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Cobalt(II), Nickel(II), and Copper(II) Bromide Complexes with 3-Amino-4-Ethoxycarbonylpyrazole: Syntheses, Structures, and Magnetic Properties

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Abstract—New complexes of cobalt(II), nickel(II), and copper(II) bromides with 3-amino-4-ethoxycarbonylpyrazole (L) of the composition $ML_4Br_2 \cdot 2H_2O$ (M = Co(II) and Ni(II)) and CuL_2Br_2 are synthesized. The compounds are studied by X-ray diffraction analysis (CIF files CCDC nos. 1006284 (**I**), 1006286 (**II**), and 1006285 (**III**)), IR spectroscopy, and static magnetic susceptibility. In the complexes, the metal ions are in the distorted octahedral environment and the ligand is coordinated to the metal by the N(2) atom of the pyrazole cycle according to the monodentate mode. The Co(II) and Ni(II) complexes are mononuclear, whereas CuL_2Br_2 is polynuclear due to the bridging function of the bromide ion. Complex CuL_2Br_2 possesses the thermochromic properties: the transition of the color is brown (at room temperature) ⇔ light brown (at the temperature of liquid nitrogen).

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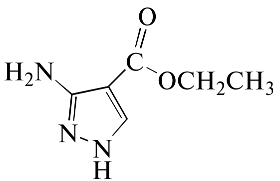
INTRODUCTION

Complexes of the first transition row metals with heterocyclic nitrogen-containing ligands attract attention of researchers as compounds with an increased response to a change in the external conditions: the temperature, pressure, or irradiation with the light of a certain wavelength. For example, the iron(II) complexes with ligands of this class have spin crossover $^1A_1 \Leftrightarrow {}^5T_2$, which is accompanied by thermochromism in many cases [1, 2]. Antiferro- or ferromagnetic exchange interactions are observed in the oligo- and polynuclear cobalt(II), nickel(II), and copper(II) complexes [3–5]. In addition, many 3*d*-metal complexes with nitrogen-containing ligands are biologically active.

We have earlier synthesized compounds with 3-amino-4-ethoxycarbonylpyrazole (L) of the composition ML_2Cl_2 (M = Co(II), Ni(II), and Cu(II)) [6]. According to the magnetochemical data, the complexes exhibit the ferromagnetic exchange interactions, whereas the transition to the magnetically ordered state (Curie temperature $T_c \cong 10–12$ K) was found for CoL_2Cl_2 and NiL_2Cl_2. It seemed reasonable to continue the work with this ligand and to study the influence of the anion on the composition and magnetic properties of the complexes. This work is devoted to the synthesis of Co(II), Ni(II), and Cu(II) bromide complexes and to the comparison of their properties with those of the earlier studied complexes of M(II) chlorides with L.



(L)

EXPERIMENTAL

The following reagents were used for the syntheses: $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $CuBr_2$ (high-purity grade), KBr (special purity grade), 3-amino-4-ethoxycarbonylpyrazole (Aldrich), and ethanol (rectificate).

Synthesis of complexes $CoL_4Br_2 \cdot 2H_2O$ (I) and $NiL_4Br_2 \cdot 2H_2O$ (II). Complex $Co(Ni)(NO_3)_2 \cdot 6H_2O$ (0.29 g, 0.001 mol) and KBr (0.71 g, 0.006 mol) were simultaneously dissolved in ethanol (10 mL), and a hot solution of L (0.62 g, 0.004 mol) was added to the obtained solution. A pink precipitate of complex **I** and a light blue precipitate of complex **II** were formed after

~1/3 of the volume of the solvents was removed and the solutions were cooled. The precipitates were filtered off and two times washed with ethanol. The obtained substances were dried in air. The yield of complex **I** was 0.63 g (75%), and that of complex **II** was 0.48 g (57%).

Synthesis of complex CuL_2Br_2 (III). Weighed samples of $CuBr_2$ (0.22 g, 0.001 mol) and L (0.31 g, 0.002 mol) were separately dissolved in ethanol (5 mL). The solutions were mixed, and a solvent excess was removed by boiling in a water bath to ~1/2 of the initial volume. The brown precipitate formed on cooling of the solution was filtered off, washed, and dried as described above. The yield was 0.45 g (85%).

For $C_{24}H_{40}N_{12}O_{10}Br_2Co$ (**I**)

anal. calcd., %:	C, 32.9;	H, 4.4;	N, 19.2.
Found, %:	C, 32.6;	H, 4.4;	N, 19.0.

For $C_{24}H_{40}N_{12}O_{10}Br_2Ni$ (**II**)

anal. calcd., %:	C, 32.9;	H, 4.4;	N, 19.2.
Found, %:	C, 31.6;	H, 4.4;	N, 18.7.

For $C_{12}H_{18}N_6O_4Br_2Cu$ (**III**)

anal. calcd., %:	C, 27.0;	H, 3.4;	N, 15.7;	Cu, 11.9.
Found, %:	C, 26.7;	H, 3.7;	N, 15.4;	Cu, 11.8.

Single crystals of compounds **I–III** suitable for X-ray diffraction analysis were obtained by slow crystallization from the mother liquors after the polycrystalline phases were separated.

Elemental analyses of the complexes were carried out at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences) on a EURO EA 3000 instrument (EuroVector, Italy). An analysis to copper was carried out by the complexonometric method after samples of the complexes were decomposed in a mixture of concentrated $HClO_4$ and H_2SO_4 (2 : 1) on reflux.

IR absorption spectra were recorded on Scimitar FTS 2000 and Vertex 80 spectrometers in a range of 4000–100 cm^{-1}. Samples were prepared as suspensions in Nujol, fluorinated oil, and polyethylene.

X-ray diffraction analysis was carried out using a standard procedure on a Bruker APEX-II CCD automated four-circle diffractometer equipped with a CCD two-coordinate detector (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator). Reflection intensities were measured by the method of φ and ω scanning of narrow (0.5°) frames. An absorption correction was applied empirically by the SADABS program [7]. Structures **I–III** were solved by a direct method and refined by the least-square method in the anisotropic approximation for non-hydrogen atoms (SHELXTL) [8]. In complex **II**, the hydrogen atoms of the organic ligands were refined in the rigid body approximation; in other cases, the refinement was performed without restraints. The main parameters of structural experiments are presented in Table 1. Selected bond lengths and bond angles are given in Table 2. The results of X-ray diffraction experiments were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1006284 (**I**), 1006286 (**II**), 1006285 (**III**); www.ccdc. cam.ac.uk/data_request/cif).

The magnetic properties of polycrystalline samples were studied on an MPMS-XL SQUID magnetometer (Quantum Design) in the temperature range 2–300 K and in a magnetic field of 5 kOe. Diamagnetic corrections were applied according to Pascal's additive scheme to calculate the paramagnetic component of the molar magnetic susceptibility (χ). In the paramagnetic region the effective magnetic moment was calculated by the formula $\mu_{eff} = \left(\frac{3k}{N_A\mu_B^2}\chi T\right)^{1/2} \approx (8\chi T)^{1/2}$, where k is the Boltzmann constant, N_A is Avogadro's number, and μ_B is Bohr's magneton.

RESULTS AND DISCUSSION

The compositions of Co(II) and Ni(II) bromide complexes **I** and **II** differ from those of the earlier obtained chloride complexes. Compounds **I** and **II** were obtained from acidified aqueous-ethanol solutions at the metal to ligand ratio equal to 1 : 4. The elemental analysis data showed that mixtures of the compounds are isolated at a lower metal to ligand ratio. The metal to ligand ratio equal to 1 : 2 was used to obtain complex **III**, as in the synthesis of the chloride complexes ML_2Cl_2 (M = Co(II), Ni(II), and Cu(II)).

The compounds crystallize as CuL_2Br_2 (**III**) and hydrates $ML_4Br_2 \cdot 2H_2O$ (M = Co (**I**), Ni (**II**)). The crystals of complexes **I** and **II** are isostructural and have the molecular structure. The metal ion lies in the inversion center, and half an ML_4Br_2 molecule is independent (Fig. 1a). The central ion has a distorted octahedral environment N_4Br_2, and the deviations of the angles from 90° do not exceed 1.3°. The M–N and M–Br distances have usual values (Table 2). The A···H–D contacts connecting the ML_4Br_2 and water molecules in the xy plane are observed in the packing of the complexes (Table 3, Fig. 2).

Complex **III** also lies on the symmetry center. The nearest environment of the copper ion consists of two nitrogen atoms of the pyrazole cycles and two bromide ions forming a nearly regular quadrangle (the deviations of the bond angles from 90° do not exceed 0.5°). The axial positions in the polyhedron are occupied by the bromide ions of the adjacent molecules bound by the translation along the x axis, and the central ion has

Table 1. Crystallographic data and experimental details for compounds **I–III**

Parameter	Value		
	I	**II**	**III**
M	875.43	875.21	533.68
Space group; Z	$P\bar{1}$; 1	$P\bar{1}$; 1	$P\bar{1}$; 1
a, Å	7.4017(4)	7.4146(2)	3.9533(3)
b, Å	9.6998(5)	9.6559(3)	6.8531(6)
c, Å	13.1902(7)	13.3816(4)	17.0301(16)
α, deg	72.355(1)	102.353(2)	97.238(3)
β, deg	74.234(1)	105.731(1)	96.001(4)
γ, deg	83.146(1)	96.757(2)	95.301(4)
V, Å^3	867.78(8)	884.96 (5)	452.59(7)
ρ(calcd.), g/cm^3	1.675	1.642	1.958
μ, mm^{-1}	2.87	2.87	5.65
θ scan range, deg	2.2–30.0	2.4–27.5	2.4–26.5
I_{hkl} measured/independent/observed	7968/5005/496	8397/4049/522	3564/1773/1382
R_{int}	0.011	0.027	0.028
Number of refined parameters	303	243	151
GOOF	1.06	1.05	0.99
R_1 for $I_{hkl} > 2\sigma(I)$	0.023	0.027	0.037
wR_2	0.059	0.072	0.078
R_1 for all I_{hkl}	0.027	0.034	0.056
wR_2	0.060	0.075	0.083
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e Å^{-3}	0.91/–0.31	0.82/–0.43	0.83/–0.57

Table 2. Selected bond lengths (Å) and bond angles (deg) in structures **I–III***

I		**II**		**III**	
Bond	d, Å	Bond	d, Å	Bond	d, Å
Co(1)–Br(1)	2.6926(2)	Ni(1)–Br(1)	2.6467(2)	Cu(1)–Br(1)	2.4904(4)
Co(1)–N(21)	2.1021(11)	Ni(1)–N(11)	2.0796(17)	Cu(1)–N(1)	1.9620(3)
Co(1)–N(11)	2.1267(11)	Ni(1)–N(21)	2.1048(16)	Cu(1)–Br(1*B*)	3.0447(5)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
N(21)Co(1)N(11)	88.73(4)	N(11)Ni(1)N(21)	89.09(6)	N(1)Cu(1)Br(1)	90.36(10)
N(21)Co(1)Br(1)	90.96(3)	N(11)Ni(1)Br(1)	89.18(5)	N(1)Cu(1)Br(1*B*)	90.81(10)
N(11)Co(1)Br(1)	90.11(3)	N(21)Ni(1)Br(1)	89.63(5)	Br(1)Cu(1)Br(1*B*)	90.59(10)

* Symmetry codes: (*B*) $x + 1, y, z$.

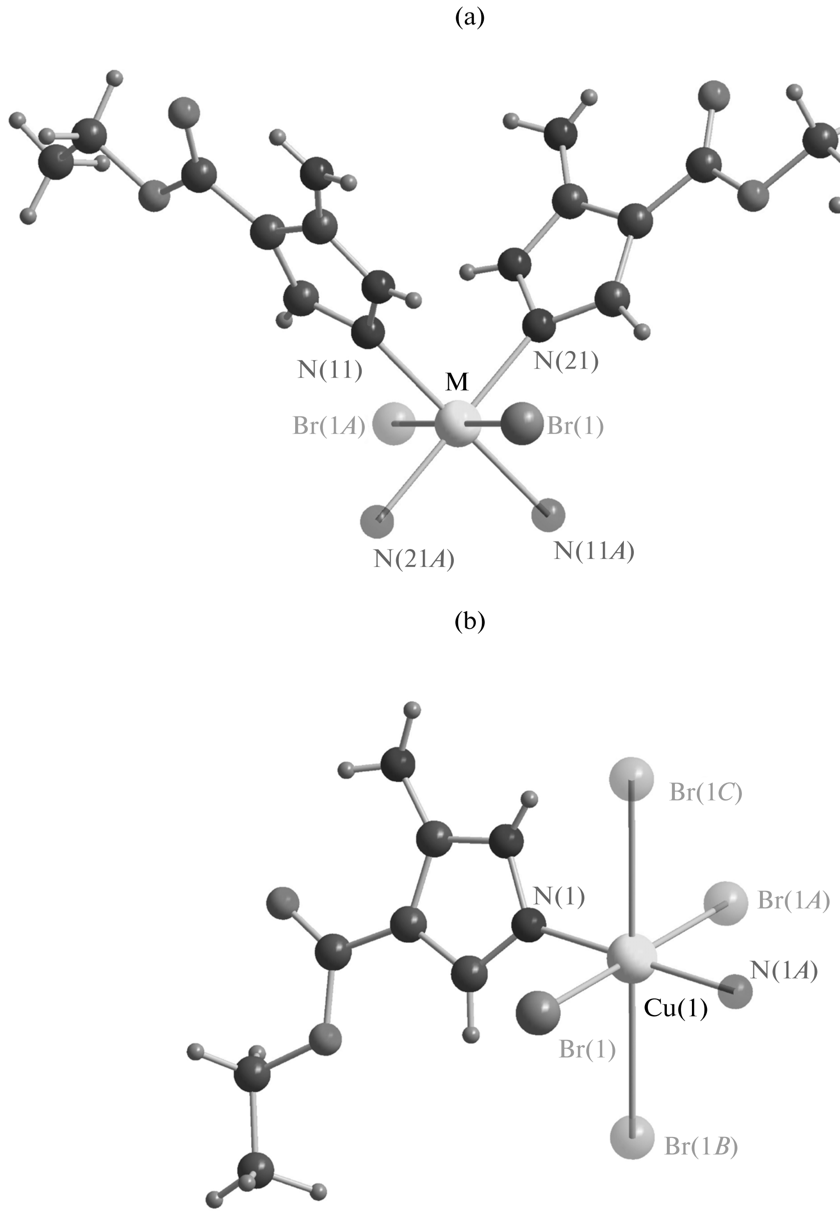


Fig. 1. Structures of the independent part in molecules (a) **I** and **II** (dependent atoms of the coordination polyhedron are multiplied by the inversion center) and (b) **III** (symmetry procedures for the coordination polyhedron: $1 - x$, $1 - y$, $1 - z$; $1 + x$, y, z; $-x$, $1 - y$, $1 - z$).

an extended tetragonal bipyramidal coordination 4+2 (Fig. 1b). The bond angles involving the axial bromide ion are also close to 90°. Molecules CuL_2Br_2 are joined into infinite chains (Fig. 3) due to the bridging function of the bromide ions (Cu–Br 2.490(1), 3.045(1) Å). The structure includes short contacts Br···H(NH_2) and Br···H(NH) (Table 3). Thus, the chains are joined by hydrogen bonds in the crystallographic direction *y*. The system of hydrogen bonds in structure **III** is shown in Fig. 4.

In all studied compounds, the geometric parameters of the ligands are usual and the deviation of the atoms of the pyrazole cycle from the root-mean-square planes do not exceed 0.004 Å.

The frequencies of the basic vibrations in the IR spectra of L and complexes **I–III** are given in Table 4. The spectra of the Co(II) and Ni(II) complexes containing water of crystallization exhibit O–H stretching vibration bands at 3590, 3515, and 3597 cm^{-1}, respectively. The shift of the bands predominantly to the high-frequency range is observed in the region of

Table 3. Intermolecular contacts A···H–D in the structures of compounds **I–III**

Contact	Distance, Å		Angle A···H–D, deg
	A···H–D	A···D	
I (II)			
Br···H(NH_2)	2.67(2.67)	3.43(3.46)	150(149)
Br···H(NH)	2.80(2.77)	3.44(3.48)	133(142)
Br···H(O*w*)	2.86(2.89)	3.60(3.65)	134(143)
O*w*···H(NH)	2.08(2.09)	2.91(2.93)	160(161)
O(C=O)···H(O*w*)'	2.13(2.19)	2.97(3.05)	168(166)
III			
Br···H(NH_2)	2.65	3.48	145
Br···H(NH)	2.89	3.57	141

stretching vibrations of the NH and NH_2 groups in the spectra of all complexes compared to the spectrum of L. The ν(C=O) bands in the spectra of complexes **I–III** are also shifted by 20–30 cm^{-1} to the high-energy region compared to the spectrum of L. This indicates that the NH and CO groups are not coordinated to the metal.

The IR spectra of the complexes become simpler in the range of stretching–bending vibrations of the pyrazole ring (1500–1580 cm^{-1}) sensitive to coordination: in the spectra of all complexes, one band shifted to the high-frequency range appears in each spectrum instead of three bands in the spectrum of L (Table 4). This pattern indicates the coordination to the nitrogen atom of the pyrazole cycle to the metal.

The magnetochemical study of the complexes shows that the value of μ_{eff} for complex **I** at 300 K is 4.88 μ_B and gradually decreases with the temperature decrease to 3.80 μ_B at 5 K. The high-temperature value of μ_{eff} is higher than the theoretical purely spin value (3.87 μ_B) for one paramagnetic center with spin $S = 3/2$ at $g = 2$. This is consistent with the orbital contribution to the magnetic susceptibility typical of the Co^{2+} ion in the octahedral environment. As the temperature decreases, the value of μ_{eff} tends to the theoretical purely spin value, indicating the absence of significant exchange interactions between the spins of the Co^{2+} ions (Fig. 5).

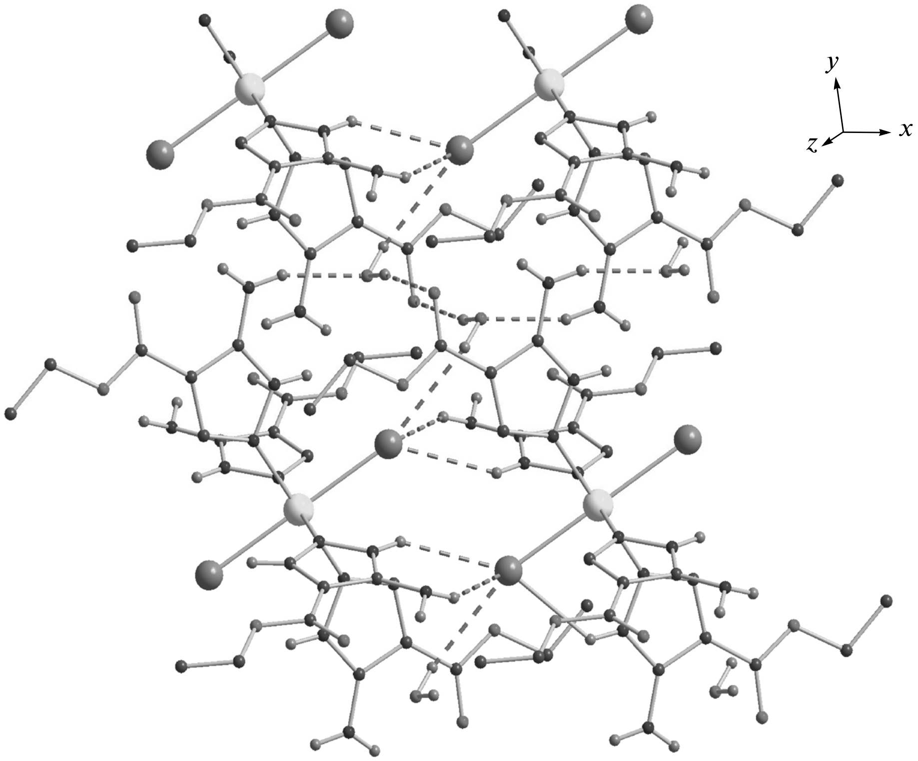


Fig. 2. Packing fragment of molecules **I** and **II**; the D–H···A interactions (dash) bind the molecules in the crystallographic planes *xy*. Hydrogen atoms of the C–H fragments are omitted.

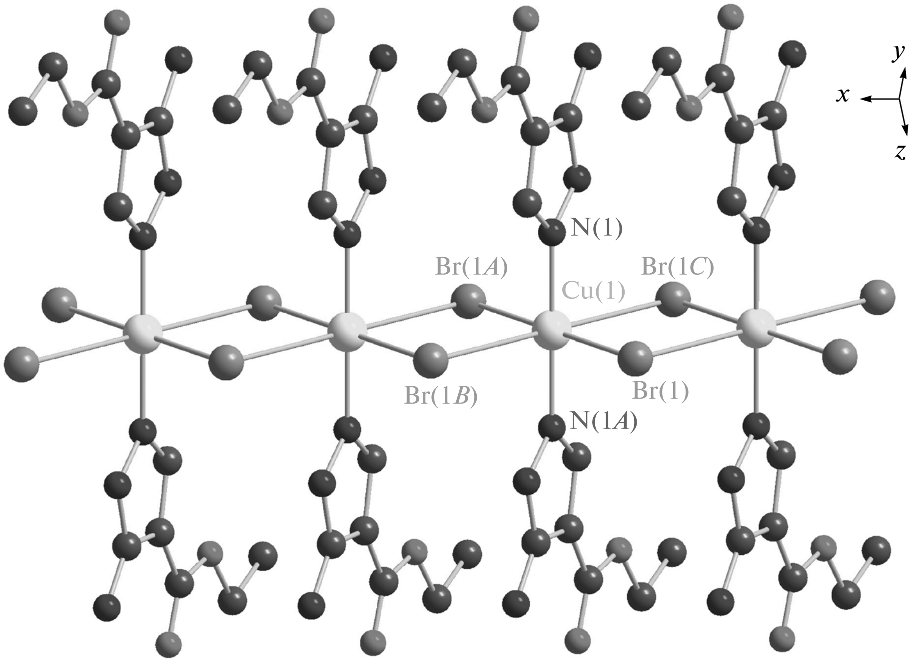


Fig. 3. Fragment of the chain in structure **III**.

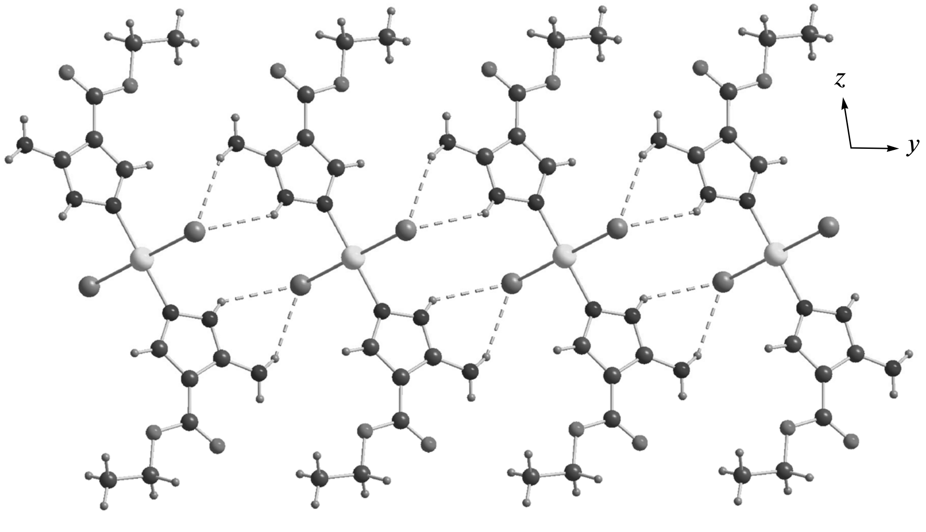


Fig. 4. Hydrogen bonds (dash) between the chains in structure **III**.

For complex **III**, the value of μ_{eff} at 300 K equal to 1.90 μ_B with the temperature decrease first gradually and below 80 K more sharply decreases to 0.64 μ_B at 5 K. The high-temperature value of μ_{eff} is slightly higher than the theoretical spin only value (1.73 μ_B) for one paramagnetic center with spin $S = 1/2$ at $g = 2$, which is due to the typical values $g > 2$ for the Cu^{2+} compounds. The decrease in μ_{eff} with the temperature decrease indicates the presence of antiferromagnetic exchange interactions between the spins of the paramagnetic centers. The dependence $\mu_{\text{eff}}(T)$ is well described by the equation for the uniform chain with the antiferromagnetic exchange (Hamiltonian $H = -2J\sum S_iS_{i+1}$) [9]. The optimal values of the g-factor and exchange interaction parameter J are 2.223 (±0.005) and −8.6 (±0.2) cm^{-1}, respectively.

Table 4. Frequencies of the main vibrations in the IR spectra of L and complexes **I–III**

L	I	II	III	Assignment
	3590	3597		ν(O–H)
	3515			
3480	3478	3454	3458	ν(NH)
3237	3461	3424	3337	
3203	3353	3322	3298	
	3329	3284		
1671	1708	1691	1703	ν(C=O)
	1695	1673		
1620	1626	1617	1624	$\delta(NH_2) + \delta(H_2O)$
1558	1572	1560	1572	R_{ring}
1522	1559		1543	
1502				

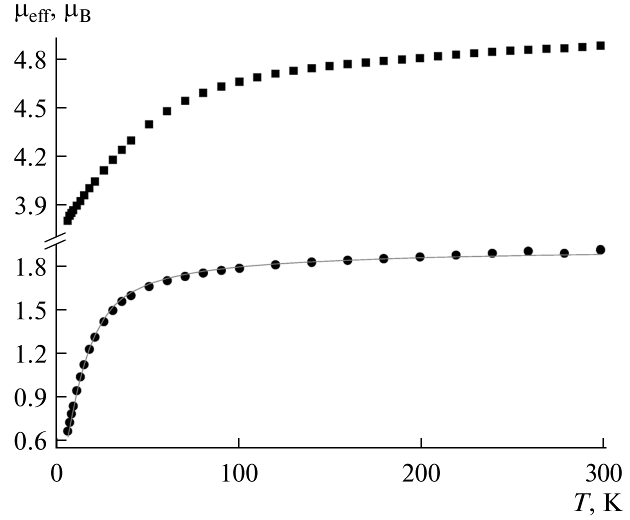


Fig. 5. Plots of $\mu_{eff}(T)$ for (■) **I** and (●) **III** (points are experimental values, and solid line is the theoretical curve).

Thus, the replacement of the chloride ion in complex CuL_2Cl_2 by the bromide ion in complex **III** results in the change of the character of exchange interactions between the copper(II) ions from ferromagnetic to antiferromagnetic.

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