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New Cu(II) and Co(II) Complexes with 2-Benzoylpyridine: Syntheses and Crystal Structures

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Abstract—Two new mononuclear complexes $[Cu(Bzpy)_2(Cl)_2]$ (**I**) and $[Co(Bzpy)_2(H_2O)_2](BF_4)_2$ (**II**) are synthesized by the reactions of 2-benzoylpyridine (Bzpy) with the copper(II) and cobalt(II) salts. It is found by X-ray diffraction analysis (CIF files CCDC nos. 1908081 (**I**) and 1908080 (**II**)) that complex **I** is molecular and complex **II** is of the ionic type. Two neutral bidentate-chelate N,O-ligands Bzpy are coordinated to the complexing atom in both complexes. The Cl^- anions supplement the coordination polyhedra to octahedra in complex **I**, and the water molecules supplement the coordination polyhedra to octahedra in complex **II**. The $[BF_4]^-$ anions in complex **II** compensate the positive charge of the complex cations and are bound to them by intermolecular hydrogen bonds O–H···F along with electrostatic interactions.

Keywords: complex compounds, Cu(II), Co(II), 2-benzoylpyridine, X-ray diffraction analysis

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INTRODUCTION

An information about the coordination geometry of the complexes formed by ions of the transition metals of the first row with 2-benzoylpyridine was obtained from the spectroscopic data when searching for selective reagents for transition metal ion extraction and studying the influence of various substituents on the coordination properties of pyridinecarboxylic acids and stereochemistry of the synthesized complexes. Then the complexes of the first row transition metals with pyridine and their derivatives were intensely studied by X-ray diffraction analysis [1]. 2-Benzoylpyridine (2-Bzpy) is a good chelating ligand in which the acyl substituent in position 2 of the pyridine ring enhances the possibilities of binding with metal ions. The coordination mode of 2-Bzpy to the central atom depends on both the metal ion used and anions and solvents. The structural studies showed that the bidentate-chelate mode can be considered as a more abundant. In the most part of cases, the carbonyl oxygen atom is coordinated to the central metal ion together with the nitrogen atom of the pyridine fragment to form the five-membered metallocycle as in [2–7]. The monodentate mode where the single nitrogen atom is used for coordination was found in three cases only [8–10]. Both mono- [3, 4, 6, 7, 11–13] and binuclear [2, 5, 13–16] complexes, as well as polynuclear complexes [5, 16–18], including coordination polymers [12, 19–21], were obtained as a result of using the N,O-coordinated ligand 2-Bzpy. However, all polynuclear compounds were synthesized involving additional ligands among which the Cu(II) complexes with Bzpy are studied to a higher extent, whereas the Co(II) complexes are poorly studied [7, 17, 18, 22, 23].

In this work, we present two new mononuclear complexes synthesized by the reactions of Bzpy with the copper(II) and cobalt(II) salts: the molecular Cu(II) complex $[Cu(Bzpy)_2(Cl)_2]$ (**I**) and the Co(II) complex of the ionic type $[Co(Bzpy)_2(H_2O)_2](BF_4)_2$ (**II**). The Cu(II) compound of the same composition $[Cu(Bzpy)_2(Cl)_2]$ was found [1, 3], which is a polymorph of compound **I**.

EXPERIMENTAL

Commercial chemicals, including solvents, were used as received.

Synthesis of complex I. Water (3 mL), methanol (3 mL), and dimethylformamide (DMF) (0.5 mL) were added to Bzpy (0.18 g, 1 mmol) and $CuF_2 \cdot 2H_2O$ (0.36 g, 1 mmol). The mixture was sealed in a reactor (V = 8 mL) with the Teflon lining and heated in an autoclave at 120°C for 72 h. Then the autoclave was slowly cooled to room temperature. The crystals obtained are soluble in methanol, ethanol, and DMF and are insoluble in ether. The yield was 21%.

For $C_{24}H_{18}N_2O_2Cl_2Cu$

Anal. calcd., %	C, 56.48	H, 3.02	N, 4.98
Found, %	C, 57.55	H, 3.63	N, 5.59

IR (ν, cm^{-1}): 3274 m, 3061 s, 2988 m, 1659 s, 1580 s, 1445 m, 1316 s, 1175 w, 946 m, 823 s, 780 w, 758 s, 656 m.

Synthesis of complex II. A mixture of Bzpy (0.18 g, 1 mmol), $Co(BF_4)_2 \cdot 6H_2O$ (0.36 g, 1 mmol), water (3 mL), methanol (3 mL), and DMF (0.5 mL) was sealed in a 8-mL reactor with the Teflon lining and heated in an autoclave at 120°C for 48 h. Then the autoclave was slowly cooled to room temperature. The crystals obtained are soluble in methanol, ethanol, and DMF and are insoluble in ether. The yield was 25%.

For $C_{24}H_{22}B_2N_2O_4F_8Co$

Anal. calcd., %	C, 45.01	H, 3.07	N, 4.02
Found, %	C, 45.40	H, 3.49	N, 4.41

IR (ν, cm^{-1}): 3380 m, 2935 s, 2924 m, 1659 s, 1555 s, 1448 m, 1370 s, 1080 w, 943 m, 761 w, 660 s, 524 w.

IR spectra were recorded on a FT-IR Perkin-Elmer Spectrum 100 spectrometer in Nujol in a range of 4000–400 cm^{-1} and in a range of 4000–650 cm^{-1} for the attenuated total reflection (ATR) mode.

X-ray diffraction analyses of the crystals of complexes **I** and **II** were carried out on an Xcalibur E diffractometer with the CCD detector at room temperature (MoK_α radiation). The unit cell parameters were refined over the whole set, and other experimental data were obtained using the CrysAlis Oxford Diffraction program package [24]. The structures were determined by direct methods, and the coordinates of nonhydrogen atoms were refined by least squares in the anisotropic variant (SHELX-97) [25]. The positions of the hydrogen atoms bound to carbon or oxygen were determined geometrically and refined isotropically in the rigid body model ($B_H = 1.2U_X$ or $1.5U_X$ (X = C, O). The main experimental characteristics and the solution and refinement parameters for the structures of complexes **I** and **II** are presented in Table 1. Selected interatomic distances and bond angles are given in Table 2.

The positions and thermal parameters for complexes **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1908081 and 1908080, respectively; www.ccdc.cam.ac.uk/conts/retrieving.html or deposit@ccdc.ca.ac.uk).

RESULTS AND DISCUSSION

The 2-Bzpy molecule (both uncoordinated and bound in the complexes) is determined by IR spectroscopy in the 4000–400 cm^{-1} range. The band at 1659–1580 cm^{-1} characteristic of the carbonyl group ν(C=O) indicates the coordination of the 2-Bzpy ligands to the central metal ion by carbonyl oxygen. The band at 1592–1570 cm^{-1} corresponds to the ν_{as}(C=N) vibration, and the band at 1285–1287 cm^{-1} is attributed to ν_s(C=N) of the pyridine group and confirms the coordination of the nitrogen atom of the pyridine fragment of the ligand to the metal ions. Complex **II** exhibits a broad medium-intensity band at 3274–3380 cm^{-1}, which can be explained by stretching vibrations of the OH groups of the water molecules. In complex **II**, the arrangement of the $[BF_4]^-$ ions in the external sphere of the complex is confirmed by the bands at 1084 $\nu_{as}(BF_4)$, 761 $\nu_s(BF_4)$, and 524 cm^{-1} δ(F–B–F).

It is found by X-ray diffraction analysis that complex **I** is molecular and complex **II** is of the ionic type.

The molecular structure of centrosymmetric complex **I** is presented in Fig. 1a. The central metal atom in the copper(II) complex has the octahedral environment. Two organic neutral Bzpy ligands are coordinated via the bidentate-chelate mode through two N,O-donor atoms to form two five-membered metallocycles located in the equatorial plane of the polyhedron. Two Cl atoms are localized on the axial coordinates of the octahedron. The coordination polyhedron of Cu(II) is formed by a set of donor atoms NOCl. The interatomic Co–N, Co–N, and Co–Cl distances are 1.977(2), 2.457(1), and 2.3184(8) Å, respectively. A similar situation was observed for the polymorphous Cu(II) complex [3], which crystallizes in the monoclinic space group *C*2/*c*, but its interatomic distances Co–N, Co–N, and Co–Cl differ noticeably: 2.006, 2.495, and 2.281 Å, respectively.

An analysis of the packing of the molecular complexes in compound **I** indicates only weak intermolecular hydrogen bonds C–H···Cl (C(2)···Cl(1) ($x + 1, y, z$) (3.703 Å) and C(3)···Cl(1) ($-x + 2, -y, -z + 2$) (3.535 Å) and intermolecular π···π interactions between the heteroaromatic cycles (centroid···centroid 3.734 Å), which dictates the formation of chains bound into layers in the crystal (Fig. 2).

Compound **II** of the ionic type is formed by the complex cation $[Co(Bzpy)_2(H_2O)_2]^+$ and $[BF_4]^-$ anions (Fig. 1b). The octahedral coordination polyhedron of the Co(II) atom is formed by the set of donor atoms N_2O_2 of two Bzpy ligands coordinated via the same mode as in complex **I** to form two pentametallocycles lying in the equatorial plane of the polyhedron and two O atoms of two water molecules on the axial coordinates. The interatomic Co–N (2.072(4) Å), Co–O 2.089(4) Å), and Co–O(*w*) (2.094(4) Å) distances differ slightly from those found in a similar

Table 1. Crystallographic data and the experimental characteristics for the structures of complexes **I** and **II**

Parameter	Value	
	I	**II**
FW	500.84	634.99
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a, Å	7.3015(7)	9.0790(5)
b, Å	8.2013(8)	11.6909(5)
c, Å	10.8395(11)	12.8702(5)
α, deg	107.777(9)	90
β, deg	95.380(8)	92.493(5)
γ, deg	113.191(9)	90
V, $Å^3$	550.91(9)	1364.77(10)
Z	1	2
ρ_{calc}, g/cm^3	1.510	1.545
μ, mm^{-1}	1.257	0.717
F(000)	255	642
Crystal sizes, mm	0.22 × 0.21 × 0.18	0.36 × 0.34 × 0.12
Range of θ, deg	2.91–25.03	3.17–25.03
Ranges of reflection indices	$-7 \le h \le 8$, $-9 \le k \le 8$, $-12 \le l \le 12$	$-6 \le h \le 10$, $-13 \le k \le 9$, $-13 \le l \le 15$
Number of measured/independent reflections (R_{int})	2910/1943 (0.0210)	4450/2399 (0.0224)
Filling, %	99.7	99.3
Number of reflections with $I > 2\sigma(I)$	1677	1717
Number of refined parameters	142	187
GOOF	1.004	1.006
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0363$, $wR_2 = 0.0910$	$R_1 = 0.0920$, $wR_2 = 0.2952$
R factors (over whole set)	$R_1 = 0.0440$, $wR_2 = 0.0980$	$R_1 = 0.1171$, $wR_2 = 0.3287$
$\Delta\rho_{max}/\Delta\rho_{min}$, e $Å^{-3}$	0.437/–0.328	0.795/–0.549

compound with perchlorate [7] in which these distances are equal to 2.077, 2.105, and 2.078 Å, respectively.

The complex anion contains coordinated water molecules involved in the intermolecular hydrogen bonds as proton donors, whereas the fluorine atoms of the $[BF_4]^-$ anions act as acceptors (Fig. 3). In the crystal, the complex cations are linked to the $[BF_4]^-$ anions into layers by electrostatic interactions and also by intermolecular hydrogen bonds O(1*w*)–H(1)···F(3) (O(1*w*)···F 2.692(7), H···F 1.88 Å, angle OHF 170°) and O(1*w*)–H(2)···F(2) ($-x + 1/2$, $y - 1/2$, $-z + 3/2$) (O(1*w*)···F 2.687(9), H···F 1.85 Å, angle OHF 160°). The layers are additionally stabilized by weak hydrogen bonds C–H···F (C(3)···F(4) ($-x + 1/2$, $y + 1/2$, $-z + 3/2$), 3.408 Å) (Fig. 2) and are joined between each other by also weak interactions C–H···F (C(1)···F(4) ($x - 1$, y, z), 3.148 Å) (Fig. 3).

Thus, the reactions of the Cu(II) and Co(II) salts with 2-benzoylpyridine gave two compounds of different types (molecular complex and ionic type compound) in which the organic ligand is coordinated via the N,O-bidentate-chelate mode to form the pentametallocycles.

Table 2. Interatomic distances and bond angles in the coordination polyhedra of Cu(II) and Co(III) in complexes **I** and **II**

Bond	*d*, Å	Angle	ω, deg
		I	
Cu(1)–N(1)	1.977(2)	N(1)Cu(1)O(1)	73.7(8)
Cu(1)–O(1)	2.4572(6)	N(1)Cu(1)Cl(1)	90.94(7)
Cu(1)–Cl(1)	2.3184(8)	O(1)Cu(1)Cl(1)	94.2(7)
		II	
Co(1)–N(1)	2.072(4)	N(1)Co(1)O(1)	78.3(2)
Co(1)–O(1)	2.089(4)	N(1)Co(1)O(1*w*)	89.2(2)
Co(1)–O(1*w*)	2.094(4)	O(1)Co(1)O(1*w*)	88.3(2)

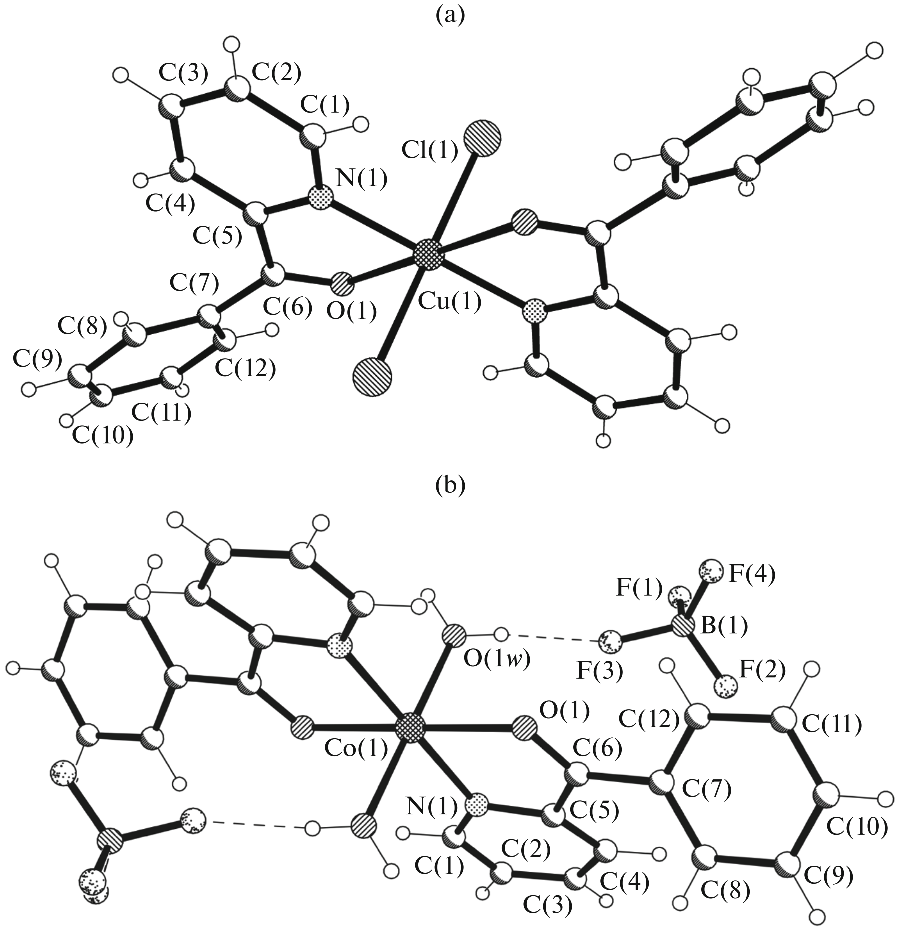

Fig. 1. Molecular structures of (a) centrosymmetric complex **I** and (b) the complex cation in compound **II**.

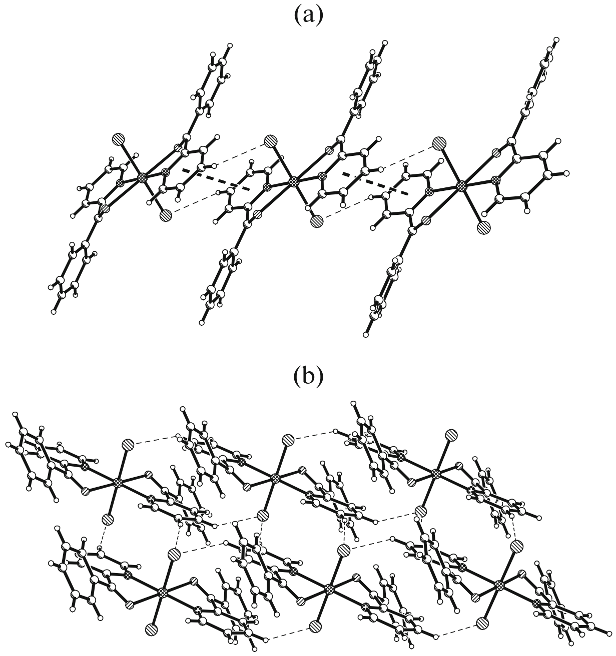

Fig. 2. (a) Formation of the chain of centrosymmetric complexes **I** and (b) the association of the chains in complex **I**.

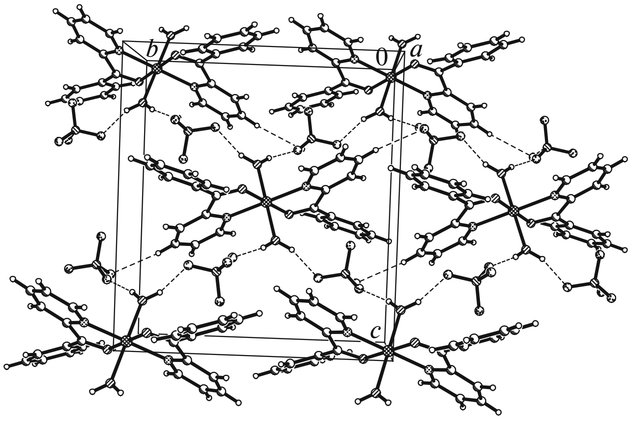

Fig. 3. Formation of the layer of the centrosymmetric complex cations and anions in compound **II**.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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