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Synthesis, Structure, and Luminescence Properties of Boron Complex with 4-Bromo-2-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenoxide Ligand

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Abstract—A boron complex with 4-bromo-2-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenoxide ligand has been synthesized, and its photoluminescence properties in solution and in the solid phase have been examined. The structure of the complex has been determined by X-ray analysis. Non-classical intermolecular interaction (halogen bond) between the bromine and fluorine atoms has been detected in the crystal structure of the complex.

Keywords: boron complex, photoluminescence, halogen bond

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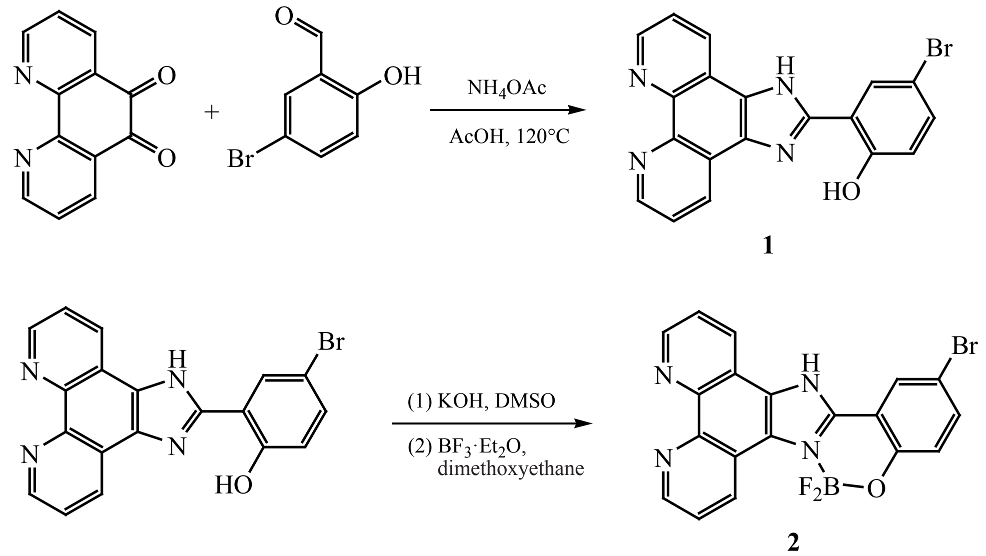
Boron complexes with N,N-, N,O-, and O,O-chelating ligands exhibit efficient photo- and electroluminescence [1–3]. The emission range of organoboron complexes covers the entire visible region, as well as the near-IR region [4]. Unlike the most efficient modern emitters based on platinum [5] and iridium compounds [6], boron complexes are advantageous due to their much lower cost, less laborious synthetic procedures, and the lack of toxicity. Therefore, studies in the field of synthesis and luminescence properties of boron compounds are continuously developing. The color and efficiency of emission of organoboron luminophores are determined mainly by ligand environment of the boron atom. In addition, luminescence properties of solid complexes are largely influenced by intermolecular interactions in the crystal structure. It was shown previously that boron complexes with ligands containing an imidazolylphenoxide fragment exhibit strong photo- and electroluminescence [7, 8].

Herein, we report the synthesis, structure, and photoluminescence properties of a new boron complex with a 4-bromo-2-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenoxide ligand. The ligand, 4-bromo-2-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenol (**1**) was synthesized according to the known procedure [9] by condensation of 1,10-phenanthroline-5,6-dione with 5-bromosalicylaldehyde in acetic acid in the presence of ammonium acetate. Phenol **1** was treated with potassium hydroxide to obtain the corresponding potassium salt which reacted with boron trifluoride–diethyl ether complex at room temperature to afford complex **2** (Scheme 1). The product was isolated in a good yield (72%) as a yellow–green finely crystalline solid which is stable in air and soluble in DMSO, DMF, and acetonitrile. By recrystallization of **2** from acetonitrile we succeeded in obtaining its single crystal suitable for X-ray analysis.

Complex **2** crystallizes as 1 : 1 solvate with acetonitrile, where the components are linked to each other through $N^{1S}\cdots H^2$ hydrogen bond (Fig. 1). The boron coordination sphere is a tetrahedron with the bond angles at the boron atom ranging from 108.263(3)° to 109.2936(16)°. The B^1–N^3 distance [1.55555(5) Å] corresponds to the sum of the covalent radii of boron and nitrogen (1.55 Å [10]); the B^1–O^1 bond [1.45025(5) Å] is slightly shorter than the sum of the covalent radii of B and O (1.50 Å [10]); and the B^1–F^1 [1.40407(3) Å] and B^1–F^2 bond lengths [1.39656(4) Å] approach the sum of the covalent radii of boron and fluorine (1.41 Å [10]). The dihedral angle between the phenoxide and imidazole ring planes is 8.0°. Molecules **2** in crystal are packed in stacks through π–π interactions between the imidazophenanthroline fragments with a distance of 3.452 Å between the centroids (Fig. 1). In addition, weak non-covalent intermolecular interactions $F^2\cdots Br^1$ like type I halogen bond [11] were detected (Fig. 2). The $F^2\cdots Br^1$ distance [2.9665(15) Å] is

Scheme 1.



shorter than the sum of van der Waals radii of fluorine and bromine (3.32 Å [12]); the $C^{16}Br^1F^2$ angle is 156.54(10)°. The existence of a bond critical point (3, –1) for the corresponding atoms was confirmed by DFT quantum chemical calculations and topological analysis of electron density distribution in the framework of Bader's quantum theory of atoms in molecule (QTAIM). The results are summarized in the table.

In fact, QTAIM analysis revealed a bond critical point (3, –1) for the intermolecular Br···F contact (type I halogen–halogen bond). This interaction is characterized by a low electron density, positive electron density Laplacian, and near-zero positive total energy density at the BCP, which are typical of non-covalent interactions. The energy of the Br···F contact was estimated at 2.2 to 3.6 kcal/mol using different known correlations (see the table). It should be noted that the calculations with both functionals used (M06 and ωB97XD) predicted similar electron densities at the BCP and Br···F interaction energies. The ratio $-G(r)/V(r) = 1.43 >> 1$ at the BCP indicates negligible contribution of the covalent component to the Br···F interaction [16].

The electronic absorption spectrum of complex **2** in acetonitrile contained bands assignable to π–π* and

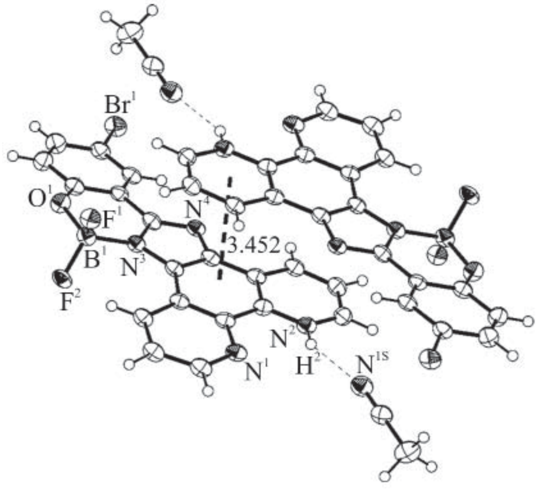


Fig. 1. A fragment of crystal packing of complex **2**; non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 30%.

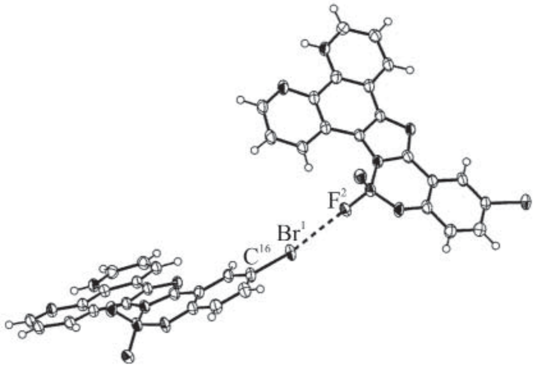


Fig. 2. Halogen bond C^{16}–$Br^1\cdots F^2$ in the crystal structure of complex **2**.

Calculated electron densities [$\rho(r)$], electron density Laplacians [$\nabla^2\rho(r)$], total energy densities (H_b), potential energy densities [$V(r)$], and kinetic energy Lagrangians [$G(r)$] at the bond critical point (3, –1) corresponding to Br···F type I halogen–halogen intermolecular contact in the crystal structure of complex **2** and energies of the Br···F interaction

Method/basis set	$\rho(r)$, a.u.	$\nabla^2\rho(r)$, a.u.	H_b, a.u.	$V(r)$, a.u.	$G(r)$, a.u.	E_{int}, kcal/mol			
						a	b	c	d
M06/DZP-DKH	0.010	0.048	0.002	–0.007	0.010	2.2	2.7	2.5	3.6
ωB97XD/DZP-DKH	0.010	0.048	0.002	–0.007	0.010	2.2	2.7	2.5	3.6

[a] $E_{int} = -V(r)/2$ [13].

[b] $E_{int} = 0.429G(r)$ [14].

[c] $E_{int} = 0.58[-V(r)]$ [15]; this correlation was proposed especially for non-covalent interactions involving bromine atoms.

[d] $E_{int} = 0.57G(r)$ [15]; this correlation was proposed especially for non-covalent interactions involving bromine atoms.

n–π* transitions in the aromatic system of the ligand (Fig. 3). The photoluminescence spectrum of **2** displayed two strong peaks with their maxima at λ 407 and 424 nm which can be assigned to transitions in an isolated molecule of the complex, as well as a broad low-intense band at λ_{max} 570 nm which may arise from emission of excimers. The solid state photoluminescence spectrum of **2** is shifted red relative to the spectrum in acetonitrile solution and is represented by a broad structureless band with λ_{max} 525 nm. The red shift is related primarily to strong intermolecular interactions in the solid state (π–π stacking and halogen bonding).

Thus, we have synthesized a new boron complex containing a 4-bromo-2-(1*H*-imidazo[4,5-*f*][1,10]-phenanthrolin-2-yl)phenoxide ligand. X-Ray analysis of the new complex has revealed π–π stacking interactions and Br···F halogen bonding in the crystal structure. The formation of Br···F halogen bond has been confirmed by quantum chemical calculations and Bader's QTAIM analysis of electron density distribution. The complex shows photoluminescence in solution and in the solid phase.

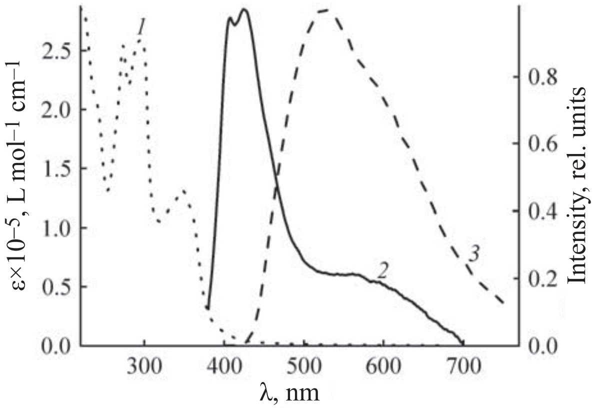


Fig. 3. (*1*) Electronic absorption spectrum of complex **2** in acetonitrile and its emission spectra in (*2*) acetonitrile and (*3*) solid phase at room temperature; λ_{excit} 360 nm.

EXPERIMENTAL

The study was performed using the facilities of the Magnetic Resonance Research Center, Chemical Analysis and Materials Research Center, and Center for X-Ray Diffraction Studies at the St. Petersburg State University.

4-Bromo-2-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenol (**1**) was synthesized as described in [9]. Boron trifluoride–diethyl ether complex (Aldrich) was used without further purification.

The ^1H, ^{13}C, ^{11}B, and ^{19}F NMR spectra were recorded in DMSO-d_6 at room temperature on a Bruker ACF-400 spectrometer at 400, 125, 160.43, and 470.50 MHz, respectively, using the residual proton and carbon signals of the solvent as reference for ^1H and ^{13}C; the ^{11}B and ^{19}F chemical shifts were measured relative to $BF_3 \cdot Et_2O$ and $CFCl_3$, respectively, as external standards. Signals were assigned with the use of two-dimensional GE-COSY and GE-HSQC techniques. The IR spectrum was recorded in KBr on a Shimadzu IR Prestige-21 spectrometer. The mass spectrum was obtained on a Bruker microTOF instrument (electrospray ionization from solution in methanol; the most abundant isotope peak is given). The electronic absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. The luminescence spectra were measured on a Horiba/Jobin Yvon Fluorolog 3 spectrofluorometer; λ_{excit} = 360 nm.

A single crystal of **2** was obtained by slow evaporation of a solution of **2** in acetonitrile at room temperature. The X-ray diffraction data were obtained at 100 K on an Agilent Technologies Supernova diffractometer equipped with an Atlas CCD detector (CuK_α radiation, λ = 1.54184 Å).

The structure was solved by the direct method and was refined using SHELXL package [17] implemented in OLEX2 software [18]. A correction for absorption was applied using CrysAlisPro [19]. The positions of hydrogen atoms were calculated by SHELX algorithms. The complete set of X-ray diffraction data for compound **2** was deposited to the Cambridge Crystallographic Data Centre (CCDC entry no. 1914231).

Quantum chemical calculations were carried out using Gaussian-09 software [20]; M06 and ωB97XD functionals, second-order Douglas–Kroll–Hess relativistic Hamiltonian, and DZP-DKH basis sets (for all atoms) were utilized [21–24]. Topological analysis of electron density distribution was carried out according to Bader's QTAIM [25] using Multiwfn [26].

Difluoro[4-bromo-2-(1*H*-imidazo[4,5-*f*][1,10]-phenanthrolin-2-yl)phenolato-κ*O*,κ*N*]boron(III). Potassium hydroxide, 0.04 g (0.71 mmol), was added to a solution of 0.2 g (0.51 mmol) of 4-bromo-2-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenol (**1**) in 5 mL of DMSO. The mixture was heated at 80°C for 4 h under continuous stirring, the liquid phase was separated from the solid precipitate, and the solvent was removed under reduced pressure. The residue (potassium salt) was dissolved in 10 mL of dimethoxyethane, the solution was cooled to 0°C, and 0.08 g (0.56 mmol) of $BF_3 \cdot Et_2O$ was added under continuous stirring. The mixture was allowed to warm up to room temperature and stirred for 8 h. The precipitate was filtered off, washed with dimethoxyethane, dried, and extracted with acetonitrile. The solvent was removed from the extract, and the residue was dried under reduced pressure at 50°C. Yield 0.16 g (72%), yellow–green crystals. IR spectrum, ν, cm^{-1}: 3543, 3207, 3185, 3151, 3098, 1619, 1573, 1548, 1500, 1480, 1457, 1321, 1256, 1056, 1032, 949. ^1H NMR spectrum, δ, ppm: 9.07 d.d (2H, 1-H, 6-H, J_{HH} = 4.8, 1.1 Hz), 8.99 d (2H, 3-H, 4-H, J_{HH} = 8.1 Hz), 8.14 d.d (2H, 2-H, 5-H, J_{HH} = 8.2, 4.9 Hz), 7.62 d (1H, 9-H, J_{HH} = 2.3 Hz), 7.24 d.d (1H, 8-H, J_{HH} = 8.8, 2.3 Hz), 6.82 s (1H, NH), 6.64 d (1H, 7-H, J_{HH} = 8.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 156.15, 150.04, 145.89, 135.51, 135.37, 134.40, 128.00, 126.20, 121.85, 119.60, 115.04, 113.87, 110.78. ^{11}B NMR spectrum, δ_B –1.27 to –1.31 ppm, m. ^{19}F NMR spectrum, δ_F, ppm: –148.16, –148.21. UV spectrum (MeCN), λ_{max}, nm ($\varepsilon \times 10^{-5}$, L mol^{-1} cm^{-1}): 273 (2.55), 293 (2.58), 350 (1.30). Mass spectrum (ESI+): *m*/*z* 439.0104 [*M* + H]$^+$. Found, %: C 51.90; H 2.39; N 12.59. $C_{19}H_{10}BBrF_2N_4O$. Calculated, %: C 51.98; H 2.30; N 12.76.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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