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Research paper

Synthesis and structure of boron difluoride binuclear β-diketonates

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ABSTRACT

Four binuclear diketonate complexes of boron difluoride have been prepared. Obtained complexes contain the following pairs of ligands connected through a sulfur atom with their central carbon atoms: acetylacetone-acetylacetone, acetylacetone-acetoacetic ester, acetylacetone-dibenzoylmethane, acetylacetone-benzoylacetone. Molecular and crystal structure have been identified for three complexes. Their structure is similar to the one of aromatic sulfides. Effect of γ-substituents on chelate cycle structure and on the substituents next to β-carbon atoms has been discussed.

1. Introduction

Boron difluoride diketonates have become popular objects for structural and photophysical investigations owing to their availability, stability, and such promising emission properties as mechanochromism [1–10], thermochromism [7,8] and solvatochromism [1,7,8], phosphorescence at room temperature [11–14]. Emission properties shown by both solutions and crystals of the complexes strongly depend on molecular design and on such weak intermolecular interactions, as hydrogen bonds, π-stacking, Van der Waals forces, yielding intermolecular self-assembly, excimers, and exciplexes [15–20]. Such a fine tuning of luminescent characteristics makes possible using diketonate complexes of tetracoordinated boron as optical chemo-, thermo- or mechanosensors, fluorescent labels, new functional materials for various applications [21–35]. Researchers put a lot of efforts to match structure and intermolecular interactions to spectral properties and luminescence [5–8,11,16–18,20]. In this regard, it is important to develop new synthetic approaches and to investigate structure of luminescent boron difluoride complexes or their counterparts promising for applications as dyes. That is why, synthesis of new complexes and their structural investigations provides data for the studies of structure-luminescent properties relationships.

This paper discusses preparation and structural investigations of binuclear boron difluoride complexes, which boron chelate fragments connected through the sulfur atom with their central (γ) carbon atoms. Complexes obtained in the work are shown on Fig. 1 along with the used abbreviations and substituent numeration in chelate cycles.

Given boron difluoride diketonates resemble aromatic compounds in terms of electronic structure and chemical properties, complexes **1–4** can be considered as counterparts of aromatic sulfides, which structure is well known. It became interesting to find out the changes that would come in case of replacing aryl radicals with boron chelate ones. Apart from that, structural investigations of the compounds **1–3** also studies interactions of substituents next to β and γ carbon atoms as well as tracks changes that are caused by the presence of large substituents next to the central carbon atom. At the moment, the structure of several substituted boron difluoride acetylacetonates has been described, however, structure of γ-substituted boron difluoride dibenzoylmethanates and acetylacetonates is practically unknown.

Earlier, the structure was studied for binuclear complexes of boron difluoride, where acetylacetonate fragments were connected with the chain of **4** carbon atoms ($F_2B(acacC_4H_8acac)BF_2$ [36]) or with disulfide group ($F_2B(acacS_2acac)BF_2$ [37]). The paper [38] described the synthesis of complex **1**. The common feature of these complexes is that both boron chelate fragments contain the same ligand – acetylacetone. Binuclear complexes with different ligands have not been studied, because there were no methods to prepare such compounds. Synthesis of boron difluoride acetylacetonates with different diketonate groups connected via sulfur atom [39] made possible fabrication of binuclear complexes with boronacetylacetonate fragment being substituted with boron chelate based on acetoacetic ester, dibenzoylmethane or benzoylacetone.

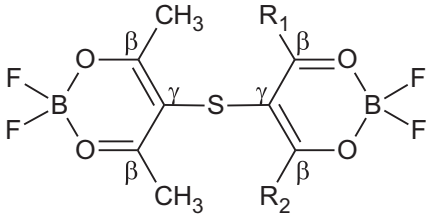
2. Experimental

2.1. Materials and methods

Synthesis of the complexes 1i-4i is given in [39]. Dried diethyl ether

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$R_1 = CH_3$ $R_2 = CH_3$ (**1**, $F_2B(acacSacac)BF_2$)
$R_1 = CH_3$ $R_2 = OCH_2CH_3$ (**2**, $F_2B(acacSacEtac)BF_2$)
$R_1 = C_6H_5$ $R_2 = C_6H_5$ (**3**, $F_2B(acacSdbm)BF_2$)
$R_1 = CH_3$ $R_2 = C_6H_5$ (**4**, $F_2B(acacSbzac)BF_2$)

Fig. 1. Structural formulas of complexes **1–4** and abbreviations for them.

Table 1
Crystal data, experimental parameters, and structure refinement parameters for **1–3**.

	1*0.5 $C_2H_4Cl_2$	**2**	**3**
Empirical formula	$C_{11}H_{14}O_4B_2F_4SCl$	$C_{11}H_{14}O_5SB_2F_4$	$C_{20}H_{16}O_4B_2F_4S$
Formula weight	375.35	355.90	450.01
Temperature/K	293.15	293.15	293.15
Crystal system	triclinic	monoclinic	orthorhombic
Space group	*P*-1	$P2_1/n$	*Pbca*
Unit cell parameters			
a/Å	7.591(4)	11.371(9)	8.368(3)
b/Å	10.496(4)	12.765(11)	18.822(7)
c/Å	10.791(5)	11.993(9)	25.534(9)
α/°	86.56(3)	90	90
β/°	85.43(2)	116.24(3)	90
γ/°	70.61(3)	90	90
Volume/Å^3	808.0(6)	1561(2)	4022(2)
Z	2	4	8
ρ_{calc}g/cm^3	1.543	1.514	1.486
μ/mm^{-1}	0.419	0.269	0.223
F(0 0 0)	382	728	1840
Crystal size/mm^3	0.83 × 0.81 × 0.39	0.39 × 0.31 × 0.27	0.93 × 0.35 × 0.09
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.7 to 82.66	6.38 to 57.8	5.82 to 58.42
Index ranges	$-14 \le h \le 14$, $-19 \le k \le 19$, $-20 \le l \le 19$	$-15 \le h \le 15$, $-17 \le k \le 17$, $-16 \le l \le 15$	$-11 \le h \le 11$, $-25 \le k \le 25$, $-34 \le l \le 34$
Reflections collected	69,665	53,701	75,569
Independent reflections	10,786 [R_{int} = 0.0382, R_{sigma} = 0.0321]	4100 [R_{int} = 0.0276, R_{sigma} = 0.0129]	5427 [R_{int} = 0.0805, R_{sigma} = 0.0307]
Data/restraints/parameters	10786/0/212	4100/0/212	5427/0/282
Goodness-of-fit on F^2	1.021	1.052	1.045
Final R indexes [I > =2σ (I)]	R_1 = 0.0669, wR_2 = 0.1788	R_1 = 0.0404, wR_2 = 0.1125	R_1 = 0.0491, wR_2 = 0.1008
Final R indexes [all data]	R_1 = 0.1200, wR_2 = 0.2078	R_1 = 0.0503, wR_2 = 0.1217	R_1 = 0.0827, wR_2 = 0.1138
Largest diff. peak/hole / e Å^{-3}	0.80/-0.79	0.29/-0.32	0.25/-0.29

and dichloroethane were used for synthesis. IR-spectra in the range 4000–550 cm^{-1} were recorded on «Infralum FT-801» instrument in KBr tablets. NMR spectra were recorded on «Bruker WH 400» instrument, solvent - $CDCl_3$. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to tetramethylsilane as an internal standard (TMS: $\delta = 0$ ppm).

2.2. Synthesis.

Method A: The mixture of $F_2B(acacSdik)H$ (1 mmol), 17 mL of ether, boron trifluoride etherate (1.5 mmol), and tributyl borate (1 mmol) was being boiled under stirring for 7 h. After cooling down the reaction mixture, obtained precipitate was filtered, washed with cool diethyl ether, dried in air and recrystallized.

Method B: a mixture of 2 mmol $F_2B(acacSdik)H$, 3 mmol boron fluoride etherate, 2 mmol tributyl borate and 6 mL of dichloroethane was being boiled for 7 h, then the reaction mixture was evaporated in vacuum. The residue was washed with three portions of hexane and recrystallized.

*$F_2B(acacSacac)BF_2$ **(1)***. Method A: after recrystallization from dichloroethane-petroleum ether mixture (90–110), colorless crystals were obtained, m.p. 173–176 °C (decomp.). Yield – 80%. Calc. for $C_{10}H_{12}B_2F_4O_4S$*0.5($C_2H_4Cl_2$): C, 35.20; S, 8.54. Found: C, 35.35; S, 8.51%. IR (ν, cm^{-1}): 1572, 1553 (C═O), 1470 (C═C), 1414, 1350, 1231 (B-F), 1177 (B-F), 1113 (B-O), 1048, 1024 (B-O). ^{1}H NMR: 2.57 (12H, s, CH_3).

Method B: after recrystallization from dichloroethane-petroleum ether mixture (90–110), colorless crystals were obtained, m.p. 173–176 °C (decomp.). Yield – 85%.

*$F_2B(acacSacEtac)BF_2$ **(2)***. Method A: after recrystallization from dichloroethane-petroleum ether mixture, colorless crystals were obtained, m.p. 150–152 °C (decomp.). Yield – 45%. Calc. for $C_{11}H_{14}B_2F_4O_5S$: C, 37.12; S, 9.01. Found: C, 36.98; S, 9.10%. IR (ν, cm^{-1}): 1578 (C═O, acEtac), 1555 (C═O, acac), 1491(C═C, acEtac), 1478 (C═C, acac), 1416, 1352, 1329, 1221 (B-F), 1177 (B-F), 1121 (B-O), 1105 (B-O), 1044. ^{1}H NMR: 1.43 (3H, t J = 7.14 Hz, CH_3(OEt)), 2.57 (3H, s, CH_3 (acEtac)), 2.61 (6H, s, CH_3 (acac)), 4.59 (2H, d J = 7.14 Hz, CH_2(OEt)).

Method B: after recrystallization from benzene-petroleum ether mixture, colorless crystals were obtained, m.p. 150–152 °C (decomp.). Yield – 50%.

*$F_2B(acacSdbm)BF_2$ **(3)***. Method B: after recrystallization from dichloroethane-petroleum ether mixture, yellow crystals were obtained, m.p. 221–224 °C (decomp.). Yield – 49%. Calc. for $C_{20}H_{16}B_2F_4O_4S$: C, 53.38; S, 7.13. Found: C, 53.22; S, 7.20%. IR (ν, cm^{-1}): 1599, 1580, 1551 (C═O, acac), 1530 (C═O, dbm), 1499 (C═C, dbm), 1480 (C═O, acac), 1453, 1439, 1352, 1225 (B-F), 1181 (B-F), 1150, 1103, 1055 (B-O). ^{1}H NMR: 1.85 (6H, s, CH_3), 7.62, 7.75, 7.95 (10*H*, t, t, d, C_6H_5).

*$F_2B(acacSbzac)BF_2$ **(4)***. Method B: after recrystallization from dichloroethane-petroleum ether mixture, colorless crystals were obtained, m.p. 181–183 °C (decomp.). Yield – 38%. Calc. for $C_{15}H_{14}B_2F_4O_4S$: C, 46.44; S, 8.27. Found: C, 46.63; S, 8.34%. IR (ν, cm^{-1}): 1597, 1580, 1553 (C═O), 1501, 1474 (C═C), 1458 (C═C),

1422, 1364, 1354, 1221 (B-F), 1184, 1163 (B-F), 1107 (B-O), 1053. ^{1}H NMR: 2.24 (6H, s, CH_3 (acac)), 2.68 (3H, s, CH_3 (bzac)) 7.56, 7.70, 7.77 (5H, t, t, d, C_6H_5).

2.3. X-ray diffraction study

Diffraction data of **1–3** were collected on a Bruker D8 Quest diffractometer with graphite-monochromated Mo K_α radiation (λ 0.71073 Å). Collection, data editing and refinement of element cell parameters, as well as absorption record were carried out using the software SMART and SAINT-Plus [40]. All calculations to determine and define structures were performed using the software SHELXL/PC [41] and OLEX2 [42]. The structures were solved by direct methods and refined by the least-squares method in anisotropic approximation for nonhydrogen atoms. The main crystallographic data and results of structure refinement are presented in Table 1. Complete atom coordinates, bond lengths, and valence angles are deposited at Cambridge structural database (No. 1910781 for **1**; 1910540 for **2**, and 1911544 for **3**, deposit@ccdc.cam.ac.uk; http://www.ccdc. cam.ac.uk).

3. Results and discussion

3.1. Synthesis of the complexes

To prepare complexes **1–4** we used substituted boron difluoride acetylacetonates containing non-chelated diketonate groups (**1i-4i**). Treatment of these compounds with the excess of boron trifluoride in the presence of tributyl borate yielded yielded complexes containing two boron chelate fragments (Scheme 1).

Earlier, formation of the complex **1** was shown to occur with good yield at heating of $(Hacac)_2S$, boron fluoride etherate with tributyl borate in the ether solution. We used this method to obtain complexes **1** and **2**. Compounds **3i** and **4i** containing dbm and bzac fragments do not enter into this reaction and remain unchanged. Apparently, this is caused by poor solubility of **3i** and **4i** complexes in the ether and due to dbm and bzac do not undergo enolization. According to ^{1}H NMR (in deuterochloroform) data, diketone fragments of **3i** and **4i** complexes are in the keto-form [38].

Ether substitution with more high-boiling dichloroethane enabled us to obtain all four complexes with a moderate yield.

Complexes **1–4** are poorly soluble in organic solvents. They are not enough volatile to be studied by the means of gas chromatography.

3.2. NMR ^{1}H spectroscopy

^{1}H NMR spectra of **1–4** complexes correspond to the suggested structures. Chelating free diketonate groups shifts the signals from β-substituents (methyl and etoxy groups) by 0.1–0.2 ppm to the weaker fields (Table 2). Signal positions of aromatic β-substituents remain almost unchanged. Signals from methyl groups of boron acetylacetonate cycle do not change considerably in complexes **1, 2, 4**. Complex **3** is an exclusion, because transformation of dibenzoylmethane fragment into dibenzoylmethanate cycle causes the shift of methyl group signal in boron acetylacetonate cycle by 0.56 ppm to the strong fields.

Table 2
NMR ^{1}H spectroscopy complexes **1i-4i** (F_2BacacSdikH) and **1–4** (F_2BacacSdikBF_2).

	CH_3 (F_2B(acac))	dikH or dikBF_2		
		CH_3	CH_2 (OC_2H_5)	CH_2 (OC_2H_5)
1i [39]	2.58	2.37		
1	2.57	2.57		
2i [39]	2.60	2.41	1.29	4.25
2	2.61	2.57	1.43	4.59
3i [39]	2.41			
3	1.85			
4i [39]	2.28	2.51		
4	2.24	2.68		

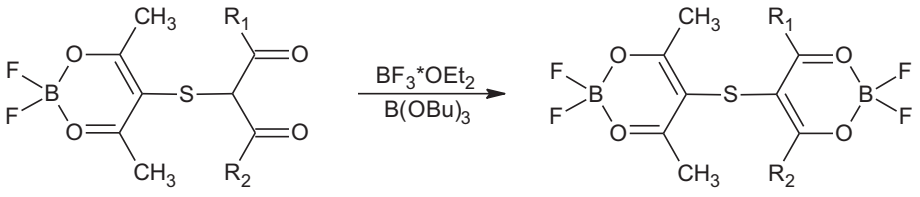
3.3. IR spectroscopy

IR spectra of the complexes **1–4** are typical for substituted boron diketonate complexes [43]. There is an intensive absorption band of C═O group in the range 1600–1500 cm^{-1}. Next to it, the more intensive absorption band of C═C bond is located in the region 1500–1400 cm^{-1}. These groups exhibit separate absorption bands arising from two different chelate cycles of complexes **2–4**. Absorption bands of B-F and B-O bonds are usually bicomponent with the high-frequency component being less intensive. This is caused by boron isotope's contribution.

3.4. Crystal structures of the complexes *1–3*

Structure of **1–3** molecules and atom indexing are given on Figs. 2–4. For convenience, main structural characteristics of the complexes **1–3** (bond lengths and angles) are given in Table 3 and Supplementary materials. Data on model compounds taken from references and from CCDC is also provided there.

Structure of the complexes **1–3** is governed by the geometry of the sulfide bond: chelate cycles are arranged at an angle of 102-105° (Cγ-S-Cγ angle), while each of the cycles is turned by 56-67° along the axis (passing through Cγ-S bond) with respect to the plane passing through Cγ-S-Cγ atoms. This structure is common for diarylsulfides with the substituents being in the ortho position. For example, C—S—C angle in dimesitylene sulfide (Mes_2S), which is structurally similar to complex **1**, is 106° and benzene cycles are turned by 54° with respect to plane



$R_1 = CH_3$ $R_2 = CH_3$ (**1i**)
$R_1 = CH_3$ $R_2 = OC_2H_5$ (**2i**)
$R_1 = C_6H_5$ $R_2 = C_6H_5$ (**3i**)
$R_1 = CH_3$ $R_2 = C_6H_5$ (**4i**)

$R_1 = CH_3$ $R_2 = CH_3$ (**1**)
$R_1 = CH_3$ $R_2 = OC_2H_5$ (**2**)
$R_1 = C_6H_5$ $R_2 = C_6H_5$ (**3**)
$R_1 = CH_3$ $R_2 = C_6H_5$ (**4**)

Scheme 1. Syntheses of complexes **1–4**.

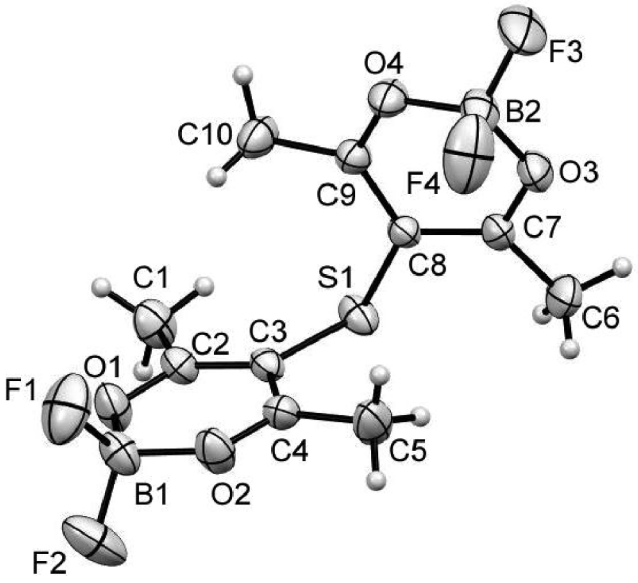


Fig. 2. Structure of compound **1**. Complex is shown without dichloroethane molecules.

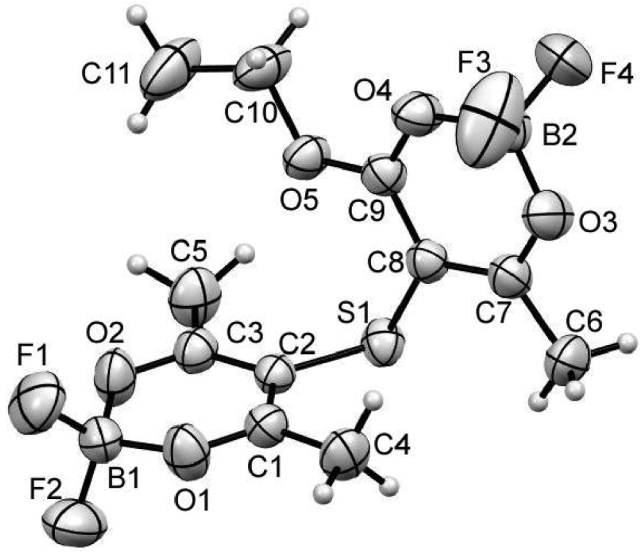


Fig. 3. Structure of compound **2**.

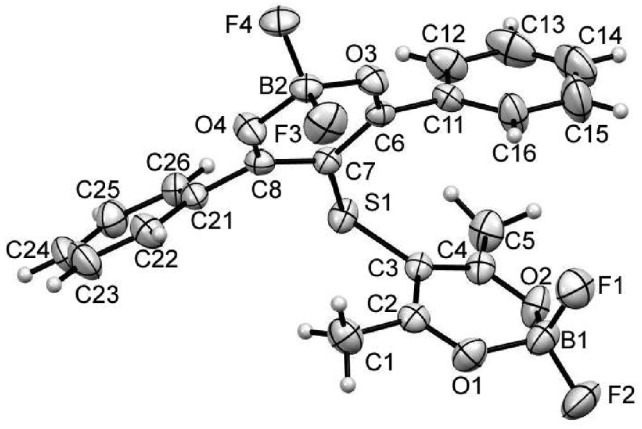


Fig. 4. Structure of compound **3**.

Table 3
Some valence angles, bend and rotation of chelate cycles in the complexes **1–3** and in model compounds, ° (Degrees).

	Cγ-S-Cγ	α*	O···O**	C···C***
F_2B(acacSacac)BF_2 (**1**)				
acac	104.58	58.45	2.27	2.84
acac		56.69	22.61	9.21
F_2B(acacSacEtac)BF_2 (**2**)				
acac	104.86	67.4	9.17	0.69
acEtac		60.83	2.64	1.94
F_2B(acacSdbm)BF_2 (**3**)				
acac	102.22	60.03	26.02	10.61
dbm		58.39	7.71	8.67
MesSMes [44]				
Mes	106.43	53.61		
Mes		54.35		
F_2B(acacSPh) [45]				
acac	104.64	76.07	163.56	175.42
Ph		6.83		
F_2B(acacH) [47]				
acac			8.44	4.19
F_2B(dbmH) [48]				
dbm			16.16	3.89

* α – rotation of chelate and aryl cycles with respect to plane passing through Cγ-S-Cγ atoms; chelate cycle plane determined as plane passing through C_β—O—O—C_β atoms.
** O…O is the angle between the planes containing B—O—O and C_β—O—O—C_β atoms in the chelate cycle.
*** C…C is the angle between the planes containing C_β—O—O—C_β and C_β-Cγ-C_β atoms in the chelate cycle.

containing this angle [44]. Obviously, sulfide atom is tetrahedrally coordinated in the complexes **1–3**, where two tetrahedral points are γ-carbon atoms and other two points are lone-electron pairs. Rotation of chelate cycles along the Cγ-S axis enables β-substituents of different cycles to be located at maximal distance from each other. It is noteworthy that structure of the complexes **1–3** is somewhat different from the one of γ-thiophenyl substituted boron difluoride acetylacetonate F_2B(acacSPh) [45], which sulfide atom is connected to chelate cycle and phenyl group. Cγ-S-C_{Ph} angle in that complex is 105°, the same as in complexes **1–3**. Benzene cycle lies in the plane of Cγ-S-C_{Ph} atoms (pretilt angle is less than 7°), while chelate cycle is almost orthogonal to it. Such changes in cycles' arrangement is caused by the absence of ortho-substituents in the phenyl ring. Mutual orthogonal arrangement of aromatic cycles, one of which is lying in C—S—C plane, is quite common for aromatic sulfides without ortho-substituents, e.g., p-O_2N-C_6H_4-S-C_6H_4-p-NH_2 [46]. C—S bond length in complexes **1–3** is 1.76–1.78 Å that is the same as in aromatic sulfides.

Thus, organic sulfides containing boron-chelate groups resemble aromatic counterparts in terms of structure.

Structure of acetylacetonate cycles in the complexes **1–3** repeats the one of unsubstituted boron difluoride acetylacetonate: chelate cycle is not planar, lengths of the paired bonds are equal. Attaching sulfur atom to central carbon atom increases B-O and C_β-Cγ bond length by 0.02–0.03 Å and 0.03–0.04 Å, respectively. At the same time, C_β-C_{Me} bond length remains practically the same. The angle between methyl group and chelate cycle (Cγ-C_β-C_{Me} angle) also does not practically change, it increases by 0.5–1.0°. Thus, methyl groups and the whole chelate cycle do not exhibit significant spatial interaction with γ-substituent. Therefore, C_β-Cγ bond length increases due to sulfur atoms weaken this bond, while spatial repulsion between β- and γ-substituents plays no role.

As in all considered complexes containing boron acetylacetonate fragment, chelate cycles in the complexes **1–3** exhibit two bends, along O…O line and along C_β…C_β, one resembling the shape of "boat".

In the compound **1**, containing two identical boronacetylacetonate fragments, one cycle is practically planar (bending over O…O and C_β…C_β lines is 2-3°, which significantly lower than in unsubstituted

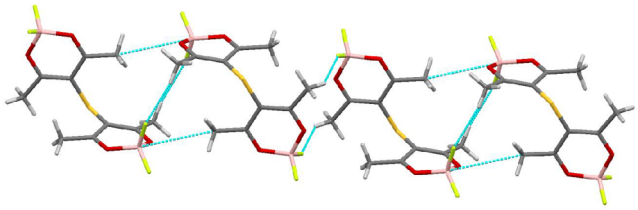


Fig. 5. Intermolecular interactions in **1**.

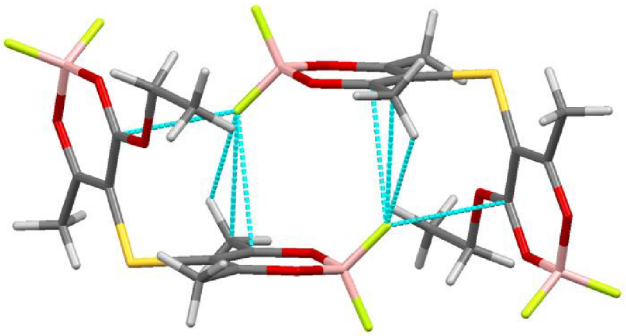


Fig. 6. Intermolecular interactions in **2**.

complex, Table 3). Bending in the second cycle of the compound **1** is 23° and 9° that is doubled compared to unsubstituted complex. Since chelate cycles in the compound 1 are equivalent, indicated differences in bending can be caused only by intermolecular interactions. Apparently, bending in chelate cycles occurs due to Coulomb interaction between fluorine atoms and closely located hydrogen atoms of methyl groups. In the bended cycle of the complex **1**, the distance between axial fluorine atom and hydrogen atom of the methyl group is 2.44 Å that is 9% lower than the sum of Van der Waals radii of fluorine and hydrogen atoms. When coming from solid to liquid phase, such interactions disappear. That is why both boronacetylacetonate cycles appear to be equivalent in ^{1}H NMR spectrum of the complex **1**, i.e., all methyl groups give rise to one signal (Table 2).

There is a limited number of structures reported for boron difluoride complexes, where acetoacetic ether acts as a ligand. Structure of the simplest compound of this type is not provided. Boron acetoacetic cycle in complex **2** is slightly different to the one containing acetylacetone as a ligand. Analogous bonds are not equal and differs by 0.04–0.05 Å. More short bonds are the ones corresponding to the double bonds in the enolized form of acetoacetic ether. Cycle is almost planar with the oxygen atom lying in the plane of chelate cycle. Boron acetylacetonate cycle is also approximately planar in the complex **2**.

Boron dibenzoylmethanate cycle is little different from the F_2B (dbmH) with respect to bond lengths and bend magnitude (Table 3). As in the case of acetylacetonate cycle, γ-substituent causes increase of C_β-$C\gamma$ bonds in the dibenzoylmethanate cycle. The largest difference between γ-substituted and original dibenzoylmethanate cycle refers to position of β-phenyl groups. In unsubstituted complex, phenyl cycles' plane is slightly out of the chelate cycle plane (3–6°). In the complex **3** this value reaches 40 and 61°. At the same time, substitution has no effect on the C_β-C_{Ph} bond length. Apparently, phenyl groups rotation aims to reduce the repulsion with thioacetylacetonate group next to central carbon atom. Bending of acetylacetonate cycle along O…O and C_β…C_β lines in the complex 3 is 26° and 11°, respectively.

Molecules of the dimer **1** are crystallized in pairs turned by 180° with respect to each other. Opposite chelate cycles are in the parallel planes. Separate pairs stay one after another forming a chain – Fig. 5. Interaction between neighbors is done via C_{Me}-H···F bonds. Complex **2** crystallizes the same way, but pairs are not aligned, therefore, eliminating chain formation – Fig. 6.

Molecules of the complex 3 crystallize forming stack of

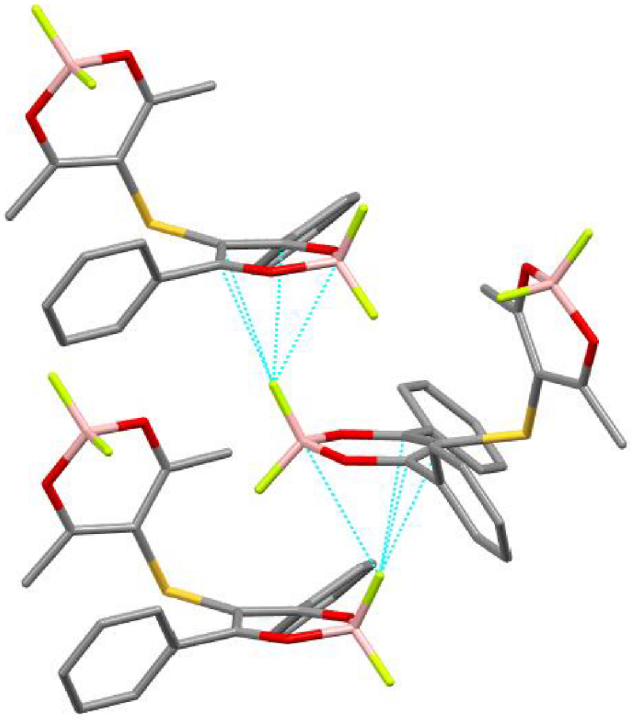


Fig. 7. Intermolecular interactions in **3**.

dibenzoylmethanate cycles, which lie in parallel planes (Fig. 7). In the neighboring layers cycles are mutually shifted and are not parallel to each other. Main interaction between the layers occurs between fluorine atom of one layers and four atoms of dibenzoyl cycle from the next layer. Apparently, indicated interaction is caused by attraction of negatively charged fluorine atoms and positively charged atoms of the chelate cycles reported earlier in the work [49].

Chelate cycles are not observed to arrange one above another for the studied complexes that excludes intermolecular interaction via π-electron systems of chelate cycles of neighboring molecules reported for some other boron chelates [10].

4. Conclusion

Thus, organic sulfides containing boron-chelate groups resemble aromatic counterparts in terms of structure. Sulfur atoms next to central carbon atom of the chelate cycle leads to increase of $C\gamma$-C_β bond length. Bulky γ-substituent breaks coplanarity of β-phenyl groups and chelate cycle for dibenzoylmethanate complex. Chelate cycle bending along O—O line in the crystal state is caused not only by the structural features of the molecule, but also by intermolecular interactions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2019.119230.

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