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Crystal Structure and Luminescence of Boron Difluoride Acetylacetonate

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Abstract—The structure of boron difluoride acetylacetonate was studied by X-ray diffraction. A pucker of the chelate ring along the line connecting the boron and γ-carbon atom was detected. The effects of geometric and electronic factors on the fluorescence intensity of boron difluoride β-diketonates were discussed.

Presently increased interest has been attached to the photophysical and photochemical properties of boron difluoride β-diketonates owing to their prospective use in laser technology [1,2]. Therefore, studying the spectral-luminescent properties of boron difluoride β-diketonates in relation to their electronic and crystal structure is topical. The information on the crystal structures of boron difluoride β-diketonates is scarce and restricted to the crystal structures benzoyl- and anisoylacetonates [3, 4].

Proceeding with our research on interrelations between the electronic structure, steric structure, and photophysical characteristics of boron difluoride β-diketonates [5], we determined the crystal and molecular structures of the simplest compound in the series of boron difluoride β-diketonates, namely acetylacetonate, and studied its spectral-luminescent properties.

The principal crystallographic parameters of the sample studied and details of the X-ray diffraction experiment and the least-squares refinement of the structural model are given in Table 1. The coordinates of basic atoms of the structure and the equivalent (isotropic) thermal parameters of the atoms (U_{eq}) are given in Table 2.

The crystal structure of boron difluoride acetylacetonate (BF_2*acac*) comprises isolated molecules that form a three-dimensional framework owing to van der Waals interactions (Fig. 1). Two oxygen atoms and the boron atom of the O_2BF_2 tetrahedron and three carbon atoms form a six-membered ring. Methyl carbon atoms are symmetrically located on two of these three atoms (Fig. 2). The bond lengths and bond angles are given in Table 3.

It is seen from a comparison of the structures of BF_2*acac* and boron difluoride benzoyleactonate

Table 1. Crystallographic data and details of the X-ray diffraction experiment and structural refinement of boron difluoride acetylacetonate

Parameter	Value
Formula	$BF_2O_2C_5H_7$
Molecular weight	147.92
Temperature, K	293(2)
Wave length	MoK_α (0.71073 Å)
Space group	$P2_1/n$
a, Å	6.669(5)
b, Å	8.525(6)
c, Å	12.596(9)
β, deg	94.074(13)
Z	4
d_{calc}, g/cm^3	2.234
μ, mm^{-1}	1.375
$F(000)$	304
Crystal habit	Sphere 0.29 mm in diameter
θ range	2.89–23.28°
Index ranges	$-7 \leq h \leq 5$, $-9 \leq k \leq 9$, $-11 \leq l \leq 13$
Reflections collected	3082
Unique reflections	1022 (R_{int} 0.0460)
Reflections with $I > 2\sigma(I)$	711
Absorption	By cut
Refinment method	Full-matrix least-squares on F^2
Refinment variables	94
S	1.008
R factors on $I > 2\sigma(I)$	R_1 0.0455, wR_2 0.1387
R factors on all reflections	R_1 0.0567, wR_2 0.1406
Extinction coefficient	0.013(8)
Residual electron density (min/max), e/Å^3	–0.196/0.194 (near C^6 atom)

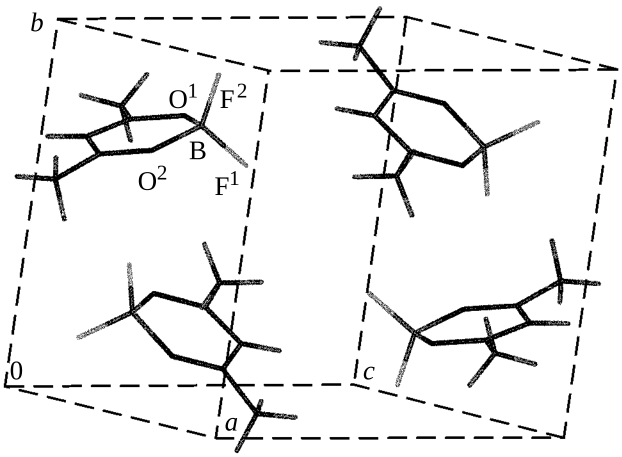

Fig. 1. Crystal structure of boron difluoride acetylacetonate.

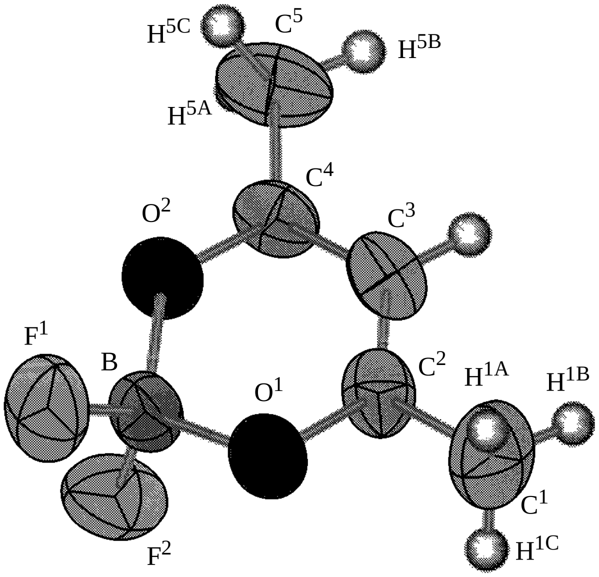

Fig. 2. Molecular structure of boron difluoride acetylacetonate.

(BF_2*bzac*) [3] that introduction of a phenyl group in the α position of the chelate ring results in an insignificant elongation of C–C and C–O bonds. Therewith, the bond lengths and bond angles in the coordination unit O_2BF_2 remain invariable. The B–O bond lengths in the series of acetylacetonates of boron diacetate [6], boron difluoride, and diphenylboron [7] increase from 1.471 to 1.530 Å.

In contrast to diphenylboron acetylacetonate [7] and boron diacetate acetylacetonate [6], where carbon and oxygen atoms of the chelate ring lie in one plane, the chelate ring in boron difluoride acetylacetonate is puckered along the line connecting of the boron atom and the γ-carbon atom C^3. The angle between the $O^1C^1C^2C^3$ and $O^2C^3C^4C^5$ planes is 172.91° (0.20). Therewith, the boron atom deviates from the

Table 2. Atomic coordinates $\times 10^4$) and equivalent isotropic thermal factors in the crystal structure ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	U_{eq}
B	2218(4)	7566(4)	3263(2)	68(1)
F^1	3611(3)	8444(2)	3836(1)	104(1)
F^2	1800(3)	6235(2)	3792(1)	101(1)
O^1	3050(3)	7176(2)	2240(1)	77(1)
O^2	360(3)	8494(2)	3095(1)	73(1)
C^1	3125(5)	6903(4)	395(2)	101(1)
C^2	2069(4)	7407(3)	1336(2)	68(1)
C^3	236(4)	8130(3)	1277(2)	73(1)
C^4	–533(4)	8712(3)	2167(2)	65(1)
C^5	–2397(4)	9660(4)	2152(3)	103(1)
H^3	–492	8225	623	88
H^{1A}	4065	7699	220	151
H^{1B}	2162	6742	–198	151
H^{1C}	3832	5941	555	151
H^{5A}	–3301	9201	2625	154
H^{5B}	–3026	9683	1443	154
H^{5C}	–2072	17010	2380	154

Table 3. Bond lengths and bond angles in boron difluoride acetylacetonate

Bond	*d*, Å	Angle	ω, deg
F^1–B	1.359(3)	F^1BF^2	110.9(2)
O^1–B	1.477(4)	F^1BO^1	107.6(2)
O^1–C^2	1.288(3)	F^1BO^2	108.5(2)
C^2–C^3	1.366(4)	C^2O^1B	122.6(2)
C^2–C^1	1.484(4)	$O^1C^2C^3$	120.9(2)
F^2–B	1.355(4)	$O^1C^2C^1$	114.9(3)
O^2–B	1.473(3)	$C^3C^2C^1$	124.1(3)
O^2–C^4	1.288(3)	$C^4C^3C^2$	120.6(2)
C^3–C^4	1.359(4)	O^1BO^2	111.1(2)
C^4–C^5	1.482(4)	F^2BO^1	108.7(2)
		F^2BO^2	110.1(2)
		C^4O^2B	122.5(2)
		$O^2C^4C^3$	121.3(2)
		$O^2C^4C^5$	115.0(3)
		$C^3C^4C^5$	123.7(3)

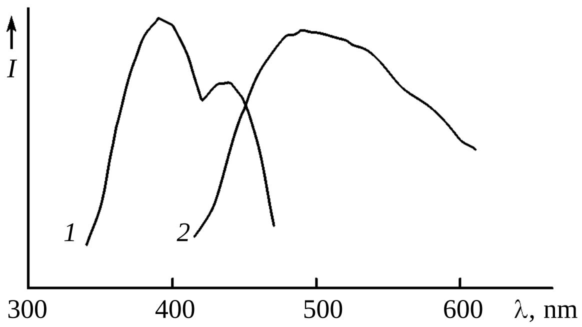

Fig. 3. (*1*) Luminescence excitation and (*2*) luminescence spectra of boron difluoride acetylacetonate.

$O^1O^2C^2C^4$ plane by 0.1223 Å and from the plane common with the C^3 atom, by 0.0489 Å.

Whereas BF_2*bzac* molecules in the crystal unit cell are coplanar [3], the angle between the normals drawn through the centers of adjacent BF_2*acac* molecules is 65.10° (0.20) (Fig. 1).

Boron difluoride acetylacetonate has the lowest fluorescence intensity among crystalline boron difluoride β-diketonates [5]. The luminescence excitation and luminescence spectra of BF_2*acac* at 77 K are given in Fig. 3. The luminescence spectrum represents a broad structureless band with a maximum at 490 nm, whereas the luminescence excitation spectrum has two maxima at 390 and 436 nm.

The fluorescence intensity of organic compounds is known to be affected by both geometric and electronic factors. The fluorescence intensity of boron difluoride acetylacetonate is lower by two orders of magnitute than that of benzoylacetonate [5]. Comparative analysis of the crystal [3] and electronic [8–10] structures of BF_2*acac* and BF_2*bzac* shows that both the factors are responsible for the low fluorescence intensity of the former.

The coplanarity of BF_2*bzac* molecules [3], where the benzene ring of one molecule is under the chelate ring of an adjacent molecule (*d* 3.44 Å), allows effective π-electron interaction and promotes strong excimer fluorescence that is similar to the fluorescence of excimers of boron difluoride dibenzoylmetahanate with alkylbenzenes [11]. At the same time, the acoplanarity of boron difluoride acetylacetonate molecules (Fig. 1) makes such intermolecular interaction impossible and weakens the luminescence intensity.

The photoelectron and UV spectral data show that the HOMO of BF_2*acac*, in contrast to β-diketonates with aromatic substituents, is substantially contributed by n^- and n^+ orbitals and that the luminescent properties are to a great extent determined by singlet and triplet $n\pi^*$ levels. It is known that organic compounds with prevailing contribution of *n* orbitals in HOMO exhibit a low fluorescence intensity [12]. We can assume that the essential contribution of *n* orbitals in the HOMO of BF_2*acac* compared to BF_2*bzac* is also responsible for the characteristic pucker of the chelate ring in the former.

EXPERIMENTAL

Boron difluoride acetylacetonate was synthesized as described in [13]. The luminescence and luminescence excitation spectra were recorded at 77 K on an apparatus assembled of an SDL-1 spectrometer and an MDR-23 monochromator with DRSh-250 and Tungsram-2500 lamps as excitation sources.

We selected the best single crystals for the X-ray diffraction study and cut out from their most perfect parts isomeric crystals which were around in water up to a spherical shape. Thus obtained samples were subjected to a preliminary X-ray diffraction study. As a result, a single crystal of 0.145 mm in radius was selected, which showed the best diffraction peak profiles and convergence of intensities of symmetrically equivalent diffraction reflections. The full X-ray diffraction study was carried out on a Bruker SMART-1000CCD system using MoK_α radiation. Data collection and edition, refinement of unit cell parameters, and conversion from integral intensities to modules of structure amplitudes were carried out by published programs [14]. The structure was solved by the direct method with subsequent refinement of positional and thermal parameters in the anisotropic approximation for all non-hydrogen atoms by programs [15]. Hydrogen atoms were located by Fourier syntheses, but it did not introduce radical novelty, and in further work we used calculated data refined by the rider model.

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