ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 8, pp. 597–608. © Pleiades Publishing, Ltd., 2009. Original Russian Text © M.B. Bushuev, V.P. Krivopalov, E.V. Peresypkina, A.V. Virovets, Yu.G. Shvedenkov, L.A. Sheludyakova, N.V. Semikolenova, V.A. Zakharov, S.V. Larionov, 2009, published in Koordinatsionnaya Khimiya, 2009, Vol. 35, No. 8, pp. 606–617.

Complexes of Copper(II) and Cobalt(II) Halides with 4-(3,5-Dimethyl-1*H*-Pyrazol-1-yl)-6-Methyl-2-Phenylpyrimidine: Synthesis, Structures, and Properties

M. B. Bushuev^{*a,b**}, V. P. Krivopalov^{*c*}, E. V. Peresypkina^{*a*}, A. V. Virovets^{*a*}, Yu. G. Shvedenkov^{*a*}, L. A. Sheludyakova^{*a*}, N. V. Semikolenova^{*d*}, V. A. Zakharov^{*d*}, and S. V. Larionov^{*a*}

^a Nikolaev Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences, pr. akademika Lavrent'eva 3, Novosibirsk, 630090 Russia

pr. akademika Lavrent eva 5, Novosibirsk, 650090 Russia

^b Novosibirsk State University, Novosibirsk, Russia

^c Vorozhtsov Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, Russia

^d Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences,

pr. akademika Lavrent'eva 5, Novosibirsk, 630090 Russia

E-mail: bushuev@che.nsk.su Received December 16, 2008

Abstract—Copper(II) and cobalt(II) complexes with 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methyl-2-phenylpyrimidine (L) of the general formula MLX₂ (M = Cu(II), X = Cl and Br; M = Co(II), X = Cl, Br, and I) were obtained. According to X-ray diffraction data, CuLBr₂ and CoLX₂ (X = Cl, Br, and I) are mononuclear molecular complexes. The ligand L is coordinated to the metal atom in a chelating bidentate fashion through the N atoms of the pyrimidine and pyrazole rings. The coordination polyhedron of the metal atom is extended to a distorted tetrahedron by two halide ions. In solution, CuLBr₂ undergoes slow transformation into CuL_(1-x)L'_xBr₂ and the binuclear (X-ray diffraction data) Cu(I) complex [CuL_{(1-x})L'_xBr]₂ (L' is 4-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methyl-2-phenylpyrimidine). The complexes MLX₂ show weak antiferromagnetic interactions between the M²⁺ ions.

DOI: 10.1134/S1070328409080077

A search for 3*d*-metal complexes, which are active components of catalytic systems, is a promising avenue in coordination chemistry and catalysis. Vanadium, iron, cobalt, and nickel complexes with nitrogen-containing organic ligands in the presence of organoaluminum compounds as cocatalysts catalyze olefin polymerization [1–6]. Complexes of CuCl₂ with bidentate α -diimino [7] and bis(benzoimidazole) ligands [8] are also active in this reaction. Most of the complexes studied contain identical coordination fragments. At the same time, attention is given to the synthesis and investigation of complexes consisting of various coordination fragments [9]. We began to synthesize 3d-metal complexes with polyheteroatomic ligands containing five- and six-membered azaheterocycles (pyrazolylpyrimidines). Because heterocyclic fragments have several N atoms and the pyrazole ring can be attached to the pyrimidine one in different positions, pyrazolylpyrimidines can be coordinated by metal atoms to form complexes with various compositions and structures [10-12]. We found that mononuclear complexes of CuCl₂ and CuBr₂ with 2-(3,5-diphenyl-1*H*-pyrazol-1yl)-4,6-diphenylpyrimidine are more active catalysts for ethene polymerization than a complex of CuCl_2 with an α -diimino ligand [13]. At present, the development of methods for targeted synthesis of complexes capable of catalyzing olefin polymerization necessitates a search for "composition–structure–property" correlations. In this step of our investigations, we should reveal correlations between the ligand structure, the nature of the central atom, and the properties of the complexes.

Additional interest in the synthesis of transition metal complexes with pyrazolylpyrimidines is due to a broad spectrum of biological activity of these nitrogeneous heterocycles [14–22]. Since complexes with similar hybrid ligands (pyrazolylpyrazines and pyrazolylpyridines) are magnetically active [23–25], pyrazolylpyrimidines can serve as potential ligands for the preparation of complexes with attractive magnetic properties (including those with spin transitions).

Earlier, we obtained a new ligand of this class, namely, 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-6-methyl-2-phenylpyrimidine (L), and its complex CuLCl₂ (I)

Complex	Content (found/calculated), %					
Complex	М	С	Н	N		
$\frac{C_{16}H_{16}N_4Cl_2Cu\left(I\right)}{CuLCl_2}$	15.6/15.9	48.4/48.2	4.1/4.0	14.1/14.0		
$\begin{array}{c} C_{16}H_{16}N_{4}Br_{2}Cu\left(\mathbf{II}\right)\\ CuLBr_{2} \end{array}$	12.6/13.0	38.6/39.4	3.3/3.3	11.2/11.5		
$\begin{array}{c} C_{16}H_{16}N_4Cl_2Co(IV)\\ CoLCl_2 \end{array}$	14.8/15.0	48.8/48.8	4.2/4.1	14.3/14.2		
$\begin{array}{c} C_{16}H_{16}N_{4}Br_{2}Co\left(V\right)\\ CoLBr_{2} \end{array}$	11.9/12.2	38.9/39.8	3.4/3.3	10.8/11.6		
$\begin{array}{c} C_{16}H_{16}N_{4}I_{2}Co\left(\textbf{VI}\right)\\ CoLI_{2} \end{array}$	10.1/10.2	30.4/33.3	3.1/2.8	9.3/9.7		

Table 1. Elemental analysis data for complexes I, II, and IV–VI

and characterized them by X-ray diffraction analysis [26].



Associated polymorphism was revealed for I: the complex crystallizes into three polymorphous modifications with different colors: light green (2G), emerald green (2EG), and orange (2O) [26]. The structures of the polymorphs mainly differs in the packing of I molecules in the solid state by means of various intermolecular π - π interactions. Thus, because of stacking, complexes of this class are of interest for the creation of molecular ensembles.

The goal of this study was to obtain complexes of Cu(II) and Co(II) halides with ligand L and examine their structures and magnetic and catalytic properties.

EXPERIMENTAL

The salts $CuCl_2 \cdot 2H_2O$, $CuBr_2$, $CoI_2 \cdot 2H_2O$ (highpurity grade), and $CoCl_2$ (analytical grade) were used; $CoBr_2$ was prepared by keeping $CoBr_2 \cdot 6H_2O$ (analytical grade) at 160°C. Fractionated EtOH, *iso*-PrOH, CHCl₃ (reagent grade), and MeCN (analytical grade) were employed as solvents. Reagent L and complex I were obtained as described in [26].

Synthesis of CuLBr₂ (II). A suspension of L (0.12 g, 0.5 mmol) in ethanol (7 ml) was added dropwise to a stirred solution of CuBr₂ (0.11 g, 0.5 mmol) in ethanol (3 ml). The mixing resulted, within a few seconds, in the formation of a reddish brown precipitate. The suspension was stirred for an hour. The precipitate was filtered off, washed with ethanol, and dried in air. The yield was 0.16 g (66%).

Reddish brown single crystals of two phases crystallized from a solution of complex **II** in *iso*-PrOH–MeCN (2 : 1). The crystals are solid solutions $\operatorname{CuL}_{(1-x)} \operatorname{L}'_x \operatorname{Br}_2$, where L' is 4-(4-bromo-3,5-dimethyl-1*H*-pyrazol-1-yl)-6methyl-2-phenylpyrimidine. X-ray diffraction analysis was carried out for crystals selected a day (**IIa**) and several days (**IIb**) after the start of the crystallization. Further crystallization gave orange single crystals of a copper(I) complex, namely, the solid solution $[\operatorname{CuL}_{(1-x)} \operatorname{L}'_x \operatorname{Br}]_2$ (**III**).

Synthesis of CoLCl₂ (IV), CoLBr₂ (V), and CoLI₂ (VI). A hot solution of ligand L (0.26 g, 1 mmol) in isopropyl alcohol (10-15 ml) was added dropwise to a stirred hot solution of an appropriate Co(II) salt $(1 \text{ mmol}; 0.13 \text{ g for CoCl}_2, 0.22 \text{ g for CoBr}_2, \text{ and } 0.35 \text{ g})$ for $CoI_2 \cdot 2H_2O$) in isopropyl alcohol (5 ml). The mixing resulted, in two to three minutes, in the formation of blue (complexes IV, V) and green precipitates (VI). The reaction mixture was heated while stirring it for 1-2 h. The precipitates were filtered off and washed in a beaker with isopropyl alcohol (3-4 ml) under heating while stirring the mixture for 1 h. The precipitates were filtered off, washed with a small amount of isopropyl alcohol, and dried in air. The yields of complexes IV, V, and VI were 0.31 g (79%), 0.31 g (64%), and 0.35 g (61%), respectively.

Single crystals of complexes IV-VI were grown by slow crystallization from their solutions in CH_2Cl_2 -MeCN (1 : 1).

The metal content of complexes I, II, and IV–VI was determined by complexometric titration following the decomposition of their samples in a mixture of concentrated H_2SO_4 and HNO_3 . An analysis for C, H, and N was performed on a Carlo Erba analyzer according to a standard procedure. The elemental analysis data are given in Table 1.

Electronic reflection spectra were recorded on a Unicam 700A spectrophotometer in the 340–2500 nm range. Electronic absorption spectra of solutions of the complexes in CHCl₃ (**II**, **V**, and **VI**) and CHCl₃–MeCN (**I** and **IV**) were recorded on a UV-3101 PC spectrophotometer (Shimadzu) in the 200–2500 nm range. IR absorption spectra were measured on Scimitar FTS 2000 (375–4000 cm⁻¹) and BOMEM MB-102 spectrophotometers (200–400 cm⁻¹).

Magnetic properties were studied on an MPMS-5s SQUID-magnetometer (Quantum Design) in the 2–300 K range with an applied magnetic field strength of 5 kOe. In calculation of molar magnetic susceptibility $\boldsymbol{\chi}$, the diamagnetism of the atoms was included via the Pascal additive scheme. The effective magnetic moment was calculated as $\mu_{eff} \approx (8\chi T)^{1/2}$.

X-ray diffraction analysis of phases IIa, IIb, and III-VI was carried out on a Bruker-Nonius X8Apex CCD automated four-circle diffractometer (Mo K_{α} radiation, $\lambda = 0.71073$ Å, graphite monochromator) according to a standard procedure. 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 for narrow frames (0.5°) up to $2\theta = 55^{\circ}$. Absorption correction was applied empirically with the SADABS program [27]. All six structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 in the anisotropic approximation for non-hydrogen atoms (SHELX-97) [28]. Since the crystals of phases IIa and **IIb** are isostructural with those of complex **I** (polymorph 2G) studied in [26], we performed structure refinement according to a known model. The H atoms were refined in the rigid-body approximation. In structures IIa, IIb, and III, the position at the C(4) atom of the pyrazole fragment of ligand L is statistically occupied by the H and Br atoms. The relative weight of the Br atom refined at fixed thermal parameters is 0.0015(2), 0.076(1), and 0.900(4) in structures **Ha**, **Hb**, and III, respectively. The crystals of complex IV are isostructural with those of complex I (20) [26]. The crystals of complexes V and VI are isostructural with each other. Atomic coordinates and thermal parameters have been deposited with the Cambridge Crystallographic Data Collection (nos. 711439-711444). Selected bond lengths and angles in six complexes are given in Table 3. The environment and molecular packing in the crystal structures were analyzed with the TOPOS 4.0 Professional program package [29].

Complexes I, II, and V were tested in ethene polymerization with methylaluminoxane as a cocatalyst ($P_{\text{ethene}} = 10 \text{ atm}, T = 35^{\circ}\text{C}, 70 \text{ ml of toluene}, [M] = 3 \times$ 10^{-5} mol/l, molar ratio Al_{cocat} : M = 500 (M = Cu and Co)).

RESULTS AND DISCUSSION

Complexes I and IV-VI were obtained by heating alcoholic solutions of appropriate metal salts and ligand L. In the synthesis of complex II, heating is unwanted because of partial reduction of complex II (the dark precipitate of the complex contains light inclusions). The precipitates of the complexes form shortly after the mixing of the solutions. The ratio M :

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY

L was 1 : 1 ($c_{\rm M} \approx 0.05-0.07$ mol/l). To avoid precipitation of some amount of the nonconsumed ligand L, the metal salt should be used in a small excess with respect to the reaction stoichiometry and the resulting precipitate should be thoroughly washed as described in the Experimental section. The complexes obtained are moderately soluble in ethanol, acetonitrile, isopropyl alcohol, dichloromethane, and chloroform and are negligible soluble in toluene. They decompose in water. Complexes I, II, V, and VI are stable in air. When stored in air, complex IV gradually decomposes for several weeks into cobalt(II) chloride hydrates and free ligand L, the IR spectrum of a stored sample no longer contains the v(OH) and v(Co-O) bands but it shows the v(Co-N) and v(Co-Cl) bands. Single crystals of complex II were not obtained because of partial bromination of ligand L in position 4 of the pyrazole ring when keeping its solution for a while. Single crystals of structures **Ha** and **Hb** are solid solutions $CuL_{(1-r)}L'_r Br_2$ (X-

ray diffraction data). The fraction of the Br atoms in position 4 of the pyrazole ring is ~1.5 and 7.6% in IIa and IIb, respectively. Thus, phase IIa corresponds to high-purity complex **II**. Apparently, the formation of such solid phases is due to the reduction of Cu(II) in complex II with Br⁻ ions in solution. This results in evolution of Br₂ and partial bromination of the pyrazole ring of ligand L. When kept for several days, the crystallization solution produces copper(I) complex III as orange crystals of the solid solution $[CuL_{(1-x)}L'_{x}Br]_{2}$

(x = 0.90). The observed reduction of Cu(II) to Cu(I) with Br-ions agrees with data in [30, 31]. In contrast to data in [13], according to which copper(II) is also reduced to copper(I) in a complex of CuBr₂ with 2-(3,5diphenyl-1*H*-pyrazol-1-yl)-4,6-diphenylpyrimidine,

this reduction is accompanied by bromination of the pyrazole ring of ligand L in our case. This is favored by the presence of less bulky and more electron-donating methyl groups compared to the phenyl substituents in 2-(3,5-diphenyl-1H-pyrazol-1-yl)-4,6-diphenylpyrimidine [13]. Similar examples of halogenation have been cited in [32–34]. The bromination at position 4 of the pyrazole ring, which is a π -abundant heterocyclic fragment in ligand L, suggests its electrophilic mechanism. Thus, the reduction of copper(II) to copper(I) occurs very slowly and is accompanied by bromination of ligand L. To elucidate the details of these transformations, further investigations are required. The overall scheme of transformations is as follows:

2009

Complex	Ша	III	Ш	N	Λ	M
Empirical formula	$C_{16}H_{15.98}Br_{2.02}CuN_4$	$C_{16}H_{15.92}Br_{2.08}CuN_4$	$C_{32}H_{30.2}Br_{3.8}Cu_2N_8$	$C_{16}H_{16}Cl_2C_0N_4$	$\mathrm{C}_{16}\mathrm{H}_{16}\mathrm{Br}_{2}\mathrm{CoN}_{4}$	$C_{16}H_{16}Col_2N_4$
M	488.87	493.61	957.58	394.16	483.08	577.06
Temperature, K	120.0(2)	293(2)	293(2)	100.0(2)	100.0(2)	91.0(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_{1}/c$	P2/n	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	7.1623(3)	7.276(2)	7.6299(4)	9.8479(3)	11.8686(4)	12.0855(3)
$b, m \AA$	11.9397(3)	11.953(3)	11.8399(6)	18.6256(5)	11.3109(3)	11.7761(3)
$c, { m \AA}$	20.5684(7)	20.794(7)	19.0505(9)	9.8362(3)	12.8776(4)	12.8893(4)
B, deg	99.9800(10)	100.579(8)	95.816(2)	109.4760(10)	95.7720(10)	93.0970(10)
$V, Å^3$	1732.31(10)	1777.7(9)	1712.11(15)	1700.95(9)	1719.98(9)	1831.73(9)
Z	4	4	2	4	4	4
p(calcd), g/cm ³	1.874	1.844	1.857	1.539	1.866	2.093
μ, mm ⁻¹	5.912	5.896	5.713	1.326	5.647	4.311
F(000)	958	966	938	804	948	1092
Crystal size, mm	$0.17 \times 0.90 \times 0.03$	$0.14 \times 0.10 \times 0.07$	$0.13 \times 0.11 \times 0.03$	$0.45 \times 0.35 \times 0.25$	$0.33 \times 0.17 \times 0.14$	$0.51 \times 0.46 \times 0.15$
θ scan range, deg	1.98–31.34	2.62–32.52	2.75–27.50	2.45–31.28	2.22–30.93	2.25-31.42
Ranges of <i>h</i> , <i>k</i> , and <i>l</i> indices	$-9 \le h \le 10$,	$-10 \le h \le 10,$	$-9 \le h \le 9,$	$-14 \le h \le 13$,	$-16 \le h \le 15,$	$-16 \le h \le 17,$
	$-10 \le k \le 10,$ $-29 \le l \le 29$	$-9 \leq k \leq 12$, $-31 \leq l \leq 31$	$-15 \le k \le 15$, $-20 \le l \le 24$	$-23 \leq k \leq 24,$ $-14 \leq l \leq 9$	$-10 \le k \le 10$, $-15 \le l \le 17$	$-10 \le k \le 11$, $-18 \le l \le 17$
Number of measured re- flections	15935	16204	12027	14673	12913	18666
Number of independent re- flections	$^{4856}_{(R_{int} = 0.0484)}$	5509 ($R_{\rm int} = 0.0336$)	3931 ($R_{\rm int} = 0.0439$)	4482 ($R_{\rm int} = 0.0186$)	4730 ($R_{\rm int} = 0.0196$)	5273 ($R_{\rm int} = 0.0302$)
Number of reflections with $I \ge 2\sigma(I)$	3231	4447	2330	4138	3893	4899
Number of parameters re- fined	213	217	211	211	211	212
GOOF	0.997	1.004	0.974	1.033	1.028	1.087
$R_1 \left(I > 2_{\sigma}(I) \right)$	0.0373	0.0483	0.0385	0.0226	0.0230	0.0188
wR_2 (for all reflections)	0.671	0.1435	0.1011	0.0594	0.0486	0.0431
Residual electron density (min/max), $e \text{ Å}^{-3}$	-0.621/0.671	-0.619/1.100	-0.421/0.571	-0.239/0.430	-0.314/0.518	-0.590/0.587

Table 2. Crystallographic parameters and a summary of data collection for structures II-VI

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 35 No. 8 2009

600

Complex	IIa (M = Cu, X = Br)	$\frac{IIb}{(M = Cu, X = Br)}$	III (M = Cu, X = Br)	IV (M = Co, X = Cl)	V (M = Co, X = Br)	VI $(M = Co, X = I)$
	((d Å	(,	(, ,	()
M(1) - X(1)	2,3536(5)	2,3503(8)	2,3632(6)	2,2389(3)	2,3604(3)	2,5519(3)
M(1) - X(2)	2.3314(5)	2.3264(8)	2.3632(6)	2.2286(4)	2.3595(3)	2.5510(3)
M(1) - M(1')*	2.001.(0)		3.0203(9)			
M(1) - N(1)	1.998(3)	2.005(4)	1.987(3)	2.0193(10)	2.0052(14)	2.0037(15)
M(1)–N(4)	2.014(3)	2.024(3)	2.455(3)	2.0634(10)	2.0929(15)	2.0875(16)
C(3)–C(4)	1.400(5)	1.406(7)	1.412(5)	1.4091(17)	1.408(2)	1.414(3)
C(3)-C(31)	1.486(5)	1.475(6)	1.470(5)	1.4870(17)	1.484(3)	1.483(3)
C(3)–N(1)	1.347(4)	1.340(5)	1.329(5)	1.3296(15)	1.330(2)	1.331(2)
C(4)–C(5)	1.369(5)	1.360(6)	1.353(5)	1.3712(16)	1.364(3)	1.364(3)
C(5)–C(51)	1.496(5)	1.493(7)	1.489(5)	1.4893(16)	1.491(2)	1.490(3)
C(5)–N(2)	1.374(4)	1.380(5)	1.370(4)	1.3809(15)	1.386(2)	1.386(2)
C(6)–C(7)	1.382(4)	1.374(5)	1.388(5)	1.3809(15)	1.380(3)	1.385(3)
C(6)–N(2)	1.406(4)	1.401(5)	1.416(4)	1.4055(14)	1.393(2)	1.395(2)
C(6)–N(4)	1.350(4)	1.344(5)	1.327(4)	1.3492(15)	1.353(2)	1.352(2)
C(7)–C(8)	1.386(5)	1.382(6)	1.381(5)	1.3951(17)	1.389(2)	1.392(2)
C(8)–C(81)	1.493(5)	1.502(6)	1.508(5)	1.4983(16)	1.500(3)	1.493(3)
C(8)–N(3)	1.349(4)	1.337(5)	1.336(5)	1.3448(17)	1.330(2)	1.354(2)
C(9)–C(10)	1.476(4)	1.483(5)	1.482(5)	1.4771(17)	1.483(2)	1.481(2)
C(9)–N(3)	1.329(4)	1.326(5)	1.335(4)	1.3373(15)	1.350(2)	1.330(2)
C(9)–N(4)	1.358(4)	1.350(5)	1.343(4)	1.3515(14)	1.357(2)	1.359(2)
C(10)-C(11)	1.394(5)	1.392(6)	1.377(6)	1.3965(17)	1.397(2)	1.403(2)
C(10)–C(15)	1.383(5)	1.375(6)	1.391(5)	1.3980(19)	1.394(3)	1.388(3)
C(11)-C(12)	1.389(5)	1.378(7)	1.375(6)	1.390(2)	1.388(3)	1.394(3)
C(12)-C(13)	1.377(5)	1.388(7)	1.360(6)	1.391(2)	1.390(3)	1.381(3)
C(13)-C(14)	1.379(5)	1.356(7)	1.376(6)	1.387(2)	1.385(3)	1.391(3)
C(14)–C(15)	1.389(5)	1.394(7)	1.380(5)	1.3910(18)	1.389(3)	1.391(3)
N(1)–N(2)	1.389(4)	1.378(5)	1.386(4)	1.3812(13)	1.382(2)	1.380(2)
C(4)–Br(3)	1.74(3)	1.784(7)	1.868(4)			
Br(3)···Br(3')*	2.83(6)	2.766(13)				
Angle		-	ω,	deg	-	
X(1)-M(1)-X(2)	101.62(2)	101.77(3)	103.87(2)**	111.053(12)	113.130(12)	112.598(10)
N(1)-M(1)-X(1)	136.60(8)	136.51(10)	111.64(9)	120.78(3)	118.73(5)	118.67(5)
N(1)-M(1)-X(2)	102.95(8)	102.94(10)	133.75(10)**	103.95(3)	110.64(4)	110.97(5)
N(4)-M(1)-X(1)	96.14(8)	96.70(9)	124.12(8)	109.43(3)	104.02(4)	103.13(4)
N(4)-M(1)-X(2)	149.03(8)	148.64(9)	109.72(7)**	129.81(3)	127.72(4)	129.17(4)
N(1)-M(1)-N(4)	80.12(11)	79.62(13)	73.50(11)	78.81(4)	79.38(6)	79.35(6)
Angle			φ,	deg		
N(3)-C(9)-C(10)-C(11)	32.2(5)	31.3(5)	17.7(6)	42.35(17)	37.89(18)	37.5(2)
C(5)–N(2)–C(6)–C(7)	15.2(6)	14.8(6)	34.0(6)	12.5(2)	18.9(3)	17.9(3)
	Dev	viation from the	plane N(1)–N(2)–	C(6)–N(4), Å	1	1
M(1)	0.426(5)	0.437(6)	0.445(7)	-0.050(2)	0.277(3)	0.275(3)
X(1)	2.316(7)	2.335(8)	-1.14(1)	1.756(3)	2.465(4)	2.642(4)
X(2)	-0.24(1)	-0.24(1)	-1.29(1)	-1.772 (3)	-1.201(5)	-1.273(5)

Table 3. Selected bond lengths *d* and bond (ω) and torsion angles (ϕ) in structures **II–VI**

Notes: * The symmetry operation code is -x + 1, -y, -z + 1.

** The angles are given for X(2) = Br(1').



Solid phases **IIa** and **IIb** are built from the molecules of mononuclear copper(II) complexes containing ligands L and L' and Br⁻ ions (Fig. 1). The coordination polyhedron of the Cu atom is a distorted tetrahedron made up of the N(1) and N(4) atoms and the bromide ions. The coordination of ligands L and L' results in closure of the five-membered chelate ring CuN₃C. In structures IIa and IIb, the degree of replacement of the H atoms by Br atoms virtually does not affect the bond lengths in the pyrazole ring: the differences do not exceed the standard deviation (Table 3). Solid phase III is built from the molecules of a binuclear copper(I) complex with two bridging Br atoms between the Cu atoms (Fig. 2). The coordination of ligands L and L' results in closure of the five-membered chelate ring CuN₃C. The degree of replacement of the H atoms by the Br atoms in position 4 of the pyrazole ring is 90%.

Removal of the solvent from the crystallization mixture gave a small amount of yellowish needlelike crystals (compound **VII**); the parameters of its face-centered monoclinic unit cell are a = 7.224(3), b =22.689(10), c = 19.151(9) Å, $\beta = 100.304(12)^\circ$, V =3088(2) Å³. The X-ray diffraction analysis performed for the space group C2/c showed that these crystals are the solid solution $L_{(1-x)}L'_x$ ($x \approx 0.6$). Unfortunately, the quality of the crystal precluded us from obtaining the *R* factor below 10% in a model allowing for pseudomerohedral twinning. The Br content is ~60% (after the refinement of position multiplicity). The atomic coordinates in compound **VII** are omitted because of the low accuracy of structure determination. The solid solution obtained is not isostructural with the starting ligand L [26]. In both structures, the conformation of pyrazolylpyrimidine is identical; the orientation of the pyrazole fragment relative to the pyrimidine one is opposite to the conformation of ligands L coordinated by the metal atom. In structure L [26], molecules are stacked by π - π -interactions, lying exactly above each other (motif AAA...). Structure $L_{0.4}L'_{0.6}$ also shows molecu-

lar π -stacking (Fig. 3). However, its molecules are alternately rotated with respect to each other, thus making the sequence ABAB... Apparently, the presence of the Br atoms makes the stacking motif AAA... unfeasible because a very short intermolecular contact Br...Br (~3.5 A) dictated by π -stacking interactions between



Fig. 1. Molecular structure IIa with atomic thermal displacement ellipsoids (50% probability).

the molecules becomes inevitable. To prevent this unwanted contact, the stacked molecules are rotated with partial retention of the π -stacking contacts. This is indirectly confirmed by the absence of noticeable intermolecular contacts Br...Br (< 3.95 Å characteristic of normal van der Waals contacts [35]), except for randomly occurring shortened contacts (3.75 Å) between adjacent molecules in a stack.

Complexes **IV–VI** are structurally similar (Fig. 4). The coordination polyhedra in the complexes are distorted tetrahedra CoLHal₂. Ligands L are coordinated to the metal atom in a chelating bidentate fashion through the N(1) and N(4) atoms to form five-membered chelate rings CoN₃C.

Unlike the complex CuLCl₂ [26], the complexes CoLHal₂ show no polymorphism. The crystals of complex **IV** are isostructural with those of complex **I** (polymorph 2O) [26]. In the crystal of complex **IV**, the planes of the π -systems in uneven molecular stacks are spaced at 3.55 and 4.81 Å. In polymorph 2O, the corresponding values are 3.63 and 4.67 Å, which suggests an increased fraction of pair interactions in stacks for complex **IV**. This can be due to a conformational difference between structures 2O and IV: in complex **IV**, the relative angle between the pyrimidine and pyrazole rings is greater almost by 10° than that in polymorph 2O and the angle between the planes of the phenyl substituent and the pyrimidine ring is also greater (Table 3).

Packing of isostructural crystals V and VI has no analogs among the polymorphs of CuLCl₂. In the crystal, stacked pyrimidine rings are spaced at 3.65 and 3.56 Å for V and VI, respectively, to form π -stacking dimeric ensembles. Similar dimeric ensembles have been found in complex I (polymorph 2EG) [26]. However, in complexes V and VI, the π -stacking interaction involves only the pyrimidine fragment of the ligand (Table 3), while in polymorph 2EG, both the pyrimidine and pyrazole rings participate in π - π interactions [26]. Apparently, this structural feature accounts for the existence of a new structural type for the complexes CoLX₂ (X = Br and I). In both structures, packed dimers are sloping toward each other to make a peculiar "par-



Fig. 2. Molecular structure III with atomic thermal displacement ellipsoids (50% probability).

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 35 No. 8 2009



Fig. 3. Molecular packing in the crystal structure $L_{0.4}L'_{0.6}$.

quet" stacking and their centers form a distorted bodycentered cubic packing (Fig. 5).

In ligand L, the pyrazole and pyrimidine rings absorb at $1589-1535 \text{ cm}^{-1}$ (stretching bends; Table 4). In the IR spectra of metal complexes with ligand L, the system of these bands changes substantially because of its coordination by metal atoms. In the spectrum of free



Fig. 4. Molecular structure of complexes IV–VI with atomic thermal displacement ellipsoids (50% probability).

ligand L, the band due to the phenyl ring is difficult to identify because of conjugation of the double bonds. In contrast, the spectra of the complexes show a band of the phenyl substituent at 1604–1599 cm⁻¹. This suggests a changed geometry of the coordinated ligand L, *viz.*, the diminished conjugation between the phenyl and pyrimidine rings, which agrees with X-ray diffraction data for ligand L and its complexes. In the low-frequency range, the spectra of the complexes exhibit bands due to v(M–N) and v(M–Hal) stretches (Table 4). The v(M–N) bands appear at 407–504 cm⁻¹ for all complexes. For the v(M–Hal) bands, the frequency ratios v(M–Br)/v(M–Cl) are close to the literature data (0.77–0.74) [36]; the frequency ratio v(Co–I)/v(Co–Cl) also correlates with the literature data (~ 0.65) [36].

The electronic absorption and reflection spectra of complexes I, II, and IV–VI are given in Table 5. The number and positions of the bands in the spectra of complexes IV–VI is consistent with the distorted tetrahedral structure of the coordination polyhedron of the Co atom. The spectra contain three structured bands. The close positions of analogous peaks in the electronic absorption and reflection spectra suggest the retention of the compositions and structures of the complexes upon their dissolution. The near-IR range shows a wide asymmetric band due to the transitions to the components of the term ${}^{4}T_{1}(F)$ [37]. A wide band of the term ${}^{4}T_{1}(P)$ is split into two (complexes V and VI) or three



Fig. 5. (a) Centrosymmetric π - π -stacking dimer in structure VI and (b) packing of the dimers in the crystal.

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 35 No. 8 2009

BUSHUEV et al.

Compound	$(v + \delta)$ (of the ring)	v(Ph)	v(M–N)	v(M–Hal)
L	1589, 1582, 1567, 1535 sh			
$CuLCl_{2}(\mathbf{I})$	1582, 1570, 1560 sh, 1535	1599	499, 446, 407	331, 311
$CuLBr_{2}(\mathbf{II})$	1581, 1570, 1560, 1534	1599	499, 444, 407	271, 255, 243
$CoLCl_2(IV)$	1592 sh, 1578, 1570, 1560 sh, 1540 sh, 1530	1604	504, 439, 407	342, 330, 321
$CoLBr_{2}(V)$	1579, 1571, 1560, 1541, 1527	1600	503, 440, 407	274, 251, 242
$CoLI_2(VI)$	1579, 1570, 1560, 1540, 1527	1599	504, 442, 407	230

Table 4. Selected frequencies in the IR spectra (cm⁻¹) of free ligand L and its complexes

Table 5.	Electronic absorption	and reflection spectra	of complexes I, II,	and IV–VI
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Complex	Electronic ab	sorption spectrum	Electronic reflection spectrum	Transition
	ν, cm ⁻¹	ϵ , l mol ⁻¹ cm ⁻¹	v, cm ⁻¹	
CuLCl ₂ (I)			25700	
	22800	748	21900	
	12500	190	12750	
			9490	
CuLBr ₂ (II)	22700	1075	21400	
	17400	499	17400	
	11900	274	12 260 sh	
			8900	
CoLCl ₂ (IV)			27800	
	17600	278	18100	
	16300	318		$4A_2 \longrightarrow {}^4T_1(P)$
	14800	398	15200	
	9090	25.2	9490 sh	
	7210	37.2	7400	$A_2 \longrightarrow {}^{4}T_1(F)$
$CoLBr_{2}(V)$			27800	
	17240	160	17320	
	14900	328	14900	$\int {}^{4}A_{2} \longrightarrow {}^{4}T_{1}(P)$
			9120 sh	
	7246	37.0	7370	$\int {}^{4}A_{2} \longrightarrow {}^{4}T_{1}(F)$
CoLI ₂ (VI)	24400	2218	23600	
	16100	300	16200	
	14700	657	15000	$\int {}^{4}A_{2} \longrightarrow {}^{4}T_{1}(P)$
			8770 sh	
	7100	81	7370	$\int {}^{4}A_{2} \longrightarrow {}^{4}T_{1}(F)$

components (IV); i.e., the symmetry of the coordination polyhedron is lower than T_d . The intensities of the components of both bands correlate with the literature data [37]. The high-frequency bands (at ~25000– 28000 cm⁻¹) are more intense and seem to be chargetransfer bands. For complexes **I** and **II**, the μ_{eff} values are virtually temperature-independent down to 20 K (Fig. 6); $\mu_{\text{eff}} =$ 1.78 and 1.77 μ_{B} for complexes **I** and **II**, respectively, approximate to the purely spin magnetic moment (1.73 μ_{B}) for non-interacting Cu²⁺ ions with the spin *S* = 1/2 and *g* = 2. Below the liquefaction temperature of



Fig. 6. Plots of μ_{eff} vs. *T* for complexes (a) VI and (b) I.

helium, $\mu_{eff}(T)$ for complexes I and II decreases to 1.76–1.75 $\mu_{\rm B}$, which suggests weak antiferromagnetic interactions between Cu^{2+} ions. Since the magnetic behavior of Cu(II) complexes (I and II), as well as that of Co(II) complexes (IV-VI), is virtually identical, here we present experimental curves $\mu_{eff}(T)$ only for complexes I and VI. At room temperature, μ_{eff} is 4.55, 4.58, and 4.87 μ_B for IV, V, and VI, respectively. With a decrease in the temperature to 160 K, the above μ_{eff} values show a gradual decline to 4.40, 4.39, and 4.74 $\mu_{\rm B}$. Such a run of the curve $\mu_{eff}(T)$ is mainly due to the spinorbital couplings of the Co²⁺ ions. In the temperature range from 50 to 150 K, the μ_{eff} values remain nearly constant (4.40, 4.39, and 4.74 μ_B). This is above a theoretical limit (3.87 μ_B) for non-interacting Co²⁺ ions with the spin S = 3/2 and g = 2. In this case, the orbital contribution to the magnetic moment of Co²⁺ ions also plays a part. Below 50 K, μ_{eff} decreases to 3.39, 3.43, and 3.77 $\mu_{\rm B}$ (2 K) for complexes IV, V, and VI, respectively. This suggests dominant antiferromagnetic interactions between Co²⁺ ions. According to the curves $\mu_{\text{eff}}(T)$ obtained for complexes **IV–VI**, the efficiency of these interactions is low ($\leq 1 \text{ cm}^{-1}$).

Unlike complexes of $CuCl_2$ and $CuBr_2$ with 2-(3,5diphenyl-1*H*-pyrazol-1-yl)-4,6-diphenylpyrimidine, which are active in ethene polymerization [13], complexes **I**, **II**, and **V** are inactive under the same conditions. It should be noted that the coordination polyhedra of the copper atoms in complexes **I** and **II** differ only slightly from those in the complexes described in [13]. Apparently, the catalytic inactivity of complexes **I**, **II**, and **V** can be due to the spatial and electronic features of ligand L that differ from those of 2-(3,5-diphenyl-1*H*-pyrazol-1-yl)-4,6-diphenylpyrimidine (relative positions of the pyrazole and pyrimidine rings and the presence of dissimilar substituents in positions 3 and 5 of the pyrazole ring).

ACKNOWLEDGMENTS

We are grateful to I.V. Yushina for recording the electronic absorption spectra of the complexes and to V.A. Blatov (Samara State University) for providing the TOPOS 4.0 Professional program package.

REFERENCES

- 1. Britovsek, G.J.P., Gibson, V.C., Kimberley, B.S., et al., J. Chem. Soc., Chem. Commun., 1998, no. 7, p. 849.
- 2. Britovsek, G.J.P., Bruce, M., Gibson, V.C., et al., *J. Am. Chem. Soc.*, 1999, vol. 121, no. 38, p. 8728.
- 3. Sun, W.H., Zhang, D., Zhang, S., et al., *Kinet. Catal.*, 2006, vol. 47, no. 2, p. 278.
- 4. Gibson, V.C. and Spitzmesser, S.K., *Chem. Rev.*, 2003, vol. 103, no. 1, p. 283.
- 5. Ittel, S.D., Johnson, L.K., and Brookhart, M., *Chem. Rev.*, 2000, vol. 100, no. 4, p. 1169.
- 6. Bianchini, C., Giambastiani, G., Rios, I.G., et al., *Coord. Chem. Rev.*, 2006, vol. 250, nos. 11-12, p. 1391.
- 7. Gibson, V.C., Tomov, A., Wass, D.F., et al., *Dalton Trans.*, 2002, no. 11, p. 2261.
- Stibrany, R.T., Schulz, D.N., Kacker, S., and Patil, A.O. PCT Int. Appl., WO 99/30822, 1999.
- 9. Karam, A.R., Catari, E.L., L'Pez-Linares, F., et al., *Appl. Catal.*, *A*, 2005, vol. 280, no. 2, p. 165.
- 10. Gomez de la Torre, F., de la Hoz, A., Jalon, F.A., et al., *Inorg. Chem.*, 2000, vol. 39, no. 6, p. 1152.

No. 8

2009

- 11. Escriva, E., Garcia-Lozano, J., Martinez-Lillo, J., et al., *Inorg. Chem.*, 2003, vol. 42, no. 25, p. 8328.
- 12. Elguero, J., Guerrero, A., Gomez De La Torre, F., et al., *New J. Chem.*, 2001, vol. 25, no. 8, p. 1050.
- 13. Bushuev, M.B., Krivopalov, V.P., Semikolenova, N.V., et al., *Koord. Khim.*, 2006, vol. 32, no. 3, p. 208 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 32, no. 3, p. 199].
- 14. Ikeda, M., Maruyama, K., Nobuhara, Y., et al., *Chem. Pharm. Bull.*, 1996, vol. 44, no. 9, p. 1700.
- 15. Ikeda, M., Maruyama, K., Nobuhara, Y., et al., *Chem. Pharm. Bull.*, 1997, vol. 45, no. 3, p. 549.
- 16. Sedereviciute, V., Garaliene, V., Vainilavicius, P., and Hetzheim, A., *Pharmazie*, 1998, vol. 53, no. 4, p. 233.
- 17. Hoffmann, M.G., Helmke, H., Willms, L., et al., U.S. Pat. Appl. Publ., US 2005209106A1, 2005.
- Liu, W.M., Zou, X.M., Song, H.H., et al., *Chin. J. Org. Chem.*, 2006, vol. 26, no. 11, p. 1600.
- Eriksen, B.L., Teuber, L., Hougaard, C., and Sorensen, U.S., *PCT Int. Appl.*, WO 2006100212A1, 2006.
- 20. Fischer, R., Alig, B., Bretschneider, T., et al., *Ger. Offen.*, DE 10108480, 2002.
- 21. Fischer, R., Alig, B., Bretschneider, T., et al., U.S. Pat. US 7087616B2, 2006.
- 22. Oshima, Y., Akimoto, T., Tsukada, W., et al., *Chem. Pharm. Bull.*, 1969, vol. 17, no. 7, p. 1492.
- 23. Halcrow, M.A., *Polyhedron*, 2007, vol. 26, no. 14, p. 3523.
- Thompson, A.L., Money, V.A., Goeta, A.E., and Howard, J.A.K., *Compt. Rend. Chimie*, 2005, vol. 8, nos. 8–9, p. 1365.

- 25. Carbonera, C., Costa, J.S., Money, V.A., et al., *Dalton Trans.*, 2006, no. 25, p. 3058.
- Peresypkina, E.V., Bushuev, M.B., Virovets, A.V., et al., Acta Crystallogr, Sect. B: Struct. Sci., 2005, vol. 61, no. 2, p. 164.
- 27. SADABS. Version 2.11. Bruker Advanced X-ray Solutions, Madison (WI, USA): Bruker AXS Inc., 2004.
- 28. SHELXTL. Version 6.22. Bruker Advanced X-Ray Solutions, Madison (WI, USA): Bruker AXS Inc., 2005.
- 29. Blatov, V.A., Newsletter Commission on Crystallographic Computing of International Union of Crystallography, 2006, no. 7, p. 4.
- 30. Schneider, W. and Zelewsky, A.V., *Helv. Chim. Acta*, 1963, vol. 46, no. 6, p. 1848.
- 31. Barnes, J.C. and Hume, D.N., *Inorg. Chem.*, 1963, vol. 2, no. 3, p. 444.
- 32. Dick, A.R., Hull, K.L., and Sanford, M.S., *J. Am. Chem. Soc.*, 2004, vol. 126, no. 8, p. 2300.
- 33. Wan, X., Ma, Z., Li, B., et al., *J. Am. Chem. Soc.*, 2006, vol. 128, no. 23, p. 7416.
- 34. Roh, S. and Bruno, J.W., *Inorg. Chem.*, 1986, vol. 25, no. 17, p. 3105.
- Zefirov, Yu.V., *Kristallografiya*, 1997, vol. 42, no. 1, p. 122 [*Crystallogr. Rep.* (Engl. Transl.), vol. 42, no. 1, p. 111].
- Nakomoto, K., Infrared and Raman Spectra of Inorganic and Coordination Compounds, New York: Wiley, 1986.
- 37. Lever. A.B.P., *Inorganic Electronic Spectroscopy*, Amsterdam: Elsevier, 1984, vol. 2.