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Structures of boron chelates of mono- and diacylketene aminals

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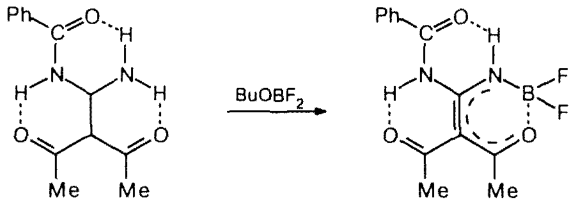
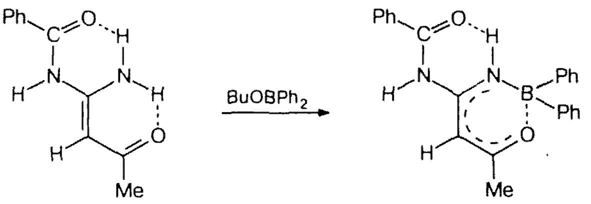
The molecular and crystal structures of diphenylboron chelates of acetylketene *N*-benzoylaminal and 2-(*N*-benzoyl)diaminomethylene-4-dimethylaminomethylene-cyclohexane-1,3-dione and the structure of the difluoroboron complex of diacetylketene *N*-benzoylaminal were established. It was found that the aminovinylcarbonyl fragment of the ligand is involved in the formation of a boron-containing ring. A delocalized π-electron system over the NCCCO fragment of the chelate ring is characteristic of the molecules studied both in crystals and solutions.

Key words: difluoro- and diphenylboron chelates, acyl- and diacylketene aminals; X-ray structural analysis.

α-Oxoketene aminals containing an unsubstituted NH_2 group are convenient blocks for designing heterocyclic systems.[1,2] The ability of these compounds (which are functionalized enaminones) to form chelates of boron and transition metals makes it possible to search for new unconventional methods of heterocyclic synthesis based on the difference in the chemical properties of the ligands and their complexes.[3–6] In this connection, ketene aminals and their chelates are interesting models for studying structural rearrangements of the ligand during chelate formation.



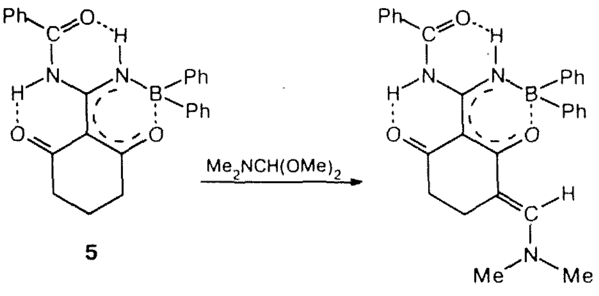
1 **2**



4 **3**

Previously,[7] we reported the crystal and molecular structure of diacetylketene *N*-benzoylaminal (**1**). It was noted that the characteristic feature of this compound, which is a push-pull ethylene, is the involvement of the O and N atoms in the formation of three six-membered H-rings through intramolecular N—H...O hydrogen bonds.

In this work, we report the results of an X-ray structural study of difluoroboron chelate **2**, which was obtained from ketene aminal **1**,[3] and diphenylboron chelate **3**, which was synthesized by the reaction of $BuOBPh_2$ with acetylketene *N*-benzoylaminal (**4**). The molecular and crystal structure of the product of condensation of 2-(*N*-benzoyl)diaminomethylenecyclohexane-1,3-dione diphenylboron chelate (**5**) with *N*,*N*-dimethylformamide dimethyl acetal was also established. Previously,[4] we assigned the structure of chelate **6** to this product based on the spectral data.



5 **6**

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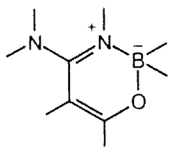
Figures 1, 2, and 3 show the overall views of molecules **2**, **3**, and **6**. (The crystal of **2** consists of two independent molecules **2a** and **2b**. The differences in their geometric parameters are no greater than the experimental error, and, therefore, the average values are given.)

The data obtained confirm the structures assigned to chelates **2**, **3**, and **6**. Therefore, ketene aminals are coordinated to boron through the aminovinylcarbonyl fragment, *i.e.*, through the site of the strongest intramolecular hydrogen bond. It was unambiguously established that the CH_2 group of complex **5** that is adjacent to the boron-containing ring is involved in condensation with *N*,*N*-dimethylformamide acetal. The diaminoethylene fragment of molecule **6** has an *E* configuration. The planes of the substituents at the boron atom, F(1)BF(2) (**2**) and $C_{Ph}BC_{Ph}$ (**3** and **6**), are virtually orthogonal to the plane of the chelate ring (the corresponding angles are 90.20°, 89.93°, and 90.5°, respectively). In molecule **2**, the B—O (1.473 Å) and B—N (1.526 Å) bonds are substantially shorter than those in **3** and **6** (1.539 and 1.574 Å in **3** and 1.508 and 1.561 Å in **6**, respectively). Furthermore, these bonds are the shortest known bonds of these types in the six-membered chelates in which the B atom is coordinated both through the N and O atoms.[8—11] In molecule **2**, the B—O bond is even shorter than the ordinary covalent B_{sp^3}—O bond found in the molecule of diphenylboron chelate of 2-hydroxymethylaminopyridine (1.485 Å).[8] Apparently, such substantial shortening of the B—N and B—O distances in chelate **2** is caused by the inductive effect of electronegative fluorine atoms. The other corresponding bonds (C(1)—N(1), C(1)—C(2), and C(2)—C(3)) in the B-chelate rings of molecules **2**, **3**, and **6** are comparable in length; these bond lengths are in the ranges of 1.305—1.311, 1.426—1.454, and 1.377—1.415 Å, respectively. The C(3)—O(1) bonds in **2** and **3** are virtually identical (1.307 Å). In molecule **6**, in which the chelate ring is fused with the cyclohexane ring, the C(3)—O(1) bond (1.332 Å) is somewhat longer than in **2** and **3**. However, the general pattern of delocalization of multiple bonds in the boron-containing rings of compounds **2**, **3**, and **6** remains virtually unchanged. Noteworthy also is the substantial contribution of the resonance structure of type **A**.



A

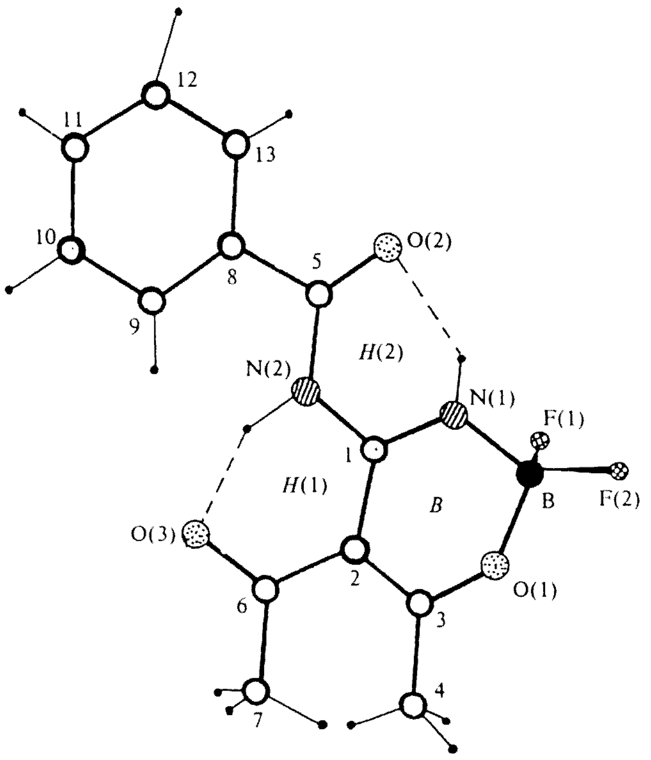


Fig. 1. Molecular structure of chelate **2**.

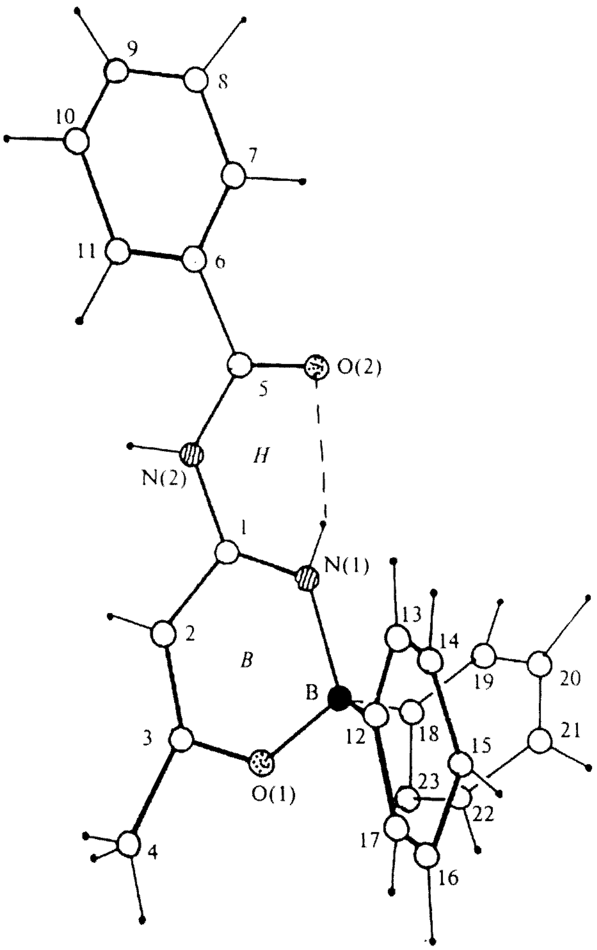


Fig. 2. Molecular structure of chelate **3**.

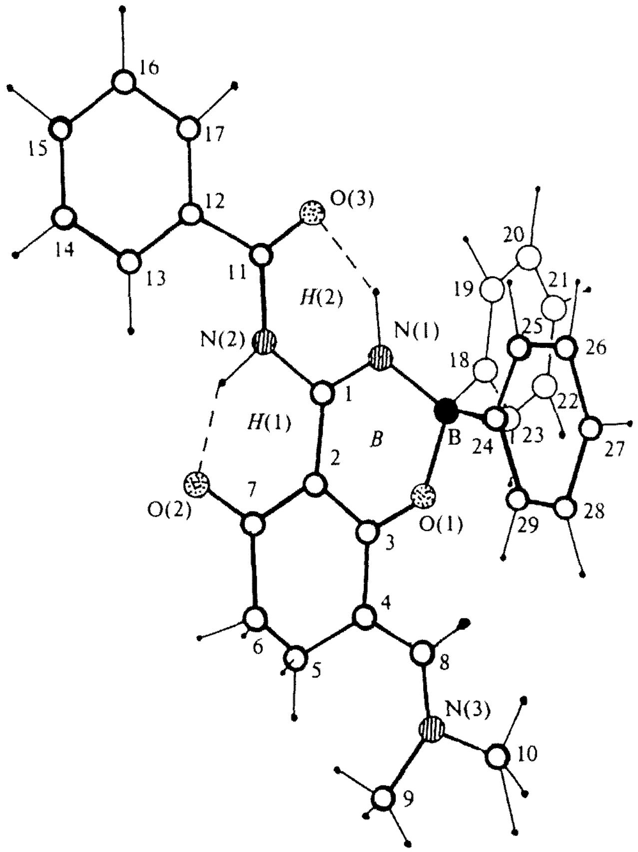


Fig. 3. Molecular structure of chelate **6**.

In the molecules of the initial ligands of the corresponding ketene aminals, pronounced conjugation between the "donor" and "acceptor" fragments occurs. However, a comparison of the structural data on ketene aminal **1** and chelate **2** demonstrated that in molecule **2** the C(1)—N(1) and C(2)—C(3) bonds are shortened ($\Delta = -0.020$ and $\Delta = -0.055$ Å, respectively) and the C(1)—C(2) and C(3)—O(1) bonds are lengthened ($\Delta = 0.033$ and $\Delta = 0.060$ Å), *i.e.*, delocalization of π electrons in the boron-containing ring of chelate **2** differs from "push-pull" delocalization in the molecule of the initial ligand **1**.

It is noteworthy that F atoms as substituents at the B atom stabilize the B-chelate ring. In this case, the ring becomes virtually planar (in molecule **2**, deviations of the atoms of the chelate ring from the mean plane of this ring are no more than 0.04 Å), whereas the chelate ring in **3** has a *twist* conformation (the B and C(1) atoms deviate from the plane through the other atoms of the cycle by −0.21 and 0.17 Å, respectively). In molecule **6**, the chelate ring adopts a half-chair conformation with the B atom lying at the top (its deviation from the mean plane of the ring is 0.39 Å).

The characteristic feature of the structures of boron chelates **2**, **3**, and **6** is the formation of H-rings through intramolecular hydrogen bonds. Thus, two H-rings are formed in molecule **2** through intramolecular hydrogen bonds: O(3)—C(6)—C(2)—C(1)—N(2)—H (*H*(1), with the following parameters: N(2)...O(3) 2.55 Å, H(N(2))...O(3) 1.70 Å; the O(3)...H—N(2) angle is 147.0°) and O(2)—C(5)—N(2)—C(1)—N(1)—H (*H*(2), with the following parameters: N(1)...O(2) 2.70 Å, H(N(1))...O(2) 2.05 Å; the O(2)...H—N(1) angle is 129.3°). Although the geometries of molecules **2a** and **2b** are similar, the degrees of puckering of the *H*(1) rings are different. In both molecules, this ring adopts a poorly pronounced *twist* conformation, but in **2a**, the C(6) and O(3) atoms deviate from the plane of the ring by −0.11 and 0.08 Å, respectively, whereas in **2b**, by −0.22 and 0.30 Å, respectively. The *H*(2) rings in **2a,b** are planar (the deviations of the atoms are no more than 0.05 Å) and are virtually coplanar with the boron-containing and phenyl rings (the angles of rotation are no more than 6°). The C(6)—O(3)—C(7) and C(3)—O(1)—C(4) groups are twisted relative to the plane of the N(1)N(2)C(1)C(2) fragment by 20.3° and 6.8°, respectively, in molecule **2a** (*cis* orientation), and by 29.4° and −3.8° in **2b** (*trans* orientation).

In compound **3**, one planar H-ring (*H*) forms with the following parameters of the intramolecular hydrogen bond: N(1)...O(2) 2.68 Å, H(N(1))...O(2) 1.79 Å, the O(2)...H—N(1) angle is 132.6°. (The deviations of the atoms from the plane are no more than 0.05 Å.) The dihedral angle *B*/*H* is 6.03°, *i.e.*, as in chelate **2**, the central fragment of the molecule retains the planar conformation.

In molecule **6**, the conformation of the bicyclic system is stabilized through two strong intramolecular hydrogen bonds, which close two H-rings, namely, O(2)—C(7)—C(2)—C(1)—N(2)—H (*H*(1), the H(N(2))...O(2) distance is 1.71 Å, and the O(2)...H—N(2) angle is 143.9°) and O(3)—C(11)—N(2)—C(1)—N(1)—H (*H*(2), the H(N(2))....O(3) distance is 1.86 Å, and the O(3)...H—N(1) angle is 137.2°). Both H-rings are flattened (deviations of nonhydrogen and hydrogen atoms from the mean plane of the ring are no more than 0.05 and 0.12 Å, respectively). The dihedral angles between the planes *H*(1,2)/*B* and *H*(1)/*H*(2) are approximately 7.5°. The other bond lengths and bond angles (in the benzoyl and acetyl groups that are not involved in chelate formation) in molecules **2**, **3**, and **6** correspond to the standard values.[12]

In solutions, the structures of chelate complexes **2**, **3**, and **6** undergo only slight changes. The IR spectra of these compounds are characterized by intense absorption in the region of 1550—1600 cm^{-1}, which corresponds to a delocalized π-bond system. The data from the IR and NMR spectra also confirm the formation of intramolecular NH...O hydrogen bonds in the chelate molecules.

Previously,[4] when comparing the ^{13}C NMR spectra of α,α-dioxoketene aminals and their boron chelates, we demonstrated that the CO signal of the acyl group,

Table 1. Principal bond lengths (*d*) and bond angles (ω) for the structure of **2** averaged over two independent molecules **2a** and **2b**

Bond	d/Å	Bond	d/Å
B—O(1)	1.472(7)	C(5)—O(2)	1.215(6)
C(6)—C(7)	1.493(7)	C(2)—C(6)	1.478(7)
B—N(1)	1.525(7)	C(6)—O(3)	1.220(6)
B—F(1)	1.368(8)	C(3)—C(4)	1.479(7)
B—F(2)	1.380(10)	C(3)—O(1)	1.307(7)
N(1)—C(1)	1.305(6)	C(2)—C(3)	1.387(7)
N(2)—C(5)	1.375(5)	C(5)—O(2)	1.215(6)
N(2)—C(1)	1.376(6)	C(5)—C(8)	1.493(7)
C(1)—C(2)	1.454(6)		
Angle	**ω/deg**	**Angle**	**ω/deg**
N(1)—B—F(1)	111.0(8)	C(1)—C(2)—C(3)	116.7(7)
N(1)—B—F(2)	110.2(3)	C(1)—C(2)—C(6)	119.7(6)
O(1)—B—F(1)	108.8(3)	C(2)—C(3)—O(1)	121.6(6)
O(1)—B—F(2)	108.0(7)	C(2)—C(3)—C(4)	127.5(7)
N(1)—B—O(1)	108.3(7)	O(1)—C(3)—C(4)	110.9(6)
F(1)—B—F(2)	109.9(8)	B—O(1)—C(3)	127.2(6)
B—N(1)—C(1)	124.5(5)	C(2)—C(6)—C(3)	120.3(6)
N(1)—C(1)—N(2)	120.2(5)	C(2)—C(6)—C(7)	122.3(8)
N(1)—C(1)—C(2)	122.2(6)	O(3)—C(6)—C(7)	117.1(7)
N(2)—C(1)—C(2)	116.6(6)	C(1)—N(2)—C(5)	126.3(7)
C(1)—C(2)—C(3)	116.7(7)	N(2)—C(5)—O(2)	123.1(7)

which is directly involved in coordination with boron, shifts substantially to the higher field with respect to the signals of C atoms of free carbonyl groups of the ligand and chelate. The chemical shifts of CO of the acetyl fragment of chelate **3** (180.37 ppm in $CDCl_3$) and ketene aminal **4** (see Ref. 13) differ by almost 13 ppm.

Experimental

The ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer. The ^{13}C NMR spectra were obtained on a Bruker AM-300 spectrometer. The ^{11}B NMR spectra were recorded on a Bruker AC-200 P instrument. The IR spectra were recorded on a Perkin-Elmer 577 instrument. The mass spectra were obtained on a Varian MAT-311A spectrometer (EI, 70 eV).

***N,O*-[3-(*N*-Benzoyldiaminomethylene)pentane-2,4-dionato]difluoroboron (2)** was synthesized from ketene aminal **1** according to the known procedure.[3] Mass spectrum, *m/z*: 294 $[M]^+$. IR ($CHCl_3$), ν/cm^{-1}: 3265 (br, NH); 3180—2900 (w.br, NH); 1698 (C=O amide); 1654 (C=O), 1606, 1557, 1495. ^1H NMR ($CDCl_3$), δ: 2.59 (s, 3 H, Me); 2.64 (s, 3 H, Me); 7.53 (m, 2 H, Ph); 7.66 (m, 1 H, Ph); 7.98 (m, 2 H, Ph); 10.87 (br.s, 1 H, NH); 13.61 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 27.21 ($\underline{Me}$COB); 32.98 ($\underline{Me}$CO); 104.98 (MeCO$\underline{C}$); 127.88, 129.31, 134.25 (Ph); 159.28 (NCN); 169.23 (CONH); 187.58 (COB); 281.10 (CO). ^{11}B NMR ($CHCl_3$), δ: −0.78.

***N,O*-[2-(*N*-Benzoyldiaminomethylene)-4-dimethylaminomethylenecyclohexane-1,3-dionato]diphenylboron (6)** was prepared from ketene aminal **5** according to the procedure described previously.[4]

Acetylketene *N*-benzoylaminal **4** was synthesized according to the known procedure.[13]

***N,O*-[4-(*N*-Benzoyldiamino)-3-buten-2-onato]diphenylboron (3).** A mixture of ketene aminal **4** (0.18 g, 0.88 mmol) and Ph_2BOBu (0.35 g, 1.47 mmol) in xylene (3.5 mL) was refluxed for 2 h. The solution was concentrated *in vacuo* to the half of the initial volume, and then pentane (20 mL) was

Table 2. Bond lengths (*d*) and bond angles (ω) for molecule **3**

Bond	d/Å	Bond	d/Å
O(1)—B	1.539(8)	B—C(12)	1.591(8)
O(1)—C(3)	1.308(8)	B—C(18)	1.607(8)
O(2)—C(5)	1.216(8)	C(1)—C(2)	1.428(10)
N(1)—B	1.574(9)	C(2)—C(3)	1.377(9)
N(1)—C(1)	1.311(9)	C(3)—C(4)	1.502(9)
N(2)—C(1)	1.378(10)	C(5)—C(6)	1.482(8)
N(2)—C(5)	1.389(9)		
Angle	**ω/deg**	**Angle**	**ω/deg**
O(1)—B—N(1)	106.2(5)	C(1)—C(2)—C(3)	117.9(5)
O(1)—B—C(12)	108.3(6)	C(2)—C(3)—O(1)	123.7(7)
O(1)—B—C(18)	108.8(5)	C(2)—C(3)—C(4)	122.3(5)
N(1)—B—C(12)	110.3(5)	O(1)—C(3)—C(4)	114.0(8)
N(1)—B—C(18)	111.1(6)	C(1)—N(2)—C(5)	126.6(7)
C(12)—B—C(18)	111.9(5)	N(2)—C(5)—O(2)	121.8(8)
B—O(1)—C(3)	119.7(7)	N(2)—C(5)—C(6)	116.3(6)
B—N(1)—C(1)	120.9(7)	O(2)—C(5)—C(6)	121.9(7)
N(1)—C(1)—C(2)	121.3(9)	C(5)—C(6)—C(7)	122.8(8)
N(1)—C(1)—N(2)	121.3(8)	C(5)—C(6)—C(11)	118.1(5)
C(2)—C(1)—N(2)	117.4(6)		

Table 3. Bond lengths (*d*) and bond angles (ω) for molecule **6**

Bond	d/Å	Bond	d/Å
B—N(1)	1.561(6)	N(3)—C(10)	1.455(7)
B—O(1)	1.508(6)	O(3)—C(11)	1.238(6)
B—C(18)	1.603(9)	C(11)—C(12)	1.492(5)
B—C(24)	1.623(7)	C(2)—C(7)	1.431(7)
N(1)—C(1)	1.303(7)	O(2)—C(7)	1.250(5)
C(1)—C(2)	1.426(8)	C(4)—C(5)	1.509(6)
C(2)—C(3)	1.415(5)	C(5)—C(6)	1.527(5)
O(1)—C(3)	1.332(6)	C(6)—C(7)	1.499(5)
C(3)—C(4)	1.427(7)	C(4)—C(8)	1.386(5)
C(1)—N(2)	1.386(5)	N(2)—C(11)	1.355(6)
N(3)—C(8)	1.327(6)	N(3)—C(9)	1.462(5)
Angle	**ω/deg**	**Angle**	**ω/deg**
O(1)—B—N(1)	106.3(8)	C(2)—C(3)—C(4)	123.4(7)
O(1)—B—C(18)	108.5(3)	O(1)—C(3)—C(4)	116.9(5)
O(1)—B—C(24)	110.2(4)	B—O(1)—C(3)	123.5(4)
N(1)—B—C(18)	110.1(5)	C(3)—C(4)—C(5)	116.9(5)
N(1)—B—C(24)	109.4(3)	C(3)—C(4)—C(8)	115.5(6)
C(18)—B—C(24)	112.2(8)	C(5)—C(4)—C(8)	127.6(3)
B—N(1)—C(1)	122.2(4)	C(4)—C(5)—C(6)	112.2(5)
N(1)—C(1)—C(2)	122.1(6)	C(5)—C(6)—C(7)	113.3(4)
N(2)—C(1)—C(2)	117.5(7)	C(2)—C(7)—C(6)	117.3(6)
N(2)—C(1)—N(1)	120.3(4)	C(2)—C(7)—O(2)	124.3(4)
C(1)—N(2)—C(11)	126.6(7)	C(6)—C(7)—O(2)	118.2(6)
C(1)—C(2)—C(3)	118.4(6)	O(3)—C(11)—C(12)	120.1(3)
C(1)—C(2)—C(7)	121.7(5)	N(2)—C(11)—O(3)	122.6(6)
C(3)—C(2)—C(7)	119.9(4)	N(2)—C(11)—C(12)	117.2(6)
C(2)—C(3)—O(1)	119.7(3)	C(4)—C(8)—N(3)	130.9(7)
C(8)—N(3)—C(9)	119.5(7)		
C(8)—N(3)—C(10)	127.3(7)		
C(9)—N(3)—C(10)	112.8(4)		

Table 4. Atomic coordinates (nonhydrogen $\times 10^4$, hydrogen $\times 10^3$) and equivalent isotropic temperature factors for nonhydrogen atoms ($B_{\text{iso}}^{\text{eq}}$) for molecules **2a**, **2b**, **3**, and **6**

Atom	x	y	z	$B_{\text{iso}}^{\text{eq}}$/Å^2
		Molecule **2a**		
B	1096(4)	3604(5)	3843(9)	4.4(3)
O(1)	0215(2)	4117(3)	2821(5)	4.9(3)
O(2)	1724(2)	0410(3)	7729(5)	4.1(3)
O(3)	−1368(2)	1095(3)	5422(6)	4.8(4)
N(1)	1025(2)	2400(3)	5093(5)	4.2(2)
N(2)	0278(2)	0867(3)	6431(5)	3.2(3)
C(1)	0279(3)	1971(4)	5299(6)	3.5(2)
C(2)	−0568(3)	2620(4)	4333(7)	3.4(1)
C(3)	−0540(3)	3702(4)	3083(7)	3.1(1)
C(4)	−1280(4)	4501(5)	1851(8)	2.9(1)
C(5)	0977(3)	0164(4)	7661(7)	4.7(2)
C(6)	−1401(3)	2125(4)	4716(7)	3.7(2)
C(7)	−2313(3)	2834(6)	4393(9)	5.4(2)
C(8)	0741(3)	−0942(4)	8877(7)	3.4(2)
C(9)	1431(3)	−1731(4)	9998(7)	3.1(2)
C(10)	1239(4)	−2773(4)	11153(7)	3.8(3)
C(11)	0396(4)	−3016(4)	11214(7)	4.6(3)
C(12)	−0300(4)	−2244(4)	10098(8)	4.1(2)
C(13)	−0122(4)	−1196(4)	8942(7)	4.2(3)
F(1)	1717(3)	3584(4)	2574(6)	3.6(2)
F(2)	1308(3)	4281(4)	4881(7)	4.1(2)
H(N(1))	148(3)	200(4)	569(7)	4.2(2)
H(N(2))	−030(3)	068(4)	633(6)	4.3(3)
		Molecule **2b**		
B(1)	4045(3)	−1716(4)	9793(6)	2.8(2)
O(1)	4970(2)	−2346(2)	10175(4)	4.4(3)
O(2)	3321(2)	−8310(2)	16725(5)	2.8(2)
O(3)	6359(2)	0304(2)	5765(4)	4.4(3)
N(1)	4064(2)	−0511(3)	8465(5)	3.4(2)
N(2)	4759(2)	−9070(3)	16553(5)	5.9(3)
C(1)	4790(2)	−0174(3)	7724(5)	3.1(2)
C(2)	5658(2)	−0912(3)	8148(6)	3.0(2)
C(3)	5679(2)	−2006(3)	9374(6)	3.9(3)
C(4)	6464(3)	−2946(4)	9922(7)	5.0(3)
C(5)	4055(2)	−8192(3)	16123(5)	5.1(3)
C(6)	6454(2)	−0485(3)	7237(6)	5.4(2)
C(7)	7381(3)	−0936(4)	8136(8)	4.1(2)
C(8)	4252(2)	−7076(3)	14885(5)	3.9(3)
C(9)	3597(3)	−6131(3)	14565(6)	1.4(3)
C(10)	3742(4)	−5074(4)	13406(8)	2.6(3)
C(11)	4537(3)	−4970(4)	12572(7)	4.1(3)
C(12)	5179(3)	−5899(4)	12853(7)	4.1(2)
C(13)	5047(3)	−6960(3)	14033(6)	2.9(2)
F(1)	3712(1)	−1674(2)	11435(3)	4.9(2)
F(2)	3532(2)	−2295(2)	8987(4)	3.1(2)
H(N(1))	348(4)	000(6)	817(9)	5.3(3)
H(N(2))	533(4)	−899(5)	1609(8)	5.4(2)
		Molecule **3**		
B	1991(7)	3191(3)	−0585(5)	5.4(2)
O(1)	2780(6)	3710(3)	0267(4)	6.2(2)
O(2)	1858(7)	0954(3)	−0237(4)	7.2(2)
N(1)	2243(7)	2403(3)	−0109(4)	5.5(2)
N(2)	3745(7)	1543(3)	0889(5)	6.3(3)
C(1)	3449(9)	2245(4)	0544(5)	5.4(3)
C(2)	4478(5)	2796(3)	0960(5)	7.5(2)
C(3)	4025(6)	3508(3)	0838(5)	6.6(1)
C(4)	4920(7)	4123(3)	1373(5)	9.0(2)
C(5)	2923(6)	0928(3)	0560(4)	6.1(1)
C(6)	3399(6)	0241(3)	1116(4)	6.0(1)
C(7)	4642(10)	0185(5)	1790(7)	9.3(2)
C(8)	5019(9)	−0501(5)	2256(7)	9.2(2)
C(9)	4214(7)	−1072(3)	2105(5)	9.3(1)
C(10)	2889(9)	−1000(4)	1480(6)	9.2(2)
C(11)	2439(9)	−0320(4)	1029(6)	6.3(1)
C(12)	0244(6)	3382(3)	−0728(4)	5.9(1)
C(13)	−0813(6)	2922(3)	−1269(4)	6.4(1)
C(14)	−2335(7)	3077(3)	−1442(5)	7.9(1)
C(15)	−2854(8)	3721(4)	−1077(6)	9.3(1)
C(16)	−1858(11)	4185(5)	−0530(7)	10.0(2)
C(17)	−0330(9)	4010(4)	−0323(6)	10.8(2)
C(18)	2745(6)	3281(3)	−1704(4)	4.9(1)
C(19)	3076(6)	2703(3)	−2370(4)	6.3(1)
C(20)	3650(7)	2800(3)	−3382(5)	7.6(1)
C(21)	3896(7)	3489(3)	−3728(5)	9.0(2)
C(22)	3649(7)	4079(3)	−3096(5)	9.2(2)
C(23)	3033(6)	3980(3)	−2111(4)	7.0(1)
H(N(1))	166(7)	194(3)	−044(5)	7.1(2)
H(N(2))	447(9)	150(4)	149(6)	6.9(1)
		Molecule **6**		
B	3734(4)	3517(2)	9431(6)	0.8(20)
O(1)	4949(2)	3816(1)	9678(3)	1.4(1)
O(2)	3321(3)	5441(1)	6330(3)	2.7(1)
O(3)	0459(3)	4502(1)	7795(4)	2.4(1)
N(1)	2736(3)	4044(1)	8724(4)	1.1(1)
N(2)	1948(3)	4940(1)	7330(4)	2.5(2)
C(1)	2896(4)	4513(2)	8034(4)	0.7(1)
C(2)	4037(4)	4613(2)	7980(5)	0.9(1)
C(3)	5073(3)	4254(1)	8867(4)	0.7(1)
C(4)	6283(3)	4357(2)	8994(4)	0.9(1)
C(5)	6458(4)	4918(1)	8228(4)	3.0(2)
C(6)	5818(4)	5045(2)	6903(5)	3.0(2)
C(7)	4151(4)	5061(2)	7058(5)	1.5(2)
C(8)	7175(3)	3937(1)	9855(4)	1.0(1)
C(9)	9079(4)	3353(2)	10987(5)	3.0(2)
C(10)	[illegible]	[illegible]	9856(4)	2.0(2)
C(11)	0789(4)	4914(2)	7214(4)	1.2(1)
C(12)	−0082(3)	5430(1)	6404(4)	0.9(1)
C(13)	−1263(3)	5407(1)	6274(4)	1.9(2)
C(14)	−2109(4)	5883(1)	5578(4)	2.6(2)
C(15)	−1775(4)	6378(2)	4974(4)	2.6(2)
C(16)	−0604(4)	6395(2)	5070(4)	2.5(2)
C(17)	0259(4)	5921(2)	5780(5)	1.7(2)
C(18)	3778(4)	3330(2)	10861(5)	0.9(1)
C(19)	4892(4)	3231(2)	12000(5)	1.6(1)
C(20)	4932(4)	3038(2)	13223(4)	2.7(2)
C(21)	3867(5)	2946(2)	13352(4)	3.3(2)
C(22)	2754(4)	3046(2)	12248(5)	2.9(2)
C(23)	2724(4)	3240(2)	11036(5)	1.7(1)
C(24)	3452(4)	2899(2)	8439(4)	3.0(2)
C(25)	2327(4)	2583(2)	7954(5)	1.6(1)
C(26)	2058(4)	2044(4)	7124(5)	2.4(2)
C(27)	2916(4)	1803(2)	6755(4)	3.0(2)
C(28)	4044(4)	2104(2)	7220(2)	3.4(2)
C(29)	4304(4)	2648(2)	8051(4)	2.4(1)
H(N(1))	194(6)	407(3)	874(6)	2.5(2)
H(N(2))	221(6)	526(3)	682(6)	2.6(2)

added. The precipitate was filtered and washed with pentane. Chelate **3** was obtained in a yield of 0.27 g (87%), m.p. 216—217 °C (hexane—benzene, 1 : 1). Found (%): C, 75.35; H, 5.94; B, 2.98; N, 7.68. $C_{23}H_{21}BN_2O_2$. Calculated (%): C, 75.02; H, 5.75; B, 2.94; N, 7.61. Mass spectrum, *m/z*: 291 $[M-Ph]^+$. IR ($CHCl_3$), ν/cm^{-1}: 3440 (NH, amide); 3330 (br, NH); 1700 (C=O amide); 1645, 1565, 1555. ^{1}H NMR ($CDCl_3$), δ: 2.13 (s, 3 H, Me); 4.71 (s, 1 H, CH); 7.10—7.80 (m, 10 H, 2 Ph); 7.83 (br.s, 1 H, NH); 9.74 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 23.77 (Me); 88.04 (CH); 150.0 (B—C); 126.08, 127.21, 129.15, 131.45, 131.74, 131.77, 133.77, 134.65 (other aromatic C atoms); 156.35 (NCN); 168.62 (CONH); 180.37 (COB). ^{11}B NMR ($CHCl_3$), δ: 3.09.

Chelate 2. Single crystals were grown from THF as colorless elongated tetrahedral prisms. The crystals are triclinic: *a* = 15.077(3) Å, *b* = 12.473(3) Å, *c* = 7.582(2) Å, α = 71.69(2)°, β = 91.76(2)°, γ = 82.03(2)°, *V* = 1336.42 Å^3, space group $P\bar{1}$, *Z* = 4, $C_{13}H_{13}BF_2N_2O_3$, 2485 independent reflections, the final value *R* was 0.060. Four fragments of the molecules, which are coupled by an inversion center in pairs, were revealed from the initial E synthesis calculated in space group *P*1. The coordinates of this inversion center were determined, and the origin of the unit cell was located at this point. The crystal structure of **2** was solved in space group $P\bar{1}$. The bond lengths and bond angles for compound **2** are given in Table 1.

Chelate 3. The colorless transparent platelet-like crystals are monoclinic: *a* = 8.924(1) Å, *b* = 18.432(2) Å, *c* = 12.354(1) Å, β = 95.83(1)°, *V* = 2021.77 Å^3, space group $P2_1/n$, *Z* = 4, $C_{23}H_{21}BN_2O_2$, 1302 reflections, *R* = 0.071. The bond lengths and bond angles for compound **3** are given in Table 2.

Chelate 6. Bright yellow crystals were grown from a 1 : 1 benzene—hexane mixture. The crystals are monoclinic: *a* = 12.1256(1) Å, *b* = 20.777(2) Å, *c* = 11.036(2) Å, β = 116.27(1)°, *V* = 2493.16 Å^3, space group $P2_1/a$, *Z* = 4, $C_{29}H_{28}BN_3O_3$, 2596 reflections, *R* = 0.058. The hydrogen atoms were placed in the geometrically calculated positions. The bond lengths and bond angles for compound **6** are given in Table 3.

X-ray structural study of chelates 2, 3, and 6. The unit cell parameters and experimental data sets with $I \geq 2\sigma(I)$ for chelates **2**, **3**, and **6** were measured on an automated four-circle RED-4 diffractometer (λ(Cu-Kα) radiation, graphite monochromator, θ/2θ scanning technique). The structures of **2**, **3**, and **6** were solved by direct methods. Coordinates of nonhydrogen atoms were refined anisotropically by the least-squares method; hydrogen atoms were refined isotropically. The calculations were carried out using the AREN-90 program.[14] The atomic coordinates and equivalent isotropic thermal parameters are given in Table 4.

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