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Synthesis and Structure of Di(μ-$O_{phenoxy}$)-bis{nitrato-2-[2-(hydroxyethylimino)-methyl]-phenoloimidazolecopper}

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Abstract—The crystal structure of di(μ-$O_{phenoxy}$)-bis{nitrato-2-[2-(hydroxyethylimino)-methyl]-phenoloimidazolecopper} was determined. The crystals are monoclinic: a = 10.222(2) Å, b = 13.810(3) Å, c = 10.620(2) Å, β =103.67(3)°, space group $P2_1/n$, Z = 2, R = 0.050. The copper atom coordinates the singly deprotonated 2-[2-(hydroxyethylimino)-methyl]-phenol molecule, imidazole, and nitrate ion. The coordination polyhedron of the central atom is an extended tetragonal bipyramid with imine and imidazole nitrogen atoms and phenol and alcohol oxygen atoms lying in its base. One axial vertex of the bipyramid is occupied by the oxygen atom of the nitrato group and the other vertex, by phenol oxygen atom of the neighboring complex joined with the initial complex by the symmetry center. Two bridging phenol oxygen atoms unite the complexes into a centrosymmetrical dimer.

Previously [1–3], copper(II) nitrate and 2-[2-(hydroxyethylimino)-methyl]-phenol (H_2L) were found to give different coordination compounds with antimicrobial properties. Their structures were studied using spectral [4], magnetochemical [5], and X-ray diffraction [6–9] methods. It was established that monomeric or polynuclear coordination compounds are formed depending on the nature of the proton-accepting agent, pH and temperature of a reaction mixture. The structure of these compounds, dentate number of the nitrato group, the physicochemical properties and antimicrobial activity are determined by the nature of their amines. In the previously studied compounds, only pyridine and picolines were used as amines; therefore, it was of interest to study how the replacement of six-membered heterocyclic amine by five-membered amine influences the structure of the complex. In this work, the compound [Cu(Im)(HL)NO_3] (**I**) (Im is imidazole) was synthesized and its crystal structure was determined.

EXPERIMENTAL

Synthesis. Compound **I** was synthesized by reacting a hot (45–50°C) alcohol solution containing 10 mmol of [Cu(HL)NO_3] in 50 ml of ethanol with a solution containing 10 mmol of imidazole in 20 ml of ethanol. On cooling of the reaction mixture, dark green precipitate formed (yield 68%), which was filtered off on a glass filter, washed with a small amount of alcohol, and dried in air. Complex **I** is readily soluble in dimethylformamide, dimethyl sulfoxide, in alcohols on heating. Its composition was determined from the elemental analysis data.

For $C_{12}H_{16}CuN_4O_5$

anal. calcd. (%): C, 40.00; H, 4.44; Cu, 17.78; N, 15.56.

Found (%): C, 40.09; H, 4.37; Cu, 17.58; N, 15.51.

Single crystals of **I** suitable for X-ray diffraction analysis were obtained after recrystallization of the title compound from an ethanol–dimethylformamide (4 : 1) solution.

X-ray diffraction analysis was carried out on a Bruker AXS Smart diffractometer with a CCD detector (MoK_α radiation, λ = 0.71073 Å, room temperature). The absorption correction was applied using the SHELXTL-NT V5.1 programs [10].

Structure **I** was solved by direct methods and refined by the least-squares method (SHELXL97 [11]) in anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms were isotropically refined; their positions were determined from the Fourier difference syntheses.

Details of data collection are presented in Table 1, the coordinates of basis atoms and their thermal parameters are given in Table 2, the bond lengths and angles are listed in Table 3.

RESULTS AND DISCUSSION

In structure **I** (Fig. 1), the copper atom coordinates the singly deprotonated 2-[2-(hydroxyethylimino)-methyl]-phenol molecule, imidazole, and nitrate ion. The coordination polyhedron of the central atom is an extended tetragonal bipyramid with the imine and

Table 1. Crystallographic data, details of data collection, and results of refinement of structure **I**

M	715.62
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell parameters	
a, Å	10.222(2)
b, Å	13.810(3)
c, Å	10.620(2)
β, deg	103.67(3)
V, Å^3	1456.8(5)
Z	2
ρ(calcd), g/cm^3	1.631
μ_{Mo} (mm^{-1})	1.529
F(000)	732
Crystal size, mm	0.2 × 0.3 × 0.4
Angles θ, deg	2.46–30.24
Range of reflection indices	$-13 \le h \le 4$, $-18 \le k \le 19$, $-13 \le l \le 14$
Total number of reflections measured	10764
Number of independent reflections	3918 (R_{int} = 0.021)
Number of refined parameters	251
GOOF	0.978
R-factors ($I > 2\sigma(I)$)	R_1 = 0.0350, wR_2 = 0.100
R factors on all reflections	R_1 = 0.050, wR_2 = 0.109
Δρ(max) and Δρ(min) (e Å^{-3})	0.723 and –0.692

Table 2. Coordinates of atoms (×10^4) and their isotropic equivalent thermal parameters (×10^3) in structure **I**

Atom	x	y	z	U_{eq}, Å^2
Cu(1)	3699(1)	277(1)	584(1)	32(1)
O(1)	4117(2)	627(1)	–1032(1)	35(1)
O(2)	3032(2)	–130(1)	2189(2)	43(1)
N(1)	2677(2)	–837(1)	–163(2)	35(1)
N(2)	4563(2)	1437(1)	1480(2)	36(1)
N(3)	5450(3)	2910(2)	1814(4)	83(1)
C(1)	2139(2)	–965(2)	–1370(2)	38(1)
C(2)	2454(3)	–1514(2)	827(3)	48(1)
C(3)	2083(3)	–925(2)	1881(3)	51(1)
C(4)	3362(2)	392(2)	–2184(2)	33(1)
C(5)	3587(3)	882(2)	–3270(2)	43(1)
C(6)	2853(3)	664(2)	–4507(2)	55(1)
C(7)	1875(3)	–53(3)	–4711(3)	60(1)
C(8)	1644(3)	–550(2)	–3679(2)	49(1)
C(9)	4842(3)	2271(2)	884(3)	48(1)
C(10)	5539(2)	2475(2)	2958(2)	43(1)
C(11)	5006(3)	1601(2)	2739(3)	46(1)
C(12)	2381(2)	–351(2)	–2395(2)	36(1)
N(4)	1210(2)	1767(2)	1145(2)	48(1)
O(3)	1407(2)	1272(2)	226(2)	57(1)
O(4)	716(3)	2576(2)	937(2)	83(1)
O(5)	1509(2)	1437(2)	2276(2)	65(1)

inidazole N(1) and N(2) atoms and phenol and alcohol O(1) and O(2) atoms in its base. The N(1), N(2), O(1), and O(2) atoms extend, on average, by 0.003 Å from their mean planes, the copper atom extends by 0.078 Å from this plane. The bond lengths are as follows: Cu(1)–O(1) 1.925(2), Cu(1)–O(2) 2.058(2), Cu(1)–N(1) 1.923(2), Cu(1)–N(2) 1.963(2) Å. One of axial vertices of bipyramid is occupied by the O(3) atom of monodentate nitrato group (Cu(1)–O(3) 2.665 Å). This bond is not coplanar to the nitrato group, but forms the angle of 54.3° with its plane. The angles formed by the Cu(1)–O(3) bond and the atoms lying in the base of the coordination bipyramid vary within the 78.9°–96.6° range. The other axial vertex is occupied by the phenol O(1*A*) atom of the neighboring complex joined with the initial complex by the symmetry center. The Cu(1)–O(1*A*) distance is equal to 2.503 Å, the O(3)Cu(1)O(1*A*) angle is equal to 177.1°. Two bridging phenol atoms (O(1) and O(1*A*)) join the complexes into a centrosymmetric dimer; the Cu(1)···Cu(1*A*) distance is equal to 3.279 Å. The angles that the Cu(1)–O(1*A*) bond forms with the basal atoms of the coordination bipyramid lie within 88.4°–99.3°. The Cu(1)–O(3) and Cu(1)–O(1*A*) bonds in structure **I** are, respectively, 0.029 and 0.027 Å longer than the analogous bonds in nitrato-2-[2-(hydroxyethylimino)-methyl]-phenolo-3-picolinecopper (**II**) [6], where analogous dimers are formed. The apical Cu–O(1*A*) bond in structure **I** is longer than the analogous bridging bonds in the dimeric copper salicylaldiminate complexes [12, 13], whose copper atoms have a tetragonal-pyramidal coordination, unlike tetragonal-bipyramidal coordination observed in complex **I**. The Cu–O_{br} distances in the above-mentioned two structures are equal to 2.450 and 2.398 Å.

The Cu(1)–O(1) distance in compound **I** is longer than the corresponding distances in nitrato-2-[2-(hydroxyethylimino)-methyl]-phenolocopper (**III**) (1.888(5) Å) [7], nitrato-2-[2-(hydroxyethylimino)-methyl]-phenolo-4-picolinecopper (**IV**) (1.888(5) Å) [8], 2-[2-(hydroxyethylimino)-methyl]-phenolocopper (**V**) (1.894(5) Å) [9], pyrazole-N-(S)-N-salicylidenalanito-(O',N,O)-copper(II) (**VI**) (1.890 Å) [14]. Note that unlike compound **I**, the phenol O(1) atom in complexes **III–VI** is not the bridging atom. In nitrato-3-

Table 3. Selected bond lengths and angles in structure **I**

Bond	*d*, Å	Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Cu(1)–N(1)	1.923(2)	C(9)–C(1)	1.447(3)	N(1)Cu(1)O(1)	92.68(7)	O(1)C(4)C(5)	118.0(2)
Cu(1)–O(1)	1.925(2)	C(4)–C(5)	1.402(3)	N(1)Cu(1)N(2)	172.41(8)	O(1)C(4)C(9)	124.1(2)
Cu(1)–N(2)	1.963(2)	C(10)–C(11)	1.322(4)	O(1)Cu(1)N(2)	93.33(7)	C(5)C(4)C(9)	117.9(2)
Cu(1)–O(2)	2.058(2)	C(10)–N(3)	1.339(5)	N(1)Cu(1)O(2)	82.46(8)	N(1)C(1)C(9)	124.2(2)
O(1)–C(4)	1.324(3)	C(5)–C(6)	1.383(4)	O(1)Cu(1)O(2)	173.39(7)	C(11)C(10)N(3)	108.2(2)
O(2)–C(3)	1.450(3)	C(2)–C(3)	1.504(4)	N(2)Cu(1)O(2)	91.18(8)	C(6)C(5)C(4)	121.3(3)
N(2)–C(11)	1.326(3)	C(12)–N(3)	1.360(4)	C(4)O(1)Cu(1)	124.02(14)	N(1)C(2)C(3)	107.4(2)
N(2)–C(12)	1.377(3)	C(8)–C(7)	1.361(4)	C(3)O(2)Cu(1)	110.8(2)	C(10)C(11)N(2)	111.2(3)
N(1)–C(1)	1.282(3)	C(6)–C(7)	1.387(5)	C(11)N(2)C(12)	105.2(2)	N(3)C(12)N(2)	108.5(3)
N(1)–C(2)	1.464(3)	O(3)–N(4)	1.246(3)	C(11)N(2)Cu(1)	129.5(2)	O(2)C(3)C(2)	107.7(2)
C(9)–C(4)	1.416(3)	O(5)–N(4)	1.253(3)	C(12)N(2)Cu(1)	125.3(2)	C(7)C(8)C(9)	121.4(3)
C(9)–C(8)	1.420(3)	N(4)–O(4)	1.225(3)	C(1)N(1)C(2)	121.8(2)	C(5)C(6)C(7)	120.8(3)
				C(1)N(1)Cu(1)	125.9(2)	C(8)C(7)C(6)	119.4(2)
				C(2)N(1)Cu(1)	112.1(2)	C(10)N(3)C(12)	106.8(3)
				C(4)C(9)C(8)	119.2(2)	O(4)N(4)O(3)	119.6(2)
				C(4)C(9)C(1)	123.2(2)	O(4)N(4)O(5)	120.1(2)
				C(8)C(9)C(1)	117.5(2)	O(3)N(4)O(5)	120.3(2)

hydroxypropylsalicylaldiminatopyridinecopper (**VII**) [15], where one oxygen atom of the nitrato group lies in the base of the tetragonal bipyramid of the copper atom, while the other $O(NO_3)$ atom and the alcohol O(2) atom are at the apical positions, the Cu(1)–O(1) distance (2.060(5) Å) is longer than that in **I**. The Cu(1)–N(1)

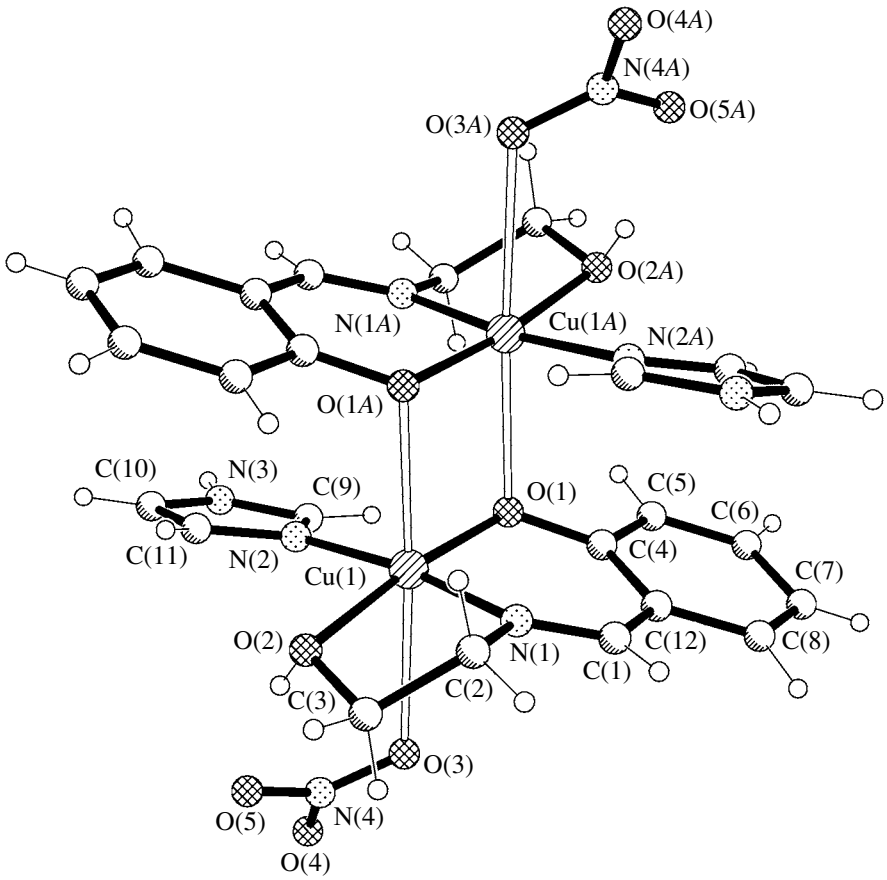


Fig. 1. The structure of complex **I**.

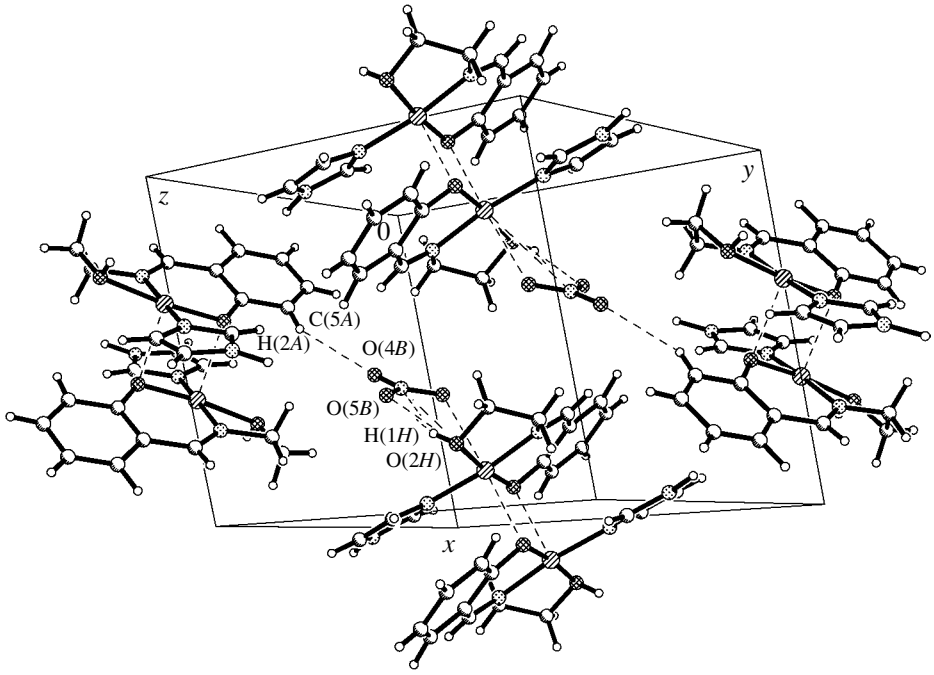


Fig. 2. Packing of the structural units in crystal **I**.

distance (1.904(6) Å) in complex **VII** is 0.019 Å shorter than the analogous bond in **I**.

In compound **I**, the six-membered metal cycle Cu(1)O(1)N(1)C(1)C(4)C(9) is bent along the O(1)···N(1) line. Dihedral angle between the Cu(1)O(1)N(1) and O(1)N(1)C(1)C(4)C(9) planes is equal to 20.6°. In compounds **II** and **VII**, this angle is equal to 14.9° and 22.7°, respectively, while in **III**–**V**, no bending of the metal cycle is observed. The benzene ring lies virtually in the plane of chelating fragment of the six-membered metal cycle; the angle between their planes is equal to 1.8°. This fragment Cu(1)O(2)N(1)C(2)C(3) has a skewed conformation: the torsion angles Cu(1)N(1)C(2)C(3), N(1)C(2)C(3)O(2), Cu(1)O(2)C(3)C(2), C(3)O(2)Cu(1)N(1) are equal to 43.3°, –46.8°, 30.3°, and –6.0°, respectively. The imidazole molecule and nitrato group are almost planar; the angle between their planes is equal to 46.0°. The Im molecule is rotated about the Cu(1)O(1)N(1) fragment through 20.5°.

With the exception of the O(1)–C(4) distance, the bond lengths in the organic ligand HL^- in structure **I** are typical of analogous compounds [6–9, 16–18]. In the copper salicylaldiminate complexes [6, 12, 13, 19], where the phenol O atom additionally interacts with the metal atom of the neighboring molecule or is involved in hydrogen bond [8], this distance lies within the 1.321–1.344 Å range. In structure **I**, the O(1)–C(4) distance is equal to 1.324(3) Å. In the complexes, where the phenol O(1) atom does not enter the additional interactions with the atoms of other molecules, the O(1)–C(4) distance is reduced to 1.29–1.31 Å.

The packing of the structural units in crystal **I** is shown in Fig. 2. Dimers are joined into chains through the hydrogen bonds (O(5*B*)···O(2H) 2.68; O(5*B*)···H(1H) 1.93 Å, angle O(5*B*)H(1H)O(2H) 166°, O(4*B*)···C(5*A*) 3.29, O(4*B*)···H(2*A*) 2.57 Å, angle O(4*B*)H(2*A*)C(5*A*) 142°); parameters of the latter H bond agree with the values reported in [20]. These chains multiplied by the sliding reflection plane are joined through the hydrogen bond (O(2)···O(5)' 2.68, H(O(2))···O(5)' 1.93 Å, the O(2)H(O(2))O(5)' angle 166°) involving the NO_3 group and the alcohol oxygen atom.

Thus, in copper(II) nitrate complexes with 2-[2-(hydroxyethylimino)-methyl]-phenol containing amines such as 3- or 4-picoline and imidazole, the nitrato group is monodentate; if these amines are absent, the nitrato group is bidentate.

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