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Halide Complexes [(2-Br-5-MePy)$_2$ZnX$_2$] (X = Cl, Br): Structure and Noncovalent Interactions in the Crystal Structure

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Abstract—The heteroligand complexes [(2-Br-5-MePy)$_2$ZnX$_2$] (X = Cl (**I**), Br (**II**)) were prepared by the reaction of zinc(II) chloride or bromide with 2-bromo-5-methylpyridine and studied by X-ray diffraction (CCDC nos. 2204966 (**I**) and 2204967 (**II**)). The crystals of **I** and **II** contain Cl···Br and Br···Br halogen bonds, which connect the [MX$_2$L$_2$] moieties into supramolecular chains. The energies of these noncovalent interactions were estimated using quantum chemical calculations.

Key words: zinc complexes, N-donor ligands, halogen bonds, crystal structure, quantum chemical calculations

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INTRODUCTION

Halogen bond (XB) is a specific type of noncovalent interactions [1]. Currently, study of halogen bonds is a hot issue of supramolecular chemistry [2–8], which is related, to a high extent, to materials science, because the ability to form XBs can affect various properties, including magnetic [9–11], luminescence [12–14], and other.

The search for new building blocks able to form XBs is a relevant issue. Quite a few studies are devoted to the use of perfluorinated iodo- and bromoarenes for this purpose [15–18]; other promising candidates are haloalkanes [19, 20], haloalkenes [21, 22], polyhalides [23–25], high-valence iodine derivatives [26–29], etc. In addition, there are a number of studies addressing characteristic features of XBs in neutral complexes such as [M^{II}L$_2$X$_2$], where L is a monodentate halogen-substituted N-donor ligand (halogenated pyridines, quinolines, etc.), X is Cl, Br, or I. These complexes are known for most *d*-elements [30–33], with Cu(II) complexes being studied most comprehensively [10, 34–36]. As a rule, XBs are formed between halide ligands and the halogen atoms of N-donor ligands in the solid state. It is noteworthy that the first publication devoted to Zn(II) complexes of [(2-XPy)$_2$ZnY$_2$] type (X and Y = Cl, Br, and I) appeared only a year ago [37] (a series comprising nine compounds was obtained). In continuation of these studies, we obtained two new Zn(II) complexes with 2-bromo-5-methylpyridine, [(2-Br-5-MePy)$_2$ZnX$_2$] (X = Cl (**I**) and Br (**II**)), which were characterized by X-ray diffraction; halogen bonds were studied using quantum chemical calculations.

EXPERIMENTAL

The synthesis was carried out in air. The initial reagents were obtained from commercial sources; ethanol was purified according to the standard procedure.

Synthesis of [(2-Br-5-MePy)$_2$ZnX$_2$] (X = Cl (I), Br (II)). A weighed portion of ZnCl$_2$·4H$_2$O (52 mg, 0.25 mmol for **I**) or ZnBr$_2$·2H$_2$O (65 mg, 0.25 mmol for **II**) was dissolved in ethanol (6 mL), then 2-Br-5-MePy (86 mg, 0.5 mmol) was added. The gradual evaporation of solutions to ~1/4 of the initial volume gave colorless crystals of **I** and **II**. The yields were 88% (**I**) and 90% (**II**).

For C$_{12}$H$_{12}$N$_2$Cl$_2$Br$_2$Zn (**I**)

Anal. calcd., %	C, 30.26	H, 2.54	N, 5.87
Found, %	C, 30.37	H, 2.62	N, 5.99

For C$_{12}$H$_{12}$N$_2$Br$_4$Zn (**II**)

Anal. calcd., %	C, 25.54	H, 2.15	N, 4.97
Found, %	C, 25.60	H, 2.27	N, 5.09

Single-crystal X-ray diffraction study of **I** and **II** was carried out at 150 K using an Agilent Xcalibur diffractometer with an AtlasS2 X-ray detector

Table 1. Crystallographic data, X-ray experiment parameters, and structure refinement details for **I** and **II**

Parameter	Value	
	I	**II**
Molecular formula	$C_{12}H_{12}N_2Cl_2Br_2Zn$	$C_{12}H_{12}N_2Br_4Zn$
M	480.33	569.25
System, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a, Å	8.6821(4)	8.8120(11)
b, Å	14.5854(6)	14.7299(16)
c, Å	12.8533(6)	12.9352(13)
β, deg	101.820(5)	100.798(4)
V, Å^3	1593.13(13)	1649.3(3)
Z	4	4
ρ(calcd.), g/cm^3	2.003	2.293
μ, mm^{-1}	6.88	11.17
F(000)	928	1072
Scanning range of θ, deg	2.6–28.1	2.6–32.6
Range of hkl indices	$-10 \le h \le 8$, $-14 \le k \le 17$, $-13 \le l \le 15$	$-10 \le h \le 10$, $-17 \le k \le 17$, $-15 \le l \le 14$
N_{hkl} measured/unique	6518/3031	17304/3126
R_{int}	0.028	0.048
N_{hkl} with $I > 2\sigma(I)$	2560	2759
R ($F^2 > 2\sigma(F^2)$), wR (F^2), S	0.041, 0.108, 1.03	0.032, 0.079, 1.05
Residual electron density (max/min), e/Å^3	1.38/−0.96	0.94/−0.44

($\lambda(\text{Mo}K_\alpha)$ = 0.71073 Å, ω-scan mode) for **I** and a Bruker D8 Venture diffractometer with a CMOS PHOTON III detector (φ- and ω-scan modes) for **II**. The integration, application of absorption corrections, and determination of unit cell parameters were carried out using the CrysAlisPro and SADABS program packages for **I** and **II**, respectively. The crystal structures were solved using the SHELXT program and refined by full-matrix least squares method in the anisotropic (except for hydrogen atoms) approximation using the SHELXL program [38]. The hydrogen atom positions in organic ligands were calculated geometrically and refined by the riding model. The crystallographic data and X-ray diffraction experiment parameters are given in Table 1.

The full tables of interatomic distances and bond angles, atom coordinates, and atomic displacement parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2204966 (**I**) and 2204967 (**II**); https://www.ccdc.cam.ac.uk/structures/).

Quantum chemical calculations were carried out using the Gaussian-09 program package (M.J. Frisch et al., Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford, CT, 2010). The ωB97XD functional [39], second-order Douglas–Kroll–Hess relativistic Hamiltonian, and DZP-DKH basis sets were used for all atoms [40, 41]. The topological analysis of electron density distribution by the QTAIM method [42] was performed using the Multiwfn program (version 3.7) [43].

RESULTS AND DISCUSSION

The Zn(II) coordination environment in the structure of **I** and **II** (Fig. 1) is tetrahedral. The Zn–N bond

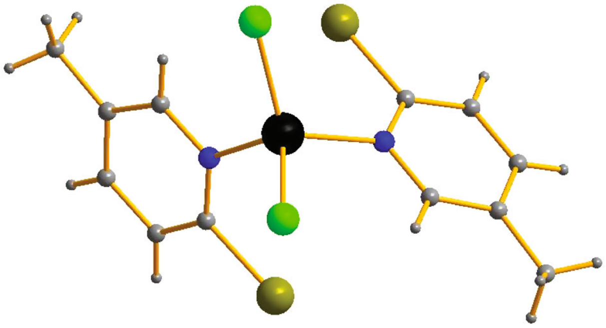

Fig. 1. Structure of **I**. Here and below: Zn is black, Cl is light green, Br is olive-colored, C and H are gray, and N is blue.

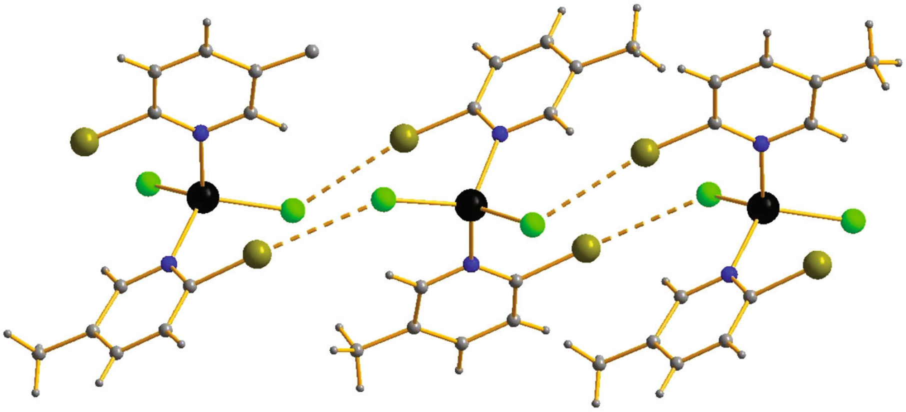

Fig. 2. Supramolecular associates in **I** (the halogen bond is shown by a dashed line).

lengths in **I** and **II** are 2.073–2.082 and 2.084–2.091 Å, respectively, and the Zn–Cl and Zn–Br bond lengths are 2.220–2.230 and 2.362–2.374 Å, respectively; these values are in line with published data for complexes of this type [37]. Compounds **I** and **II** are isostructural.

Analysis of the interatomic distances in the crystals of **I** and **II** and their comparison with the sums of the corresponding Bondi van der Waals radii (3.58 Å for Cl and Br and 3.66 Å for two Br atoms, respectively [44, 45]) suggest the presence of noncovalent interactions. The system of contacts between Br atoms of 2-Br-5MePy and chloride (Cl···Br, 3.309–3.292 Å) or bromide (Br···Br, 3.418–3.466 Å) ligands connects the $[ML_2X_2]$ moieties into infinite supramolecular chains (Fig. 2). The corresponding angles (ZnClBr, 128.3°–136.2°; CBrCl, 170.6°–173.2°; ZnBrBr, 126.1°–134.6°; and CBrBr, 169.5°–173.0°) indicate that these contacts can be classified as true halogen bonds (type II contacts) [46].

The energies of the above noncovalent interactions were estimated using the approach that was successfully employed previously to study similar systems [7, 8, 27, 28, 47]. Quantum chemical calculations were performed for model dimeric associates, the atomic coordinates for which were taken directly from X-ray diffraction data without geometry optimization. As follows from Table 2, halogen bond energies are in the 1.8–2.2 kcal/mol range, which is typical of compounds of this class.

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Table 2. Values of electron density, ρ(**r**); electron density Laplacian, $\nabla^2\rho(\mathbf{r})$; total energy density, H_b; potential energy density, $V(\mathbf{r})$; kinetic energy Lagrangian $G(\mathbf{r})$ (atomic units) at the (3, –1) bond critical points corresponding to noncovalent Cl···Br and Br···Br contacts in the crystal structures of **I** and **II**, and bond energies E (kcal/mol) of these contacts

Contact	ρ(**r**)	$\nabla^2\rho(\mathbf{r})$	λ_2	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	E_{int}*
I							
Br···Cl, 3.309 Å	0.011	0.037	–0.011	0.002	–0.006	0.008	2.2
Br···Cl, 3.392 Å	0.009	0.030	–0.009	0.001	–0.005	0.006	1.8
II							
Br···Br, 3.418 Å	0.011	0.031	–0.011	0.001	–0.006	0.007	2.2
Br···Br, 3.466 Å	0.010	0.028	–0.010	0.000	–0.006	0.006	2.2

* $E_{int} = 0.58(-V(\mathbf{r}))$ (the correlation was specially developed to estimate the energy of noncovalent interactions involving bromine atoms) [48].

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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