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Heteroleptic Binuclear Iodoacetate Copper(II) Complexes with 3-Bromopyridine and 4-Ethylpyridine: Crystal Structures and Peculiarities of Contacts Halogen···Halogen

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Abstract—The reactions of $[Cu_2(IOAc)_4(H_2O)_2]$ with 3-bromopyridine and 4-ethylpyridine in acetone afford heteroligand complexes $[Cu_2(IOAc)_4(3\text{-}BrPy)_2]$ (**I**) and $[Cu_2(IOAc)_4(4\text{-}EtPy)_2]$ (**II**). Their structures are determined by X-ray diffraction analysis (CIF files CCDC nos. 1945900 (**I**) and 1945901 (**II**)). Specific noncovalent interactions I···I and Br···I leading to the formation of supramolecular polymers are observed in the crystal structure of complex **I**. The energies of the contacts are determined using quantum chemical methods.

Keywords: copper, N-donor ligands, halogen bond, crystal structure, quantum chemical calculations

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INTRODUCTION

During last years, the halogen bond, a special type of noncovalent interactions involving halogen atoms, attracts increasing attention of researchers [1–7]. The search for new "building blocks" capable of halogen bonding is an interesting task from the viewpoint of supramolecular coordination chemistry. In particular, neutral complexes of the $[M^{II}L_2X_2]$ type (X = Cl, Br, I; L is the halogen-containing N-donor ligand) [8–11], polyhalides [12, 13], perfluorinated arenes [14, 15], etc. are considered as candidates to this role. In spite of many presently described complexes with anions of halogen-containing carboxylic acids [16–18] and intensive investigation of the carboxylate complexes as a whole [19–26], they are rarely considered as fragments of supramolecular systems based on halogen bonds. From the point of view of the electronic structure, the iodoacetate anion is especially interesting in the context of hydrogen bonds. At the same time, the structural chemistry of the iodoacetate complexes is poorly studied. The structures of only four Cu(II)-based compounds are presently described [27–30], and the structures of one compound based on Fe [31], Sb [32], and Pb [33] are known.

We have previously shown that $[Cu_2(IOAc)_4(H_2O)_2]$ can be used as a precursor for the synthesis of heteroleptic complexes by the substitution of H_2O by the N-donor ligands. Depending on the nature of the latter, the system of halogen bonds of these compounds in the solid state can change significantly [30].

Continuing these studies, we synthesized complexes $[Cu_2(IOAc)_4(3\text{-}BrPy)_2]$ (**I**) and $[Cu_2(IOAc)_4(4\text{-}EtPy)_2]$ (**II**) and studied their structures by X-ray diffraction analysis. The formation of systems of contacts Br···I and I···I is observed in the crystal structure of compound **I**, and the energies of the contacts were estimated by quantum chemical calculations.

EXPERIMENTAL

The syntheses were carried out in air. The $[Cu_2(IOAc)_4(H_2O)_2]$ complex was synthesized according to the described procedure [29], and other reagents were purchased from commercial sources. Acetone was purified using a standard procedure.

Synthesis of $[Cu_2(IOAc)_4(3\text{-}BrPy)_2]$ (I). A weighed sample of $[Cu_2(IOAc)_4(H_2O)_2]$ (50 mg, 0.055 mmol) was dissolved in boiling acetone (15 mL), and a solution of 3-bromopyridine (11 μL, 0.11 mmol) in acetone (1 mL) was added. The mixture was slowly cooled to room temperature. The cooling and gradual evaporation of the solvent (to ~1/2 of the initial volume) led to the formation of blue crystals of complex **I** suitable for X-ray diffraction analysis.

For $C_{18}H_{16}N_2O_8Br_2I_4Cu_2$

Anal. calcd., %	C, 18.3	H, 1.4	N, 2.4
Found, %	C, 18.5	H, 1.5	N, 2.4

Synthesis of $[Cu_2(IOAc)_4(4\text{-}EtPy)_2]$ (II) was carried out similarly to that of complex **I** using 4-ethylpyridine (13 μL, 0.11 mmol) instead of 3-bromopyridine. Blue crystals of complex **II** suitable for X-ray diffraction analysis are formed.

For $C_{22}H_{26}N_2O_8I_4Cu_2$

Anal. calcd., %	C, 24.5	H, 2.4	N, 2.6
Found, %	C, 24.6	H, 2.5	N, 2.6

X-ray diffraction data for complexes **I** and **II** were obtained at 130 K on an Agilent Xcalibur automated diffractometer equipped with an Atlas S2 two-coordinate detector (graphite monochromator, $\lambda(MoK_\alpha)$ = 0.71073 Å, ω scan mode). Integration, absorption correction application, and unit cell parameter determination were carried out using the CrysAlisPro program package. The crystal structures were solved using the SHELXT program and refined by full-matrix least squares in the anisotropic (except for hydrogen atoms) approximation using the SHELXL program [34]. The positions of the hydrogen atoms of the organic ligands were calculated geometrically in the riding model. The crystallographic data and details of diffraction experiments are presented in Table 1.

The full tables of interatomic distances and bond angles, coordinates of atoms, and atomic shift parameters for the structures were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1945900 (**I**) and 1945901 (**II**); https://www.ccdc.cam.ac.uk/structures).

RESULTS AND DISCUSSION

As mentioned previously [30], the work describing the synthesis and structure of $[Cu_2(IOAc)_4(H_2O)_2]$ [29] remained unnoticed for a long time, although this compound can be considered as a convenient precursor for the preparation of heteroligand complexes. In addition to 3-BrPy and 4-EtPy, we carried out the reactions with a series of substituted pyridines (Py, 4-MePy, etc.). It is most likely that complexes of the $[Cu_2(IOAc)_4L_2]$ type were initially formed in all cases. However, sometimes they are not stable in the mother liquor: the color of the solution and precipitate changed to brown within 2–3 days, and no crystalline products can be isolated.

The structures of complexes **I** and **II** are typical of the binuclear copper(II) carboxylates. The Cu···Cu distances are 2.643 and 2.709 Å, respectively (compare with 2.663 and 2.634 Å in $[Cu_2(IOAc)_4(3.5\text{-}ClPy)_2]$ and $[Cu_2(IOAc)_4(H_2O)_2]$, respectively [29, 30]). The Cu–O bond lengths vary in ranges of 1.962–1.974 and 1.942–2.007 Å, respectively. The Cu–N bond lengths are 2.156 and 2.109–2.112 Å. The ethyl substituents in both 4-EtPy ligands in the structure of compound **II** are disordered.

An analysis of possible halogen···halogen contacts in the structures of complexes **I** and **II** demonstrates that the I···I distances in complex **II** (the shortest distance is 4.212 Å) significantly exceed the sum of the van der Waals radii according to Bondi (3.96 Å [35, 36]), which assumes that the structure contains no noncovalent interactions. On the contrary, the Br···I and I···I distances in the structure of complex **I** are shorter than the sum of the corresponding van der Waals radii. The first of them are 3.787 Å (compare with 3.81 Å [36]), which suggests the contacts involving the 3-BrPy fragments and two of four iodoacetate ligands of each “building block” $[Cu_2(IOAc)_4(3\text{-}BrPy)_2]$. All the four iodoacetate ligands are involved in the I···I interactions (3.921 Å). On the whole, both systems of contacts lead to the formation of one-dimensional supramolecular chains (Fig. 1). The values of the CIBr, CBrI, and CII angles (156.57°, 125.15°, and 98.92°, respectively) make it possible to ascribe the contacts to types I and II, respectively [37], i.e., to classify some of them as halogen bonds.

In order to estimate the energies of the aforementioned contacts, we performed quantum chemical calculations in the framework of the density functional theory (M06/DZP-DKH) [38–40] using the Gaussian-16 program package and the topological analysis of the electron density distribution by the QTAIM method (R. Bader’s quantum theory “Atoms in Molecules”) [41] using the Multiwfn program (version 3.6) [42]. This approach is widely used for studying noncovalent interactions of various types [4, 43–47]. The results are presented in Table 2. The diagram of the contour lines of the Laplacian electron density distribution $\nabla^2\rho(\mathbf{r})$, bonding routes, and zero flux surfaces corresponding to the noncovalent interactions I···Br and I···I in the crystal of complex **I** are presented in Fig. 2. The values of the electron density, Laplacian electron density, total energy density, potential energy density, and Lagrangian kinetic energy at the critical bond points (3, –1) corresponding to the noncovalent interactions I···Br and I···I in the crystal of complex **I** are quite typical of supramolecular contacts of this kind involving halogen atoms. The estimated values of the energy of the noncovalent interactions I···Br and I···I in complex **I** vary in ranges of 1.3–2.1 and 1.3–2.5 kcal/mol, respectively, depending on the estima-

Table 1. Crystallographic data and structure refinement parameters for compounds **I** and **II**

Parameter	Value	
	I	**II**
FW	1182.83	1081.13
Crystal system	Triclinic	Tetragonal
Space group	$P\bar{1}$	$P4_12_12$
a, Å	8.6878(4)	14.2890(4)
b, Å	9.1042(5)	14.2890(4)
c, Å	10.8343(5)	15.1342(4)
α, deg	113.997(4)	90
β, deg	100.592(4)	90
γ, deg	103.429(4)	90
V, Å^3	723.17	3090.03(19)
Z	1	4
ρ_{calc}, g/cm^3	2.716	2.324
μ, mm^{-1}	8.55	5.42
F(000)	542	2024
Crystal size, mm	0.28 × 0.22 × 0.21	0.31 × 0.29 × 0.18
Scan range over θ, deg	3.4–28.9	3.4–29.1
Range of indices *hkl*	$-11 \le h \le 10$, $-12 \le k \le 11$, $-13 \le l \le 13$	$-19 \le h \le 14$, $-13 \le k \le 17$, $-20 \le l \le 14$ $h = -19 \rightarrow 14$, $k = -13 \rightarrow 17$, $l = -20 \rightarrow 14$, $h = -19 \rightarrow 14$, $k = -13 \rightarrow 17$, $l = -20 \rightarrow 14$
Number of measured/independent reflections	5443/3120	8491/3512
R_{int}	0.030	0.040
Reflections with $I > 2\sigma(I)$	2629	3056
GOOF	1.02	1.10
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0366$, $wR_2 = 0.0746$	$R_1 = 0.0518$, $wR_2 = 0.1338$
R factors (for all reflections)	$R_1 = 0.0451$, $wR_2 = 0.0796$	$R_1 = 0.0618$, $wR_2 = 0.1417$
Residual electron density (max/min), e/Å^3	1.36/–1.27	1.75/–1.27

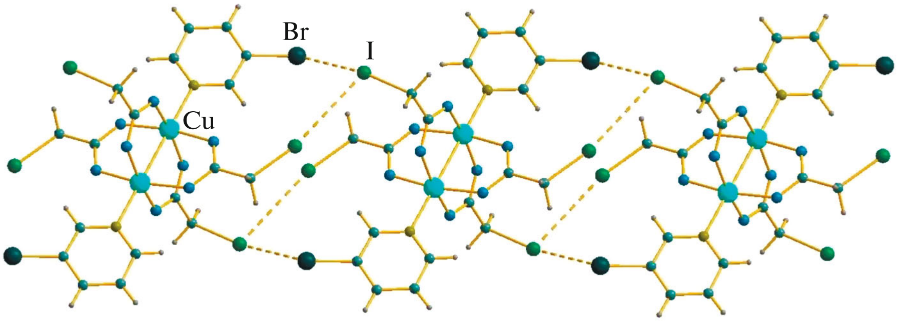

Fig. 1. Contacts I···Br (shown by dashed lines) in the structure of compound **I**.

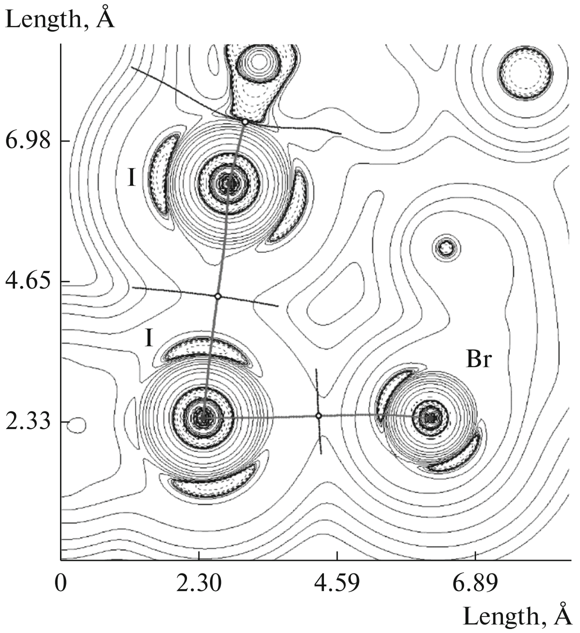

Fig. 2. Diagram of contour lines of the Laplacian electron density distribution $\nabla^2\rho(\mathbf{r})$, bonding routes, and zero flux surfaces corresponding to the noncovalent interactions I···Br and I···I in the crystal of compound **I**. Critical bond points (3, –1) are white circles, and critical nuclei points (3, –3) are gray circles.

Table 2. Electron density ($\rho(\mathbf{r})$), Laplacian electron density ($\nabla^2\rho(\mathbf{r})$), total energy density (H_b), potential energy density ($V(\mathbf{r})$), and Lagrangian kinetic energy ($G(\mathbf{r})$) (au) at the critical bond points (3, –1) corresponding to the noncovalent interactions I···Br and I···I in the crystal of compound **I** and the lengths of these contacts (l, Å) and their energies (E, kcal/mol) estimated using various correlations proposed in the literature

Supramolecular contact	$\rho(\mathbf{r})$	$\nabla^2\rho(\mathbf{r})$	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	E^a	E^b	E^c	E^d	l^e
I···Br	0.007	0.022	0.001	–0.004	0.005	1.3	1.3	1.7	2.1	3.787
I···I	0.007	0.027	0.001	–0.004	0.006	1.3	1.6	1.7	2.5	3.921

[a] $E = -V(\mathbf{r})/2$ (correlation was developed for the estimation of the energies of hydrogen bonds) [48].

[b] $E = 0.429G(\mathbf{r})$ (correlation was developed for the estimation of the energies of hydrogen bonds) [49].

[c] $E = 0.68(-V(\mathbf{r}))$ (correlation was specially developed for the estimation of the energies of noncovalent interactions involving iodine atoms) [50].

[d] $E = 0.67G(\mathbf{r})$ (correlation was specially developed for the estimation of the energies of noncovalent interactions involving iodine atoms) [50].

[e] The shortest van der Waals radii for bromine and iodine atoms are 1.83 and 1.75 Å, respectively [35].

tion method [48–50]. The ratio of the potential energy density and Lagrangian kinetic energy at the critical bond points (3, –1) corresponding to the noncovalent interactions I···Br and I···I in complex **I** indicate that these supramolecular contacts contain no substantial fraction of the covalent component.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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