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Crystal Structure of the Heteroligand Complex [(2-Br-5-MePy)$_2$CoCl$_2$] · (2-Br-5-MePy): Formation of Supramolecular Associates due to the Halogen Bond

S. A. Adonin[a, b, c, d, *], A. S. Novikov[e], and V. P. Fedin[a, d]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[b] *Tyumen Industrial University, Tobolsk Industrial Institute (Branch), Tobolsk, Russia*
[c] *Southern Ural State University, Chelyabinsk, Russia*
[d] *Novosibirsk National Research University, Novosibirsk, 630090 Russia*
[e] *St. Petersburg State University, St. Petersburg, 199164 Russia*
**e-mail: adonin@niic.nsc.ru*

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Abstract—The reaction of $CoCl_2$ with 2-bromo-5-methylpyridine (2-Br-5-MePy) in ethanol affords the heteroligand complex [(2-Br-5-MePy)$_2$CoCl$_2$] · (2-Br-5-MePy) (**I**), the structure of which is determined by X-ray diffraction analysis (CIF file CCDC no. 1921405). Specific noncovalent interactions Cl···Br (halogen bond) are observed in the crystal structure and lead to the formation of unidimensional supramolecular polymers. The energies of these contacts are determined using quantum-chemical methods.

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

Halogen bond represents a specific type of noncovalent interactions recently attracting special attention of researchers in the field of supramolecular chemistry [1–4]. Along with purely fundamental interest, the target design of "building blocks" capable of forming halogen bonds is urgent in the context of using this property in the development of functional materials, especially sensors [5, 6]. Many halogen-containing structural fragments and individual substances, in particular, halogenalkanes, [7–9], polyhalides [10–15], perfluorinated iodoarenes [16–18], etc. are considered as candidates to this role. Metal complexes containing halogen-substituted N-donor ligands, in particular, pyridine derivatives, are of special interest: it has previously been shown that similar fragments can easily be involved into halogen bond formation, which results in assembling of unusual supramolecular associates in the solid state [19–25]. The family of complexes of the [$M^{II}L_2X_2$] type (M = Cu [23, 26], Ni [27], Cd [22], Co [28], Pd [29, 30], etc.; X = Cl, Br, I; L is halogen-substituted pyridine) should be distinguished among the most attractive "building blocks" of this kind. Their distinctive feature is simple synthesis, and they represent an almost ideal objects from the viewpoint of hydrogen bonding. Note that the chemistry and structures of similar compounds with 2-halogenpyridines are studied to a weaker extent than those with 3- and especially 4-halogenpyridines. For example, similar complexes are unknown for Ni(II) and Zn(II), whereas the structure of [Co(2-BrPy)$_2$Br$_2$] only was described for Co(II) [31]. Although many other 2-halogenpyridines, for example, 2-bromo-5-methyl- and 2-bromo-4-methylpyridines, are commercially available reagents, their ability to act as ligands was not almost described in literature.

In this work, we synthesized the heteroligand complex [Co(2-Br-5-MePy)$_2$Cl$_2$] · (2-Br-5-MePy) (**I**) and determined its structure by X-ray diffraction analysis. The energies of the halogen bond (Cl···Br) were estimated using quantum-chemical calculations.

EXPERIMENTAL

The synthesis was carried out in air. The initial reagents were purchased from commercial sources, and ethanol was purified according to a standard procedure.

Synthesis of complex I. A weighed sample of $CoCl_2 \cdot 6H_2O$ (100 mg, 0.42 mmol) was dissolved in ethanol (5 mL), and a solution of 2-bromo-5-methylpyridine (145 mg, 0.84 mmol) in ethanol (2 mL) was added. The gradual evaporation of the solvent (to ~3 mL) resulted in the formation of blue crystals of complex **I**

Table 1. Crystallographic data and experimental and structure refinement parameters for compound **I**

Parameter	Value
FW	645.91
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	12.4449(6)
b, Å	13.7541(6)
c, Å	14.0515(7)
β, deg	112.892(6)
V, Å^3	2215.7(2)
Z	4
ρ_{calc}, g/cm^3	1.936
μ, mm^{-1}	6.44
F(000)	1252
Crystal size, mm	0.21 × 0.20 × 0.18
Scan range over θ, deg	3.4–29.1
Range of indices *hkl*	$-17 \le h \le 13$, $-13 \le k \le 18$, $-13 \le l \le 19$
N_{hkl} for measured/independent reflections	11229/4944
R_{int}	0.029
N_{hkl} for $I > 2\sigma(I)$	4038
GOOF for F^2	1.01
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0292$, $wR_2 = 0.0555$
R factors (for all reflections)	$R_1 = 0.0418$, $wR_2 = 0.0597$
Residual electron density (max/min), e/Å^3	0.50/−0.58

suitable for X-ray diffraction analysis. The yield was 62% (based on the ligand).

For $C_{18}H_{18}N_3Cl_2Br_3Co$

Anal. calcd., %	C, 33.7	H, 2.8	N, 6.5
Found, %	C, 33.3	H, 2.8	N, 6.5

X-ray diffraction analysis. The diffraction data for a single crystal of compound **I** were obtained at 130 K on an Agilent Xcalibur automated diffractometer equipped with an AtlasS2 two-coordinate detector (graphite monochromator, $\lambda(MoK_\alpha) = 0.71073$ Å, ω scan mode). The integration, application of an absorption correction, and determination of the unit cell parameters were performed 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 [32]. The positions of the hydrogen atoms of the organic ligands were calculated geometrically and refined 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 were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1921405; https://www.ccdc.cam.ac.uk/structures/).

RESULTS AND DISCUSSION

The geometric parameters of compound **I** resemble those of other representatives of complexes of the $[CoL_2Cl_2]$ family [33–41]. The Co–Cl and Co–N distances in compound **I** are 2.247–2.254 and 2.056–2.059 Å, respectively, which is consistent with the published data (Table 2). It can be noted that there are

Table 2. Lengths of the Co–Cl and Co–N bonds in the complexes of the $[CoL_2Cl_2]$ type

Ligand	Co–N, Å	Co–Cl, Å	References
4-MePy	2.034–2.068	2.230–2.235	34
4-(NH_2COCH_2)Py	2.046	2.242	35
3-MePy	2.022–2.033	2.223–2.242	36
2-NH_2-3-MePy	2.034–2.039	2.230–2.264	37
2-NH_2-4-MePy	2.030–2.035	2.248–2.251	38
2-CH_3NHPy	2.042–2.049	2.244–2.249	39
2-(Ph_3C)NHPy	2.051–2.054	2.239–2.242	40

no correlations, most likely, between the bond lengths and basicity of substituted pyridine acting as a ligand, which is probably explained by the influence of both steric factors and a set of noncovalent interactions in the crystal packing (hydrogen bond, as a rule).

Complex **I** is a cocrystallizate including one 2-bromo-5-methylpyridine molecule and one molecule of $[Co(2\text{-Br-5-MePy})_2Br_2]$. Interestingly, both hydrogen and halogen bonds between these fragments are absent (in all cases, the distances substantially exceed the sums of the corresponding van der Waals radii). The single exception is the weak (2.551 Å) contact between the nitrogen atoms of free 2-Br-5-MePy and the *m*-proton of one of the corresponding ligands. An analysis of the interatomic distances shows specific interactions between the chloride ligands and bromine atoms of coordinated 2-Br-5-MePy (3.295–3.349 Å, which is substantially less than the sum of the corresponding van der Waals radii (3.58 Å [42, 43])). Each of the $[Co(2\text{-Br-5-MePy})_2Br_2]$ fragments participates in the formation of four such contacts leading to the formation of infinite supramolecular chains (Fig. 1). In order to establish the nature of these interactions (they can be classified as typical halogen bonds [4]), we performed quantum-chemical calculations in the framework of the density functional theory (M06/DZP-DKH) [44–46] using the Gaussian-09 program package and topological analysis of the electron density distribution by the QTAIM method (R. Bader's theory "Atoms in Molecules" [47]) using the Multiwfn program [48]. This approach was successfully used earlier for studying the properties of various noncovalent interactions [8, 49–52] in the transition metal complexes. The results are presented in Table 3. The diagram of contour lines of the Laplacian electron density distribution $\nabla^2\rho(\mathbf{r})$, bonding routes, and zero flux surfaces corresponding to the Br···Cl noncovalent interactions in the crystal of complex **I** are presented in Fig. 2. The values of 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 Br···Cl noncovalent interactions in compound **I** are quite typical of supramolecular contacts of this type involving halogen atoms [53]. The estimated values of energy of the Br···Cl noncovalent interactions in the crystal of compound **I** vary in a range of 1.9–2.9 kcal/mol depending on the method of estimation. The ratio of the potential energy density and Lagrangian kinetic energy at the critical bond points

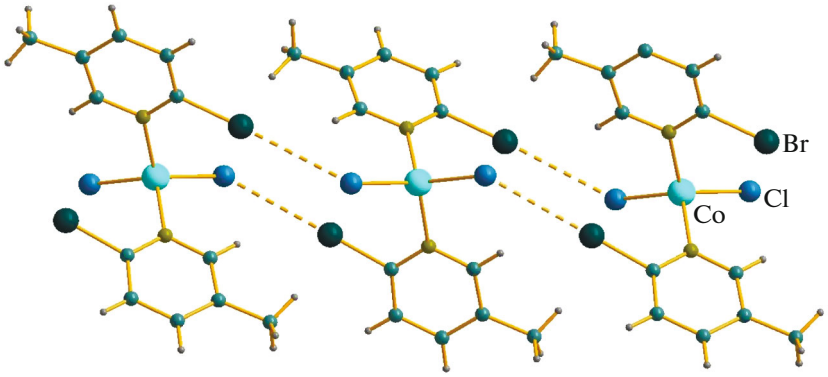

Fig. 1. Contacts Cl···Br in the structure of compound **I**.

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

ρ(**r**)	$\nabla^2\rho(\mathbf{r})$	H_b	$V(\mathbf{r})$	$G(\mathbf{r})$	E^a	E^b	E^c	E^d	L^e
0.010	0.033	0.001	−0.006	0.007	1.9	1.9	2.2	2.5	3.349
0.011	0.037	0.002	−0.006	0.008	1.9	2.2	2.2	2.9	3.295

[a] $E = -V(\mathbf{r})/2$ (correlation was developed for the estimation of the energies of hydrogen bonds) [54].
[b] $E = 0.429G(\mathbf{r})$ (correlation was developed for the estimation of the energies of hydrogen bonds) [55].
[c] $E = 0.58(-V(\mathbf{r}))$ (correlation was specially developed for the estimation of the energies of noncovalent interactions involving bromine atoms) [56].
[d] $E = 0.57G(\mathbf{r})$ (correlation was specially developed for the estimation of the energies of noncovalent interactions involving bromine atoms) [56].
[e] The shortest van der Waals radii for bromine and chlorine atoms are 1.83 and 1.75 Å, respectively [42].

(3, −1) corresponding to the Br···Cl noncovalent interactions in the crystal of complex **I** indicates the absence of a substantial fraction of the covalent component in these supramolecular contacts.

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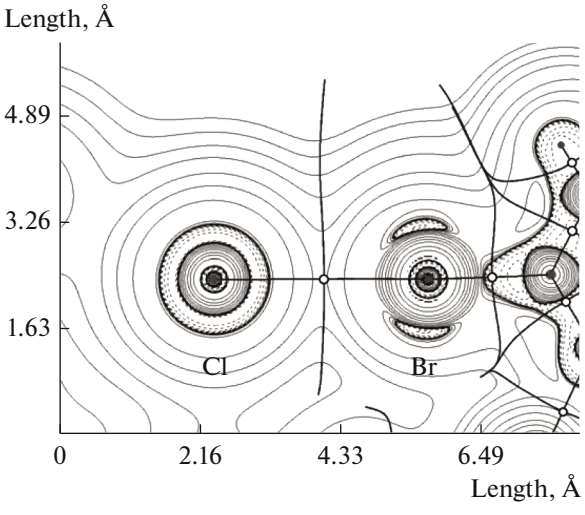

Fig. 2. Diagram of contour lines of the Laplacian electron density distribution $\nabla^2\rho(\mathbf{r})$, bonding routes, and zero flux surfaces corresponding to the noncovalent interactions Br···Cl in the crystal of compound **I**. Critical bond points (3, −1) are white circles, and critical nuclei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

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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