Pyrazolylpyrimidine L was obtained by cyclic condensation of 2-hydrazino-4,6-diphenylpyramidine with dibenzoylmethane. Complexes **I** and **II** were synthesized by reacting Cu(II) salts with L in ethanol solutions on heating. The compounds were taken at a molar ratio Cu : L = 1 : 1. A slight excess of the Cu(II) salt with respect to a stoichiometric ratio of 1 : 1 can be used in the synthesis of the complexes. In order to obtain a pure phase, the precipitate formed should be thoroughly washed as recommended above. Complexes **I–III** are stable in air. Compounds **I** and **II** are soluble in organic solvents (ethanol, MeCN, isopropyl alcohol, $CHCl_3$, and their mixtures), but are poorly soluble in water. Crystals **III** precipitated from a solution obtained after dissolution of complex **II** in a mixture of $CHCl_3$–MeCN (2 : 1), after it was allowed to stay for several days. Complex **III** is a product of reduction of compound **II** and addition of acetonitrile molecule. The bromide ion is supposed to be a reductant. Therefore, the following transformations are carried out:



(**III**) (**I** and **II**, X = Cl, Br)

Mononuclear complexes **I–III** have molecular structures. The structures of complexes **I** and **III** are shown in Fig. 1a, 1b, respectively. The coordination polyhedron of the Cu atoms in **I** and **II** is a distorted tetrahedron with two coordination sites occupied by the

Table 2. The main bond lengths (d) in structures **I–IV** and bond (ω) and torsion (τ) angles in **I–III**

Bond	d, Å				Angle	ω, τ, deg		
	I X = Cl	**II** X = Br	**III** X(1) = Br, X(2) = N(1L)	**IV** [19] X = Cl		**I** X = Cl	**II** X = Br	**III** X(1) = Br, X(2) = N(1L)
Cu(1)–X(1)	2.2065(8)	2.3165(8)	2.3874(4)	2.235	X(1)Cu(1)X(2)	108.40(3)	107.69(3)	123.64(6)
Cu(1)–X(2)	2.1848(8)	2.3399(9)	1.984(2)	2.188	N(2)Cu(1)X(1)	126.66(7)	103.88(12)	108.59(5)
N(1L)–C(2L)			1.120(3)		N(2)Cu(1)N(10)	79.85(8)	80.00(16)	77.24(7)
C(1L)–C(2L)			1.463(4)		N(10)Cu(1)X(1)	101.51(6)	139.18(12)	116.26(5)
Cu(1)–N(2)	1.986(2)	1.984(4)	2.1106(19)	2.009	X(2)Cu(1)N(2)	103.36(7)	125.89(12)	114.50(9)
Cu(1)–N(10)	2.027(2)	2.015(4)	2.1157(19)	2.000	X(2)Cu(1)N(10)	138.42(6)	101.62(12)	107.43(8)
C(3)–C(4)	1.402(4)	1.389(6)	1.406(3)	1.388				
N(1)–N(2)	1.369(3)	1.367(5)	1.376(3)	1.384	N(1)C(5)C(51)C(56)	121.9(3)	122.4(6)	131.3(3)
C(3)–N(2)	1.332(3)	1.338(6)	1.334(3)	1.379	N(2)C(3)C(31)C(32)	133.6(3)	134.5(6)	161.3(2)
C(4)–C(5)	1.358(4)	1.368(6)	1.371(3)	1.382	N(30)C(40)C(41)C(46)	12.1(4)	10.7(7)	0.1(3)
C(5)–C(51)	1.478(4)	1.467(6)	1.478(3)		N(10)C(60)C(61)C(66)	146.1(4)	140.5(5)	133.4(3)
C(5)–N(1)	1.377(3)	1.385(6)	1.381(3)	1.376	N(30)C(20)N(1)C(5)	−3.96(4)	−4.8(8)	−3.5(3)
C(20)–N(1)	1.407(3)	1.406(6)	1.420(3)	1.401				
C(3)–C(31)	1.467(4)	1.475(7)	1.473(3)		Deviation from the plane	**I**	**II**	**III**
					N(10)C(20)N(1)N(2), Å	X = Cl	X = Br	X(1) = Br, X(2) = N(1L)
C(20)–N(10)	1.345(3)	1.344(6)	1.340(3)	1.334	Cu(1)	0.0856	0.0501	0.2639
C(20)–N(30)	1.304(3)	1.307(6)	1.320(3)	1.309	X(1)	1.8917	1.3756	1.3187
C(40)–C(50)	1.387(4)	1.398(6)	1.383(3)	1.387	X(2)	1.2526	1.9559	2.4879
C(40)–N(30)	1.352(3)	1.339(6)	1.352(3)	1.318				
C(50)–C(60)	1.374(4)	1.387(6)	1.381(3)	1.368				
C(60)–N(10)	1.358(3)	1.356(6)	1.352(3)	1.356				

Table 3. The results of estimation of the catalytic activity of complexes **I** and **II** in ethylene polymerization reaction

Complex	Experimental conditions			PE yield, g	Activity, kg PE/mol Cu h atm
	cocatalyst	$P_{C_2H_4}$, atm	T, °C		
$CuLCl_2$ (**I**)	MAO	10	35	0.70	35
	TIBA			1.12	56
$CuLBr_2$ (**II**)	MAO	10	35	0.90	45
	TIBA			1.15	58
Cu(α-diimine)Cl_2	MAO	4.5	25	0.4	4.5

*The data of [12] are given for comparison ([Cu] = 2.0×10^{-4} mol/l).

**The polymerization conditions are: 70 ml of toluene (heptane), [Cu] = 3×10^{-5} mol/l, the molar ratio Al_{cocat} : Cu = 500.

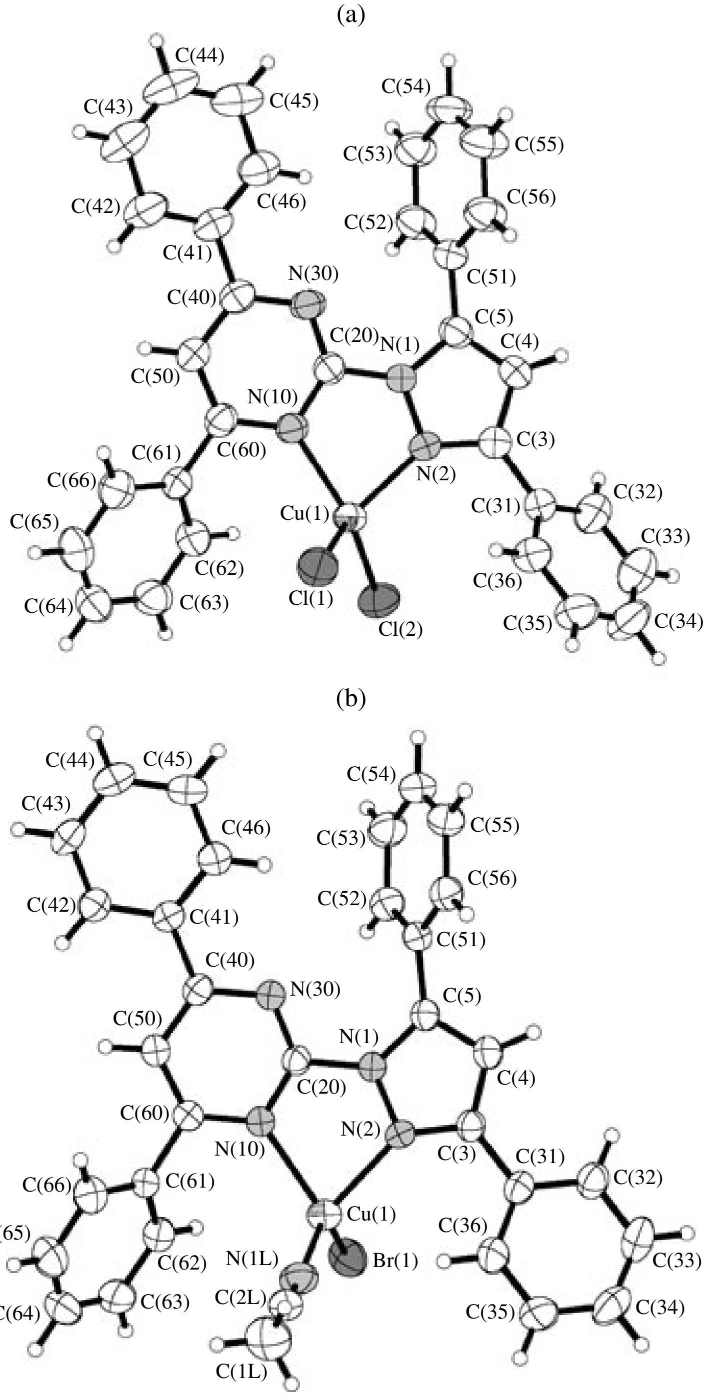


Fig. 1. The structure of (a) complex **I** and (b) complex **III** (ellipsoids of a 50% probability). The numbering schemes in **I** and **II** coincide.

N^2 atom of pyrazole and N^1 atom of pyrimidine rings of a bidentate-cyclic ligand L. The remaining two vertices of a tetrahedron in molecules **I** and **II** are occupied by the halogen atoms; in **III**, by the Br atom and the N atom of the coordinated MeCN molecule. As a result of the ligand coordination, the CuN_2C_2 chelate cycle is closed. In compounds **I** and **II**, this cycle is almost planar, while in **III**, the Cu atom noticeably deviates (by 0.264 Å) from the N_2C_2 plane (Table 2). The nitrogen-containing heterocycles are also almost planar with the maximum deviation of the atoms from their plane in **I,** **II**, and **III** being 0.031, 0.026, and 0.011 Å, respectively.

The molecular structure of complexes **I** and **II** is similar to that of compound $CuCl_2$ with symmetric α-diimine, which is catalytically active [11]. Note that

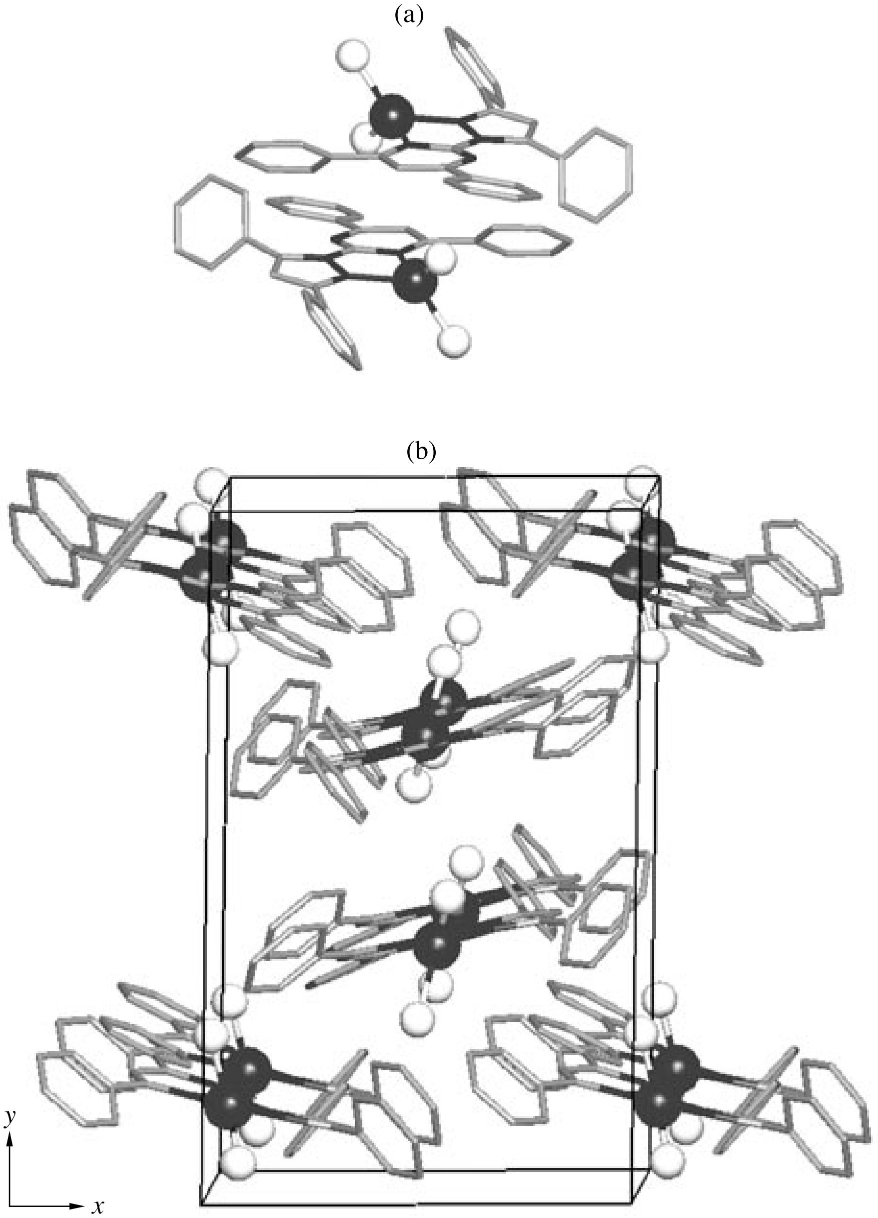


Fig. 2. (a) Molecular pair and (b) molecular packing along the *z* axis in structures **I** and **II**.

compounds **I** and **II** have substantially different lengths of the Cu–Hal bond for two halogen atoms and of the Cu–N bond for the donor N atoms of different heterocycles (Table 2). At the same time, the $CuCl_2$ complex with α-diimine, where both N atoms belong to identical fragments, does not show this difference.

The lengths of the Cu–N and Cu–Hal bonds gradually decrease on going from two Cu(II) complexes (**I** and **II**) to the Cu(I) complex (**III**). The analysis of data from CSD showed that compound **III** is the first Cu complex with oxidation state +1 and pyrazolylpyrimidine ligand. The nearest analog of complexes **I** and **II** is dichloro(4-methoxy-2-(5-methoxy-3-methylpyrazole-1-yl)-6-methylpyrimidine)copper (II) (**IV**) [19] with methyl and methoxy groups instead of phenyl substituents in pyrazole and pyrimidine rings. The bond lengths in pyrazole rings of compounds **I** and **II** are almost identical. The analysis of the C–C and C–N distances in complexes **I–III** shows that the change in the oxidation state of copper from +2 to +1 results in a higher delocalization of bonds in pyrimidine ring. It is worthwhile noting that elongation of the C^3–N^2 and C^4–C^5 bonds in complex **IV** as compared to complexes **I** and **II** is caused by a stronger positive mesomeric electronic effect of the 5-MeO group as compared to that of 5-Ph group on the electron density redistribution in a pyrazole ring.

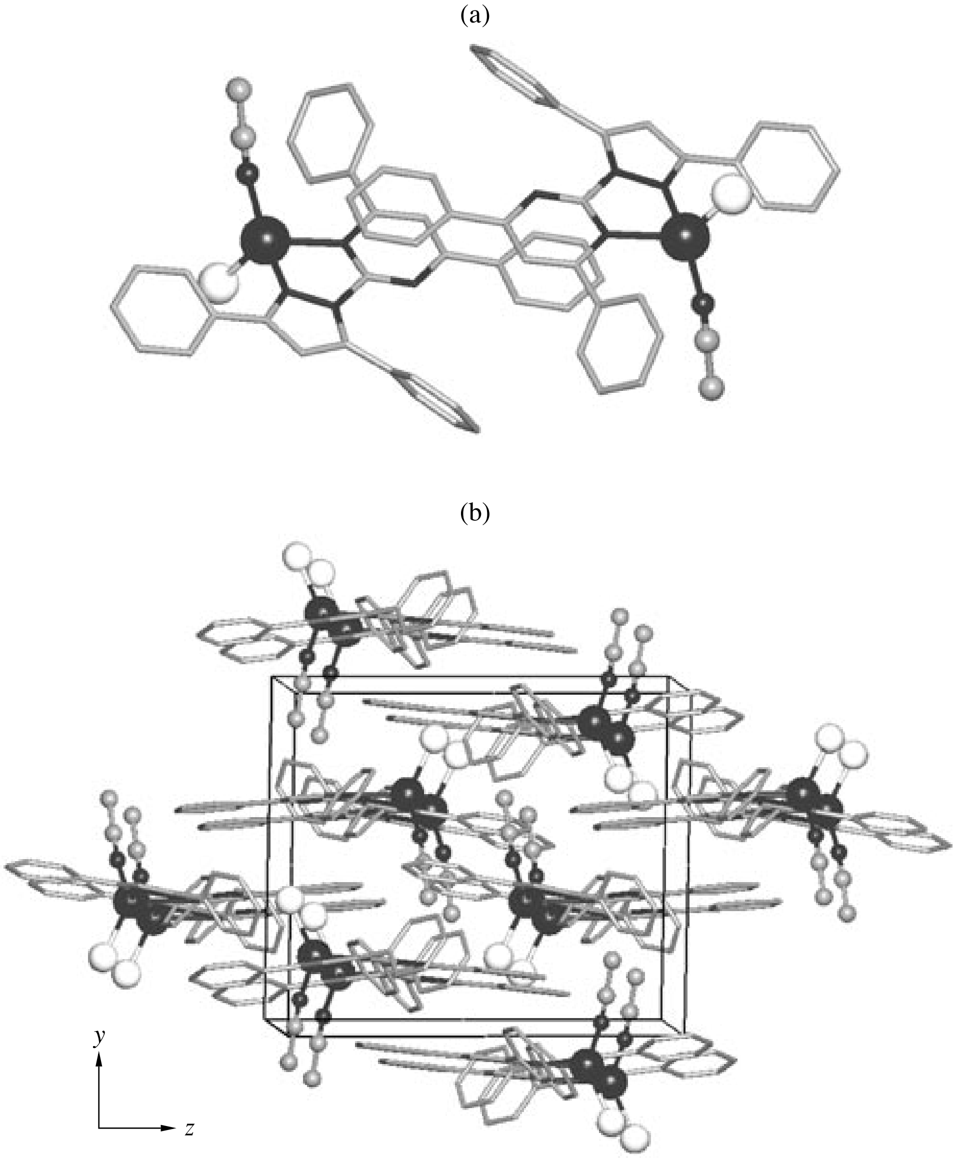


Fig. 3. (a) The dimeric molecular pair formed by stacking interaction and (b) packing along the *x* axis in structure **III**.

Crystals **I** and **II** have similar molecular packing (Fig. 2a). Each $CuLX_2$ molecule (X = Cl, Br) is surrounded by 14 neighbors (molecular C.N. 14). It was previously shown [20, 21] that the nearest surrounding of a molecule in crystal can be efficiently analyzed using the frontier surfaces, whose area and solid angle determine the surface area of a contact between the neighboring molecules and hence, the relative energy of their interaction.

The molecules of structures **I** and **II** form centrosymmetric pairs (Fig. 2a), for which the frontier surface area is maximum and is equal to about 17% and 14%, respectively, of the total surface of a central molecule. The molecules are arranged in such a way that the halogen atom of one molecule is directed toward pyrimidine ring of another molecule, which prevents stacking interactions. The remaining molecules in surrounding have lower contact area. Therefore, one can formally consider the molecular packing as a packing of molecular pairs, which, despite nonuniform surrounding of every separate molecule, realize almost perfectly uniform packing of a body-centered cubic lattice. In general, the molecular packing in crystals **I** and **II** can be considered to be mainly due to van der Waals interactions between molecules.

Crystal **III** has different molecular packing. Every molecule in this crystal is surrounded by 13 close and 2 remote neighbors. In this case, one of the surrounding molecules forms with a central molecule a frontier surface equal to ~22% of the total surface of the molecule

Table 4. The main frequencies in IR spectra (cm^{-1}) of the L ligand and complexes **I–III**

Compound	ν(Ph)	$(\nu + \delta)_{ring}$	ν(CH)	ν(Cu–N)	ν(Cu–X)
L	1602	1587, 1574, 1560, 1522	3062		
$CuLCl_2$ (**I**)	1607	1594, 1577, 1557, 1527	3059	280 sh	304, 329
$CuLBr_2$ (**II**)	1607	1593, 1577, 1557, 1526	3059	255, 264	230, 246
CuL(MeCN)Br(**III**)	1607	1592, 1577, 1554, 1526			

(Fig. 3a), whereas the contribution of any other surrounding molecule is less than 13%. As in the case of crystals **I** and **II**, in crystal **III**, a pair of nearest molecules is bonded through the symmetry center. However, the molecules of a dimer ensemble are noticeably drawn together, and the π-systems of a pyrimidine ring and of one of the phenyl rings participate in the stacking interactions (the distance between the planes of these rings is ~3.4 Å). As a whole, the molecular packing (Fig. 3b), which can be treated as a packing of dimers (where the molecules are bonded to one another stronger than to the neighboring molecules), is in fact a significantly distorted face-centered cubic lattice.

Table 4 contains IR spectroscopic data for ligand L and complexes **I–III**. The positions of the stretching-deformation vibrations of heterocyclic rings in IR spectra of complexes **I–III** are changed as compared to the spectrum of L, which, in accordance with X-ray diffraction data, suggest coordination of the L molecule. The band due to vibrations of the phenyl group in the spectra of the complexes shifts toward the high-frequency region. The low-frequency regions of the spectra of complexes **I** and **II** each contain two bands due to the stretching vibrations of the bonds Cu–Cl in **I** and Cu–Br in **II**, for which ν(Cu–Br)/ν(Cu–Cl) = 0.74–0.77. The IR spectra of complexes **I** and **II** exhibit the bands due to the stretching vibrations of the Cu–N bonds. In the spectrum of compound **I**, the bands due to vibrations ν(Cu–N) are overlapped by the intense absorption ν(Cu–Cl).

The electronic reflection spectrum of complex **I** contains in a visible region two bands with ν_{max} = 20800 cm^{-1}, while that of complex **II** contains two bands with ν_{max} = 21800 and 17100 cm^{-1}. The near-IR region of spectra of **I** and **II** has a broad band with $\nu_{max} \approx 9000$ cm^{-1}.

The results of estimation of the catalytic activity of the Cu(II) complexes (**I** and **II**) in the ethylene polymerization reaction are given in Table 3. One can see that under the indicated conditions and in the presence of MAO cocatalyst, both $CuLCl_2$ and $CuLBr_2$ exhibit a noticeable catalytic activity in the process of ethylene polymerization, which is one order of magnitude higher than the activity of the Cu(II) α-diimine complex [12] (Table 3, experiment 5). Note that TIBA also proved to be efficient cocatalyst for complexes **I** and **II** (Table 3, experiments 2 and 4).

Thus, it was shown that the Cu(II) halide complexes with a ligand containing pyrazole and pyrimidine rings are potential catalysts that can be used in the ethylene polymerization process. Therefore, further search for new catalysts, i.e., the transition 3*d*-metal complexes with the nitrogen-containing heterocyclic ligands and several N atoms in the cycles, is promising.

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