ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 3, pp. 151–156. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © L.D. Popov, S.I. Levchenkov, I.N. Shcherbakov, K.Yu. Suponitskii, V.V. Lukov, V.A. Kogan, 2016, published in Koordinatsionnaya Khimiya, 2016, Vol. 42, No. 3, pp. 131–136.

Crystal Structures of the Polymer Copper(II) Complexes with Acylhydrazones of Bromosalicylaldehyde Derivatives

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Received June 2, 2015

Abstract—Polymer copper(II) complexes with 5-bromosalicylaldehyde heptanoylhydrazone (**I**) and 3,5-dibromosalicylaldehyde acetylhydrazone (**II**) are synthesized and structurally characterized. In complex **I**, the formation of the polymer is due to the coordination of the hydrazide nitrogen atom to the copper(II) ion of the adjacent fragment. In complex **II**, polymer formation is due to the binding of the monomer fragments by dipyridyl linkers (CIF files CCDC 947908 (**I**) and 947909 (**II**)).

DOI: 10.1134/S1070328416020068

INTRODUCTION

Acylhydrazones of salicylaldehyde and its derivatives are classical tridentate O,N,O'-donor ligands. They are characterized by the formation of binuclear complexes with copper(II) ions in which two monomer fragments are dimerized through phenoxide bridges [1–4]. These complexes are convenient models for studying the structural and electronic factors affecting the exchange interaction [3–5]. At the same time, in some cases, these ligand systems are capable of forming polymer copper(II) complexes. The formation of the latter is usually due to additional donor centers in the hydrazide fragments [6–8]. Polymers are significantly rarely formed due to binding of monomer fragments by diamine linkers [9, 10] or coordination of the hydrazide nitrogen atom to the copper(II) ion of the adjacent fragment [10, 11].

In this report, we present the results of the structural study of the polymer copper(II) complexes with 5-bromosalicylaldehyde heptanoylhydrazone (H_2L) and 3,5-dibromosalicylaldehyde acetylhydrazone (H_2L') with different polymerization modes.

EXPERIMENTAL

Hydrazones H_2L and H_2L' were synthesized according to described procedures [12, 13].

Synthesis of complex I. A hot solution of copper(II) acetate (1 mmol) in methanol (10 mL) was poured to a hot solution of 5-bromosalicylaldehyde heptanoylhydrazone (H_2L) (1 mmol) in methanol (10 mL). The reaction mixture was refluxed for 1 h. The precipitate was filtered off and recrystallized from DMSO. The yield was 0.05 g (25%).

For $C_{16}H_{23}N_2O_3SBrCu$

anal. calcd., %:	C, 41.16;	H, 4.97;	Cu, 13.61.
Found, %:	C, 40.87;	H, 5.09;	Cu, 13.75.

IR (ν, cm^{-1}): 1623 ν(C=N).

Synthesis of complex II. A hot solution of copper(II) perchlorate (1 mmol) in methanol (10 mL) was poured to a hot solution of 3,5-dibromosalicylaldehyde acetylhydrazone (H_2L') (1 mmol) in methanol (20 mL), and 1,3-di(4-pyridyl)propane (5 mmol) was added. The reaction mixture was refluxed for 2 h and left to stand overnight. The precipitate was filtered off and recrystallized from DMSO. The yield was 0.18 g (30%).

For $C_{22}H_{202}N_4O_2BrCu$

anal. calcd., %:	C, 44.35	H, 3.38;	Cu, 10.67.
Found, %:	C, 44.11;	H, 3.55;	Cu, 10.80.

IR (ν, cm^{-1}): 1620 ν(C=N).

IR spectra were recorded on a Varian Scimitar 1000 FT-IR instrument in a range of 400–4000 cm^{-1} for suspensions of the samples in Nujol.

The X-ray diffraction analyses of the complexes were carried out on a Bruker SMART APEX2 CCD

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Table 1. Crystallographic data, experimental details, and refinement characteristics for complexes **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_{32}H_{46}N_4O_6S_2Br_2Cu_2$	$C_{22}H_{20}N_4O_2Br_2Cu$
FW	933.75	595.78
Crystal size, mm	0.42 × 0.26 × 0.15	0.19 × 0.11 × 0.03
Temperature, K	100(2)	100(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	$Pna2_1$
a, Å	15.4248(8)	8.4827(7)
b, Å	18.0823(9)	17.7308(15)
c, Å	27.1481(13)	14.8769(13)
V, Å^3	7572.0(7)	2237.6(3)
Z	8	4
ρ_{calcd}, g/cm^3	1.638	1.769
μ, mm^{-1}	3.391	4.574
F(000)	3792	1180
Scan θ range, deg	1.89–30.00	2.29–26.65
Number of measured reflections	93636	27351
Number of independent reflections	11049	6527
Number of reflections with $I > 2\sigma(I)$	7740	5636
Ranges of reflection indices	$-21 \leqslant h \leqslant 21, -25 \leqslant k \leqslant 25, -38 \leqslant l \leqslant 38$	$-11 \leqslant h \leqslant 11, -25 \leqslant k \leqslant 25, -20 \leqslant l \leqslant 20$
Number of refined parameters	489	281
R_1 ($I > 2\sigma(I)$)	0.0374	0.0344
wR_2 (all reflections)	0.0835	0.0639
Goodness-of-fit (all reflections)	1.012	0.985
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.786/–0.584	0.480/–0.777

diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator, ω scan mode). The initial sets of measured intensities were processed using the SAINT and SADABS programs [14, 15]. Structures **I** and **II** were solved by a direct method and refined by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms for F^2_{hkl}. Hydrogen atoms were placed in the geometrically calculated positions and included into refinement by the riding model. The structures were solved and refined using the SHELXTL program [16].

The experimental characteristics and crystallographic data for structures **I** and **II** are presented in Table 1. Selected interatomic distances and bond angles are listed in Table 2. The coordinates of atoms and temperature factors were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC 947908 (**I**) and 947909 (**II**); http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The reaction of 5-bromosalicylaldehyde heptanoylhydrazone H_2L with copper(II) acetate followed by recrystallization from DMSO gave complex **I** with the composition [CuL(DMSO)], whose structure was determined by X-ray diffraction analysis. Structure **I** is based on a binuclear fragment of the polymer chain (Fig. 1). In turn, the binuclear formula unit consists of monomer fragments with the same composition and structure but somewhat different geometric parameters. The Cu(1) and Cu(2) atoms are in the distorted square-pyramidal coordination. The axial positions are occupied by the oxygen atoms of the DMSO molecule (O(3) and O(6), respectively). For Cu(1) and

Table 2. Selected interatomic distances and bond angles in the coordination polyhedra of the copper atoms in molecules of compounds **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
	I		
Cu(1)–O(1)	1.9015(18)	Cu(2)–O(4)	1.9090(19)
Cu(1)–N(1)	1.945(2)	Cu(2)–N(3)	1.947(2)
Cu(1)–O(2)	1.9558(18)	Cu(2)–O(5)	1.9376(18)
Cu(1)–N(4)	2.007(2)	Cu(2)–N(2)	2.017(2)
Cu(1)–O(3)	2.374(2)	Cu(2)–O(6)	2.350(2)
	II		
Cu(1)–O(2)	1.920(2)	Cu(1)–N(3)	2.015(2)
Cu(1)–N(2)	1.933(3)	Cu(1)–N(4a)	2.312(3)
Cu(1)–O(1)	1.952(2)		
Angle	**ω, deg**	**Angle**	**ω, deg**
	I		
O(1)Cu(1)N(1)	93.33(8)	O(4)Cu(2)N(3)	93.33(8)
O(1)Cu(1)O(2)	172.51(8)	O(4)Cu(2)O(5)	171.25(8)
N(1)Cu(1)O(2)	80.38(8)	O(5)Cu(2)N(3)	80.27(8)
O(1)Cu(1)N(4)	91.88(8)	O(4)Cu(2)N(2)	91.60(8)
N(1)Cu(1)N(4)	167.43(9)	O(5)Cu(2)N(2)	92.42(8)
O(2)Cu(1)N(4)	93.50(8)	N(3)Cu(2)N(2)	159.35(9)
O(1)Cu(1)O(3)	95.26(8)	O(4)Cu(2)O(6)	89.12(8)
N(1)Cu(1)O(3)	90.43(8)	O(5)Cu(2)O(6)	97.22(8)
O(2)Cu(1)O(3)	88.88(8)	N(3)Cu(2)O(6)	93.97(8)
N(4)Cu(1)O(3)	100.47(8)	N(2)Cu(2)O(6)	106.16(8)
	II		
O(2)Cu(1)N(2)	92.47(10)	O(1)Cu(1)N(3)	93.00(9)
O(2)Cu(1)O(1)	169.00(9)	O(2)Cu(1)N(4a)	97.86(9)
N(2)Cu(1)O(1)	81.19(10)	N(2)Cu(1)N(4a)	95.25(10)
O(2)Cu(1)N(3)	91.49(10)	O(1)Cu(1)N(4a)	91.70(9)
N(2)Cu(1)N(3)	167.90(11)	N(3)Cu(1)N(4a)	95.53(9)

Cu(2), the azomethine nitrogen atom (N(1) and N(3)), phenoxide (O(1) and O(4)) and α-oxyazine (O(2) and O(5), respectively) oxygen atoms of one organic ligand, and the hydrazone nitrogen atom (N(4) and N(2b)) of another organic ligand lie in the equatorial plane. The latter shift from the plane of other donor atoms by 0.245 and 0.472 Å, respectively.

The five-membered chelate rings Cu(1)N(1)N(2)C(8)O(2) and Cu(2)N(3)N(4)C(24)O(5) have a conformation of the flattened envelope. Its valves are the Cu(1) and Cu(2) atoms shifting from the mean plane of other four atoms by 0.101 and 0.139 Å, respectively. The conformation of the six-membered chelate ring Cu(1)N(1)C(7)C(6)C(1)O(1) is a flattened half-chair, and the Cu(1) atom deviates from the mean plane of other five atoms of the ring by 0.134 Å. The six-membered metallocycle Cu(2)N(3)C(23)C(22)C(17)O(4) has a “half-twist” conformation due to the inflection over the C(23)···O(4) line by 9.36°. The equatorial coordination planes of the copper ions in the monomers are unfolded relatively to each other about the Cu(1)–N(4) bond by 64.3°.

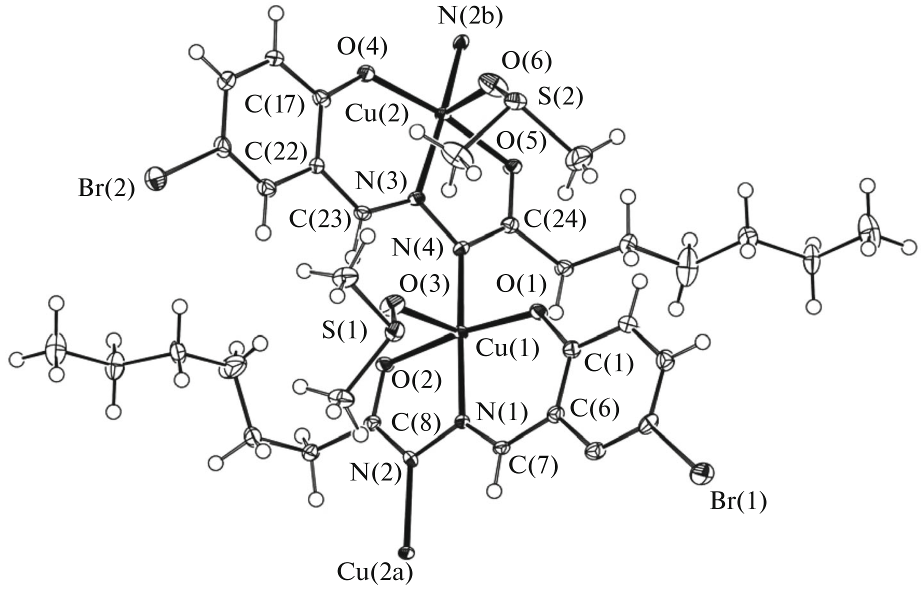

Fig. 1. Structure of the dimeric unit of complex **I** (thermal vibration ellipsoids for 50% probability).

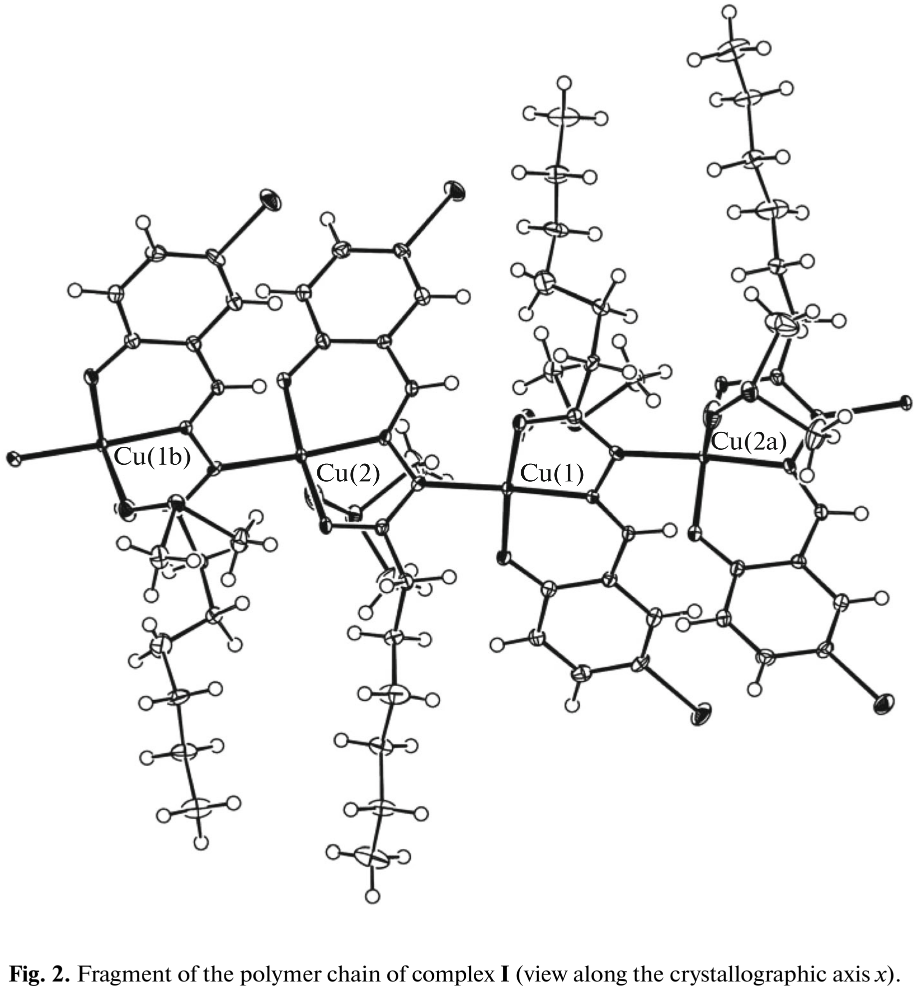

Fig. 2. Fragment of the polymer chain of complex **I** (view along the crystallographic axis *x*).

Table 3. Characteristics of intermolecular hydrogen bonds C–H···O in crystal of complex **I***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
C(16)–H(16*B*)···O(4)$^{\rm i}$	0.98	2.36	3.283(3)	157
C(32)–H(32*B*)···O(2)$^{\rm ii}$	0.98	2.51	3.468(4)	167

* Crystallographic positions: $^{\rm i}$ $-1/2 - x$, $1/2 + y$, z; $^{\rm ii}$ $-1/2 + x$, y, $-3/2 - z$.

The fragment of the polymer chain of complex **I** is shown in Fig. 2. The distances between the copper ions in the chain are similar: inside the dimeric unit the Cu(1)–Cu(2) distance is 4.7527(5) Å, and between the dimers the Cu(1)–Cu(2a) ((Cu(2)–Cu(1b)) distance is 4.7592(5) Å.

The 1D chains are packed into layers along the crystallographic axis *x* due to hydrogen bonds C–H···O between the hydrogen atoms H(16*B*) (H(32*B*)) of the methyl groups of the coordinated DMSO molecules and the oxygen atoms O(4)$^{\rm i}$ (O(2)$^{\rm ii}$) of the salicylic and hydrazide fragments (Table 3). The layers are linked to each other by hydrophobic interactions of the hexyl aliphatic groups of the hydrazide fragments of the organic ligand, and positions of their terminal atoms are substantially disordered because of conformational flexibility.

Complex **II** was synthesized by the reaction of copper(II) nitrate with 3,5-dibromosalicylaldehyde acetylhydrazone in methanol in the presence of 1,3-di(4-pyridyl)propane. The monomer fragment of complex **II** is shown in Fig. 3.

The organic ligand (L')$^{2-}$ is coordinated to the copper ion in the doubly deprotonated form through the tridentate mode. The coordination polyhedron of the Cu(1) ion is a distorted square pyramid. The azomethine nitrogen atom N(2), α-oxazine O(1) and phenozide O(2) oxygen atoms, and the N(3) nitrogen atom of the dipyridyl linker lie in the equatorial plane. The axial position is occupied by the nitrogen atom N(4a)$^{\rm iii}$ of the dipyridyl linker ($^{\rm iii}$ $3 - x$, $1 - y$, $-1/2 + z$). The Cu(1) atom shifts from the equatorial plane of the O(1), O(2), N(2), and N(3) atoms to the axial N(4a) atom by 0.176 Å. Both the five- and six-membered metallocycles in complex **II** are almost planar.

The N(4) nitrogen atom of the second pyridyl cycle of the bridging ligand is axially coordinated to the Cu(1b) copper ion of another mononuclear fragment bound by the symmetry procedure $^{\rm iv}$ $3 - x$, $1 - y$, $-1/2 + z$. Thus linked (according to the “head-to-tail” type) mononuclear complexes form infinite zigzag chains along the crystallographic axis *z* (Fig. 4).

Short interatomic contacts of the Br(1) bromine atom of one 1D chain and the O(1) oxygen and C(1) carbon atoms of the acetyl fragment of another chain are observed between the adjacent one-dimensional chains of the complexes. The Br···O distances (3.1364(19) Å) are by 0.23 Å shorter than the sum of the van der Waals radii of the Br and O atoms, and the Br···C distance (3.305(3) Å) is by 0.24 Å shorter than the sum of the van der Waals radii of the Br and C atoms. The chains bound by this interaction form layers in the *xz* plane, and no short contacts are observed between the layers.

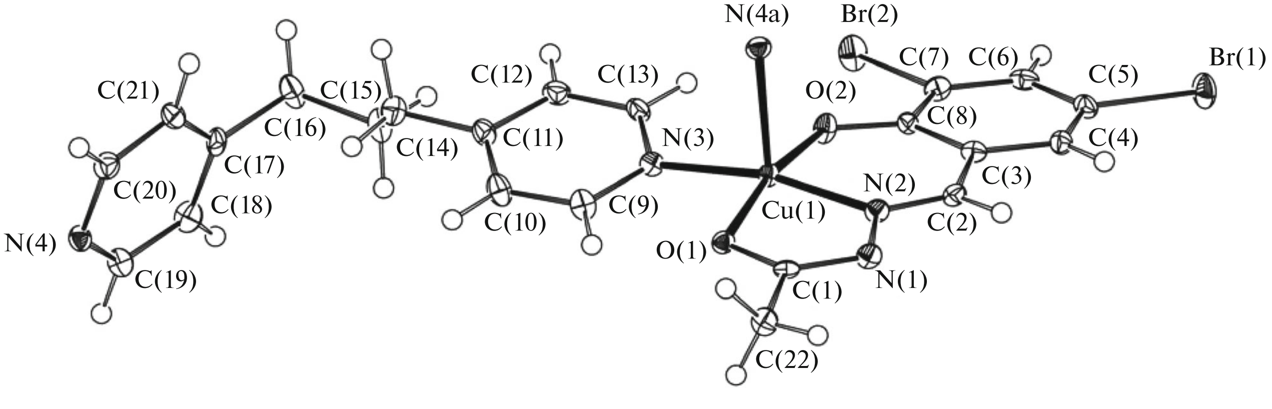

Fig. 3. Structure of the monomer fragment of complex **II** (thermal vibration ellipsoids for 50% probability).

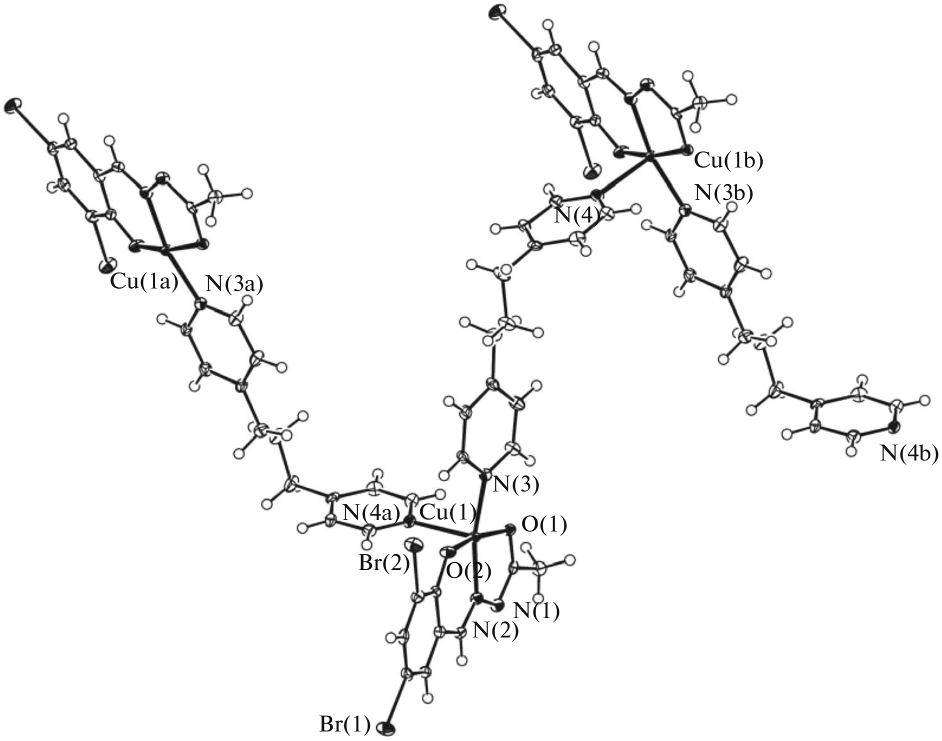

Fig. 4. Fragment of the polymer chain of complex **II** (view along the crystallographic axis *y*).

ACKNOWLEDGMENTS

This work was supported by the Southern Federal University, grant no. 213.01-07-2014/03PChVG.

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Translated by E. Yablonskaya