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New boronates prepared from 2,4-pentanedione derived ligands of the NO_2 and N_2O_2 type – comparison to the complexes obtained from the corresponding salicylaldehyde derivatives

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Abstract

2,4-Pentanedione (= acetylacetone) has been reacted with 2-aminoethanol, 1,2-diaminoethane and 1,3-diaminopropane to give the NO_2 and N_2O_2 type ligands named acacaminolH_2, acacenH_2 and acpenH_2, which are structurally and electronically related to the corresponding ligands derived from salicylaldehyde (salaminolH_2 and salenH_2). On reaction of acacaminolH_2 with phenylboronic acid a dinuclear monomeric complex has been obtained containing one three- and one four-coordinate boron atoms as well as one six-membered and one seven-membered heterocyclic ring. Since with salaminolH_2 a dimeric complex with a central 10-membered heterocycle had been reported, it becomes apparent that there may be differences in reactivity when comparing 2,4-pentanedione and salicylaldehyde derived ligands. The molecular compositions of the boron complexes prepared from acacenH_2 and acacpenH_2 are analogous to the corresponding salen and salpen derivatives, however, the presence of two methyl groups in the six-membered chelate rings generates some structural changes, the most important being the distortion of the boat conformation of the central heterocyclic ring. This was predicted by computational methods and confirmed experimentally for one of the complexes. A further important observation was that the products described in here are much more soluble than the salicylaldehyde derivatives. As lateral product the adduct of acacenH_2 with 1,3,5-triphenylboroxine was crystallized. Elemental analysis, IR and NMR (^{1}H, ^{13}C, ^{11}B) spectroscopy, mass spectrometry, ab intio theoretical calculations and X-ray crystallography have been applied to carry out this study.

Keywords: Salen; 2,4-Pentanedione; Phenylboronic acid; Boronates; X-ray crystallography; Ab initio calculations

1. Introduction

During the last few years we and others have explored the chemistry between boric acid derivatives and tridentate NO_2 [1,2] as well as tetradentate N_2O_2 type ligands derived from salicylaldehyde (Scheme 1) [3,4].

For both ligand types a series of different structures is possible, depending on the steric bulk of the substituents (R-R″) and the spatial distribution of the donating atoms in the ligand, the substituents on the boric acid, as well as the solvent and the conditions used for the reaction. As outlined in Scheme 2, in the case of the salaminol derivatives (salaminolH_2 = *N*-2-(salicylideneimino)ethanol) four different types of reaction products have been identified so far, two being monomeric (**I** and **II**) [1d,1e,1j], one being dimeric (**III**) [1e,1g–1i] and another one being polymeric (**IV**) [1i]. From an applicative point of view structure types **II** and **III** are the most

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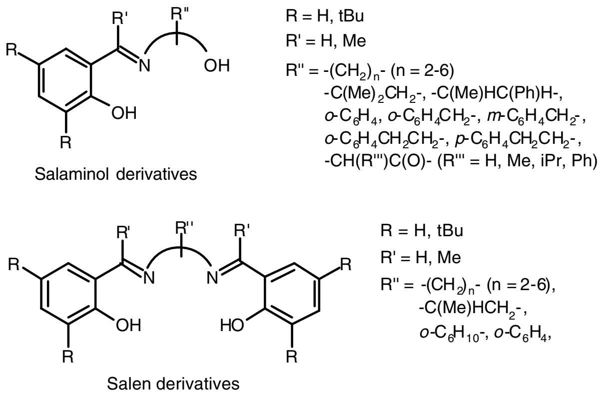
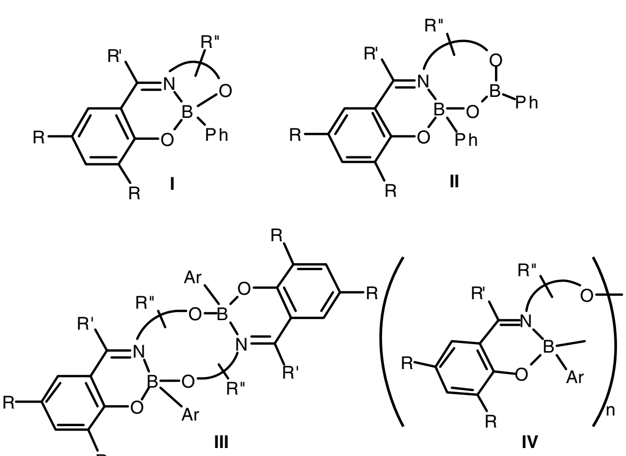
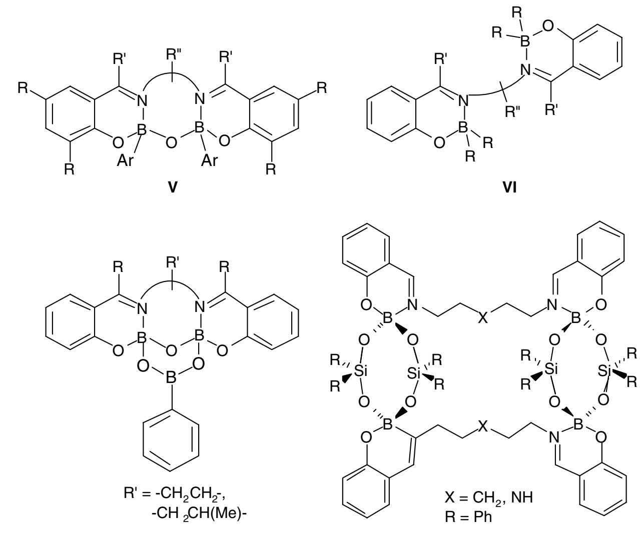


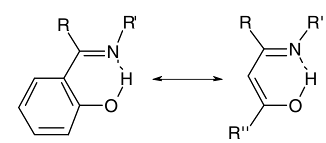
Scheme 1. Salaminol and salen type ligands used so far for the complexation of boric acid derivatives.



Scheme 2. From the reaction between a salaminol derivative as ligand and a phenylboronic acid monomeric (**I**, **II**), dimeric (**III**) and polymeric (**IV**) products can be obtained.



Scheme 3. From the reaction between a salen derivative as ligand and a phenylboronic derivative acid dinuclear (**IV**, **V**), trinuclear (**VI**) and tetranuclear (**VIII**) products can be obtained.



Scheme 4. Electronic and structural analogy between imines derived from saliylaldehyde and 2,4-pentanedione.

interesting ones, type **II** because of the presence of the Lewis acidic, tricoordinate boron atom that may be useful as catalytic center in polymerization processes or in asymmetric synthesis [2f], and type **III** because of the formation of a central macrocyclic ring (10–18 members so far), which might be useful for host–guest chemistry [5].

In the case of the salen derivatives (salenH_2 = *N*,*N'*-ethylenebis(salicylideneimine)) four different reaction products have been identified until now (Scheme 3), two being dinuclear (**V**,**VI**) [3,4], one being trinuclear (**VII**) [3b] and another one being tetranuclear containing a huge cylinder-shaped cavity in its interior (**VIII**) [4g]. In this context it should be mentioned that such a structural variety in the complexes formed from salaminol and salen type ligands is unique for the boron element, comparing its chemistry with that of the rest of the group 13 family and the whole series of other representative and transition metal elements [6].

2,4-Pentanedione (= acetylacetone) is like salicylaldehyde planar and one of its tautomers possesses a similar distribution of the π-electron density (Scheme 4). Despite of this similarity, 2,4-pentanedione based ligands have been used to a much less extent than the above mentioned salicylaldehyde derivatives. Due to the unique structural features of phenylboronates derived from salaminol [1c] and salen [3,4] type ligands in comparison to complexes with other metal ions, we decided to expand this chemistry using herein the related 2,4-pentanedione ligands and explored the reactivity of three representative ligands with phenylboronic acid. AcacaminolH_2 (acacaminolH_2 = *N*-2-(acetylacetimine)- ethanol) is a tridentate ligand comparable to salaminolH_2, while acacenH_2 (acacenH_2 = *N*,*N'*-ethylenebis(acetylacetimine)) and acacpenH_2 (acacpenH_2 = *N*,*N'*-propylenebis(acetylacetimine)) are fourdentate N_2O_2 ligands comparable to salenH_2 and salpenH_2 (salpenH_2 = *N*,*N'*-propylenebis(salicylideneimine)). The latter two ligands have been used previously for the preparation of metal complexes [7,8].

In what follows the results of these reactions are presented in a comparative way to the complexes obtained from the salicylaldehyde derivatives.

2. Experimental

2.1. Instrumental

NMR studies were carried out with Varian Gemini 200, Jeol GSX 270, Bruker 300 and Varian Inova 400 instruments. Standards were TMS (internal, ^{1}H, ^{13}C) and $BF_3 \cdot OEt_2$ (external, ^{11}B). Chemical shifts are stated in parts per million; they are positive, when the signal is shifted to higher frequencies than the standard. COSY, HMQC and NOESY experiments have been carried out in order to assign the ^{1}H and ^{13}C spectra completely. IR spectra have been recorded on a Bruker Vector 22 FT spectrophotometer. Mass spectra were obtained on a HP 5989A equipment. Elemental analyses have been carried out on Perkin–Elmer Series II 2400 and Elementar Vario ELIII instruments.

2.2. Preparative part

Commercial starting materials and solvents have been used. The acacenH_2 and acacpenH_2 ligands have been prepared according to a method reported in the literature [8].

2.3. Preparation of acacaminolH_2

The acacaminolH_2 ligand was prepared by reaction of acetylacetone (3.50 g, 35.0 mmol) with 2-ethanolamine (2.14 g, 35.0 mmol) in ethanol (20 ml). After 30 Min. of reflux in presence of a Dean-Stark trap part of the solvent was eliminated through distillation. Under cooling to room temperature a precipitate of the ligand formed, which was filtered off under vacuum and washed with small amounts of chloroform. The colorless product is soluble in all common organic solvents. Yield: 79%; m.p. 94–96 °C.

2.3.1. Spectroscopic data

IR (KBr) ν_{max}: 3277 (br, m), 2962 (w), 2933 (w), 2879 (w), 1607 (m), 1551 (s), 1437 (m), 1374 (m), 1353 (m), 1310 (m), 1245 (m), 1197 (w), 1117 (w), 1080 (w), 1057 (w), 1027 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.94 (3H, s, H-5), 1.96 (3H, s, H-1), 3.39 (dd, 2H, H-6), 3.73 (2H, t, H-7), 4.95 (1H, s, H-3) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ: 19.5 (C-5), 28.9 (C-1), 45.8 (C-6), 61.7 (C-7), 96.0 (C-3), 164.4 (C-4), 195.2 (C-2) ppm. MS (70 eV) m/z (%): 143 (M^+, 88), 128 (50), 112 (87), 100 (76), 94 (50), 84 (69), 70 (52), 58 (61), 43 (100).

2.4. Preparation of acacaminol[B(Ph)–O–B(Ph)] (**1**)

Compound **1** was prepared from one equivalent of acacaminolH_2 (0.18 g, 1.25 mmol) and two equivalents of phenylboronic acid (0.30 g, 2.46 mmol) in benzene (8 ml). After 1 h of reflux in presence of a Dean-Stark trap the solution was cooled down two room temperature, whereupon a colorless precipitate of the product formed that was filtered off under vacuum and washed with benzene. Complex **1** is soluble in benzene, toluene, chloroform, dichloromethane and THF. Yield: 80%; m.p. 154–156 °C.

2.4.1. Spectroscopic data

IR (KBr) ν_{max}: 3068 (w), 3012 (w), 2958 (w), 2888 (w), 1624 (m), 1534 (s), 1470 (w), 1439 (w), 1419 (m), 1375 (w), 1361 (m), 1344 (w), 1323 (m), 1301 (m), 1264 (m), 1250 (m), 1182 (m), 1154 (m), 1132 (m), 1098 (m), 1049 (m), 1019 (m) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ: 2.06 (3H, s, H-1), 2.14 (3H, s, H-5), 3.44, 3.74, 3.86 and 4.29 (2H, ABCD, H-6, H-7), 5.23 (1H, s, H-3), 7.26 (3H, m, *m*-H, *p*-H), 7.41 (3H, m, *m*′-H, *p*′-H), 7.47 (2H, dd, *o*-H), 8.01 (2H,dd, *o*′-H) ppm; ^{13}C NMR (67.9 MHz, $CDCl_3$) δ: 20.4 (C-5), 23.2 (C-1), 49.8 (C-6), 63.9 (C-7), 97.7 (C-3), 127.2 (C-*p*), 127.5 (C-*m*′), 127.6 (C-*m*), 130.2 (C-*p*′), 131.2 (C-*o*), 134.9 (C-*o*′), 168.6 (C-4), 176.2 (C-2) ppm; ^{11}B NMR (96 MHz, $CDCl_3$) δ: 3 ($h_{1/2} = 160$ Hz, $B_{tetrac.}$), 27 ($h_{1/2} = 520$ Hz, $B_{tric.}$) ppm; MS (70 eV) m/z (%): 334 ($M^+ + 1$, 0.3), 333 (M^+, 0.1), 256 ($M^+ - C_6H_5$, 41), 152 ($M^+ - C_{12}H_{10}BO$, 100), 126 (8), 110 (4), 104(3), 91(1), 77 (11), 51 (10). Elemental analysis (%): Calc.: C, 68.43; H, 6.35; N, 4.20. Found: C, 68.25; H, 6.43, N, 4.79.

2.5. Preparation of acacen[B(Ph)–O–B(Ph)] (**3**)

Compound **3** was prepared from one equivalent of acacenH_2 (0.25 g, 1.11 mmol) and two equivalents of phenylboronic acid (0.27 g, 2.22 mmol) in benzene (8 ml). After 1 h of reflux in presence of a Dean-Stark trap the solution was cooled down two room temperature, whereupon a colorless precipitate of the product formed that was filtered off under vacuum and washed with benzene. Complex **3** is soluble in all common organic solvents except for hexane. Yield: 41%; m.p. > 300 °C.

2.5.1. Spectroscopic data

IR (KBr) ν_{max}: 3069 (w), 3052 (w), 3002 (w), 2958 (w), 2959 (w), 1619 (s), 1529 (s), 1461 (m), 1429 (m), 1410 (m), 1370 (m), 1342 (m), 1316 (s), 1198 (s), 1129 (m), 1118 (s), 1051 (m), 1016 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.79 (6H, s, H-5), 2.09 (6H, s, H-1), 3.19 and 3.48 (4H, AA′BB′, H-6), 5.17 (2H, s, H-3), 7.14 (2H, d, H-*p*), 7.20 (4H, dd, H-*m*), 7.44 (4H, d, H-*o*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.8 (C-5), 23.4 (C-1), 46.7 (C-6), 97.9 (C-3), 126.0 (C-*p*), 126.8 (C-*m*), 132.4 (C-*o*), 167.1 (C-4), 176.4 (C-2) ppm; ^{11}B NMR (128 MHz, $CDCl_3$) δ : 4 ($h_{1/2} = 230$ Hz, $B_{tetrac.}$) ppm; MS (70 eV) m/z (%): 415 (M^++1, 0.3), 337 (M^+-C_6H_5, 100), 259 (4), 233 (54), 151 (6), 130 (17), 77(2). Elemental analysis (%): Calc.: C, 69.53; H, 6.81; N, 6.76. Found: C, 69.76; H, 6.80, N, 6.60.

2.6. Preparation of acacpen[B(Ph)–O–B(Ph)] (4)

Compound **4** was prepared from one equivalent of acacpenH_2 (0.50 g, 2.10 mmol) and two equivalents of phenylboronic acid (0.51 g, 4.20 mmol) in benzene (8 ml). After 1 h of reflux in presence of a Dean-Stark trap the solution was cooled down to room temperature, whereupon a colorless precipitate of the product formed that was filtered off under vacuum and washed with benzene. Complex **4** is soluble in all common organic solvents except for hexane. Yield: 68%; m.p. 248–251 °C.

2.6.1. Spectroscopic data

IR (KBr) ν_{max}: 3051 (w), 1627 (m), 1547 (s), 1428 (w), 1368 (w), 1325 (w), 1204 (m), 1128 (w), 1033 (w), 964 (w), 906 (w), 745 (w), 704 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.62 (2H, m, H-7), 1.85 (6H, s, H-5), 1.95 (6H, s, H-1), 3.25 and 3.48 (4H, AA′BB′, H-6), 4.90 (2H, s, H-3), 7.10 (2H, m, H-*p*), 7.18 (4H, m, H-*m*), 7.62 (4H, d, H-*o*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ: 19.9 (C-5), 23.7 (C-1), 29.0 (C-7), 46.5 (C-6), 96.4 (C-3), 126.3 (C-*p*), 126.9 (C-*m*), 131.7 (C-*o*), 166.8 (C-4), 175.8(C-2) ppm; ^{11}B NMR (64 MHz, $CDCl_3$) δ: 5 ($h_{1/2} = 200$ Hz, $B_{tetrac.}$) ppm; MS (70 eV) m/z (%): 351 (M^+-Ph, 100), 273 (16), 247 (52), 137 (39), 77 (4). Elemental analysis (%): Calc.: C, 70.09; H, 7.01; N, 6.54. Found: C, 70.62; H, 7.39, N, 6.66.

2.7. Preparation of complex 7

Compound **7** was obtained as a crystalline product, when compound **3** was recrystallized slowly from benzene. Apart from complex **7** the crystals contained 0.5 equivalents of the acacenH_2 ligand. Yield: 58%; m.p. 165–167 °C.

Elemental analysis (%): Calc.: C, 65.69; H, 6.94; N, 7.42. Found: C, 64.98; H, 6.12; N, 7.40.

2.8. X-ray crystallography

X-ray diffraction studies were performed on Bruker-AXS Smart 6000 (compounds **1** and **7**) and APEX (compound **4**) diffractometers with CCD area detectors ($\lambda_{Mo\ K\alpha} = 0.71073$ Å, monochromator: graphite). Frames were collected at $T = 293$ K (compounds **1** and **7**) and $T = 100$ K (compound **4**) via ω–rotation ($\Delta/\omega = 0.3°$) at 5 and 10 s per frame (SMART [9]). The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT [10]). Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package [11,12]. Non hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions using a riding model. For complex **7** the N–H hydrogen atoms have been localized by difference Fourier maps. In the case of compounds **4** and **7** two independent molecules are present in the asymmetric unit. Additionally, in the crystal lattice of compound **7** one acacenH_2 ligand molecule is present per asymmetric unit. Molecular structures were created by the CRYSTALS software package [13,14]. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-221127-221129. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk, www: http://www.ccdc.cam.ac.uk).

2.9. Theoretical calculations

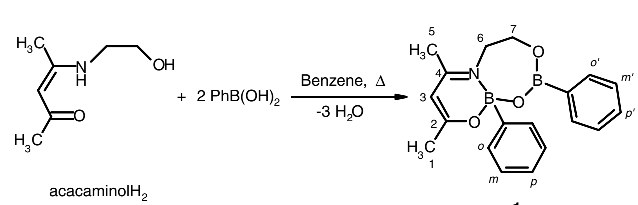
HF/6-31G(d, p) geometry optimizations were done on a PC with a Pentium III processor using the *PC GAMESS* software [15]. Structures were visualized with Molekel 4.3 [16] and Mercury 1.1.2 [17]. All geometry optimizations were followed by frequency calculations, using the same basis set, to characterize the stationary points as true minima.

3. Results and discussion

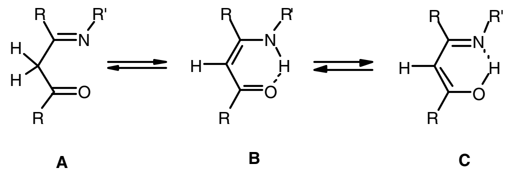
3.1. Preparation and characterization of acacaminol[B(Ph)–O–B(Ph)]

AcacaminolH_2 was prepared through a condensation reaction between 2,4-pentanedione and 2-ethanolamine in absolute ethanol with a yield of 79%. When this ligand is refluxed in benzene and in the presence of a Dean-Stark trap with an equimolar amount of phenylboronic acid, complex **1** is isolated as the only solid product in a yield of 32%. Using the ligand and phenylboronic acid in a 1:2 ratio, the yield increases to 80% (Scheme 5).

A comparative analysis of the ^{1}H and ^{13}C NMR spectroscopic data between the ligand and the boron compound shows that the distribution of the π-electron density changes. It is well known that for uncoordinated acetylacetimines there exists a tautomeric equilibrium between three species in solution, the Schiff base **A**, the



Scheme 5. Preparation of complex **1**.



Scheme 6. Species present in the tautomeric equilibria of acetylacetimines are the Schiff base **A**, the cetamine **B** and the enimine **C**.

cetamine **B** and the enimine **C** (Scheme 6), which is shifted towards the tautomer containing the acid proton at the nitrogen atom (**B**) [18].

According to the ^{1}H and ^{13}C NMR data the coordinated ligand in complex **1** possesses a distribution of the π-electron density characteristic for the enimine species **C**. This is evident from the high-field shift of the signal for the carbonyl carbon C-2, $\Delta\delta = 19.0$ ppm, and the simultaneous low-field-shift of the signal for C-4, $\Delta\delta = 4.2$ ppm, upon formation of the boronate.

The threefold coordination of the ligand to boron atoms can be deduced from the appearance of an ABCD system in the ^{1}H NMR spectrum with signals at $\delta = 3.44$ and 3.74 ppm for the NCH_2 methylene group and at $\delta = 3.86$ and 4.29 ppm for the OCH_2 group. It should be mentioned that the ^{1}H and ^{13}C NMR spectra have been completely assigned using 2D NMR experiments like COSY, HMQC and NOESY.

The fact that a dinuclear boron complex has been formed was deduced from the ^{11}B NMR spectrum showing two signals at $\delta = 3$ and 27 ppm, the first being in the shift range typical for a tetra-coordinate boron and the second one being typical for a three-coordinate boron atom [19].

Besides elemental analysis and mass spectrometry, the molecular structure of **1** was confirmed by X-ray crystallography. The most relevant crystallographic data are summarized in Table 1. Selected bond lengths, bond angles and torsion angles are listed in Table 2.

As can be seen from the molecular structure shown in Fig. 1, compound **1** contains two boron heterocycles, the first being a C_3BNO heterocycle consisting of six members and the second one being a $C_2B_2NO_2$

Table 1
Crystallographic data for compounds **1**, **4** and **7**

Crystal data	**1**[a]	**4**[b]	**7**[a]
Formula	$C_{19}H_{21}B_2NO_3$	$C_{25}H_{30}B_2N_2O_3$	$C_{62}H_{78}B_6N_6O_{10}$
Crystal size (mm)	0.18 × 0.20 × 0.22	0.16 × 0.18 × 0.42	0.29 × 0.50 × 0.70
M_w (g mol^{-1})	332.99	428.13	1132.16
Space group	$P2_1/c$	$P2_1$	$P\bar{1}$
Cell parameters			
a (Å)	11.053(2)	13.452(2)	12.162(2)
b (Å)	13.586(3)	7.4004(9)	16.114(3)
c (Å)	12.884(3)	23.038(3)	18.325(4)
α (°)	90	90	110.49(3)
β (°)	106.550(5)	96.767(2)	101.41(3)
γ (°)	90	90	92.86(3)
V (Å^3)	1854.6(7)	2277.6(5)	3269.9(11)
Z	4	4	4
μ (mm^{-1})	0.078	0.080	0.076
ρ_{calcd} (g cm^{-3})	1.19	1.25	1.15
Data collection			
θ limits (°)	$2 < \theta < 23$	$2 < \theta < 23$	$2 < \theta < 26$
hkl limits	−12, 12; −14, 15; −14, 12	−14, 14; −8, 8; −25, 25	−13, 14; −19, 18; −18, 22
No. collected refl.	9511	18544	21026
No. ind. refl. (R_{int})	2659 (0.07)	6297 (0.05)	12787 (0.05)
No. observed refl.[c]	1111	5950	4541
Refinement			
$R^{c,d}$	0.041	0.064	0.054
$R_w^{e,f,g}$	0.098	0.141	0.148
No. of variables	228	574	789
GoF	0.80	1.20	0.81
$\Delta\rho_{min}$ (e Å^{-3})	−0.10	−0.27	−0.16
$\Delta\rho_{max}$ (e Å^{-3})	0.12	0.30	0.19

[a] Data collection on a Bruker Smart 6000 diffractometer.
[b] Data collection on a Bruker Apex diffractometer.
[c] $I > 2\sigma(I)$.
[d] $R = \sum(F_o^2 - F_c^2)/\sum F_o^2$.
[e] All data.
[f] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.
[g] $w^{-1} = \sigma^2 F_o^2 + (X * P)^2 + Y * P$; $P = (F_o^2 + 2F_c^2)/3$; $X = 0.0365$ for **1**, 0.0565 for **4**, 0.0587 for **7**; Y = 0 for **1**, 1.18 for **4**, 0 for **7**.

Table 2
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for compound **1**

Bond lengths			
B1–N1	1.574(4)	N1–C4	1.302(3)
B1–O1	1.508(4)	N1–C6	1.473(3)
B1–O2	1.435(4)	O1–C2	1.302(3)
B1–C14	1.605(4)	O3–C7	1.422(3)
B2–O2	1.326(4)	C2–C3	1.339(4)
B2–O3	1.375(4)	C3–C4	1.413(4)
B2–C8	1.562(4)	C6–C7	1.501(4)
Bond angles			
O1–B1–N1	108.2(2)	B1–O1–C2	124.5(3)
O1–B1–O2	106.3(2)	B1–N1C4	123.7(3)
O1–B1–C14	108.2(3)	B1–N1–C6	114.0(3)
O2–B1–C14	113.9(3)	B2–O3–C7	127.5(3)
O2–B1–N1	109.9(3)	O1–C2–C3	121.5(3)
N1–B1–C14	110.0(2)	C2–C3–C4	123.0(3)
O2–B2–O3	126.1(3)	C3–C4–N1	118.9(3)
O2–B2–C8	119.7(3)	C4–N1–C6	122.1(3)
O3–B2–C8	114.1(3)	N1–C6–C7	113.0(3)
B1–O2–B2	137.3(3)	C6–C7–O3	116.5(3)
Torsion angles			
B1–N1–C6–C7	−81.7(3)	O1–C2–C3–C4	−2.3(5)
N1–C6–C7–O3	71.9(4)	C2–C3–C4–N1	1.1(5)
C6–C7–O3–B2	−43.2(5)	C3–C4–N1–B1	−1.6(5)
C7–O3–B2–O2	10.8(5)	C4–N1–B1–O1	2.8(4)
O3–B2–O2–B1	22.8(6)	N1–B1–O1–C2	−3.9(4)
B2–O2–B1–N1	−43.4(5)	B1–O1–C2–C3	4.0(5)
O2–B1–N1–C6	61.9(3)		

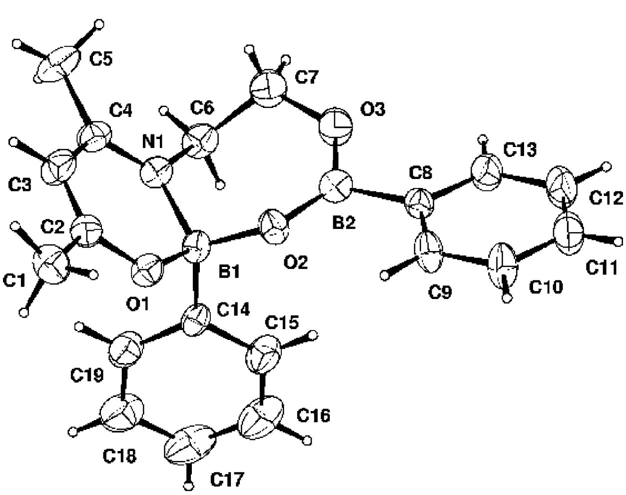
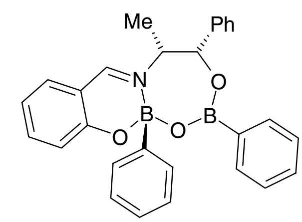


Fig. 1. Perspective view of the molecular structure of compound **1**. Ellipsoids are shown at the 20% probability level.

heterocycle of seven members. The coordination numbers and geometries of the two boron atoms are different, B1 being distorted tetrahedral with bond angles between 106.3(2)° and 113.9(3)°, and B2 being trigonal planar with bond angles between 114.1(3)° and 126.1(3)°.

An analysis of the bond lengths in the two heterocycles reveals some interesting features: the coordinative B1–N1 bond is extremely short [20a], 1.574(4) Å, and reaches almost the $N \rightarrow B$ bond length found in cubic boron nitride, 1.56 Å [20b]. On the other hand, the B1–O1 bond is rather long [1–4], 1.508(4) Å, indicating that there is still some reminiscent character of the cetamine tautomer in the coordinated ligand. That the equilibrium has been displaced in direction of the enimine tautomer can be seen from the C2–C3, C3–C4 and C4–N1 bond lengths of 1.339(4), 1.413(4) and 1.302(3) Å, respectively. The B1–O2 bond length is in the range observed for related species, 1.435(4) Å [1–4]. In comparison, for the structurally characterized, related complex **2**, the corresponding $N \rightarrow B$, B–O_{ph} and B–O_B bond lengths are 1.629(5), 1.470(6) and 1.431(5) Å [1e].



2

As expected, for the tricoordinate boron atom the B–O bonds are significantly shorter due to p_π–p_π interactions, 1.326(4) Å for B2–O2 and 1.375(4) Å for B2–O3. Interestingly, the B2–C8 bond is also significantly shorter than the corresponding B1–C14 bond, $1.562(4) \leftrightarrow 1.605(4)$ Å, indicating that there is probably some delocalization of the aromatic π-electron density to the boron atom. This observation is confirmed by the fact that the B-phenyl ring is localized almost in the same plane as the BO_2 group, the O2–B2–C8–C9 torsion angle being −9.3(5)°. Similar results have been also found for complex **2** [1e].

Finally, it should be mentioned that the B–O–B bond angle is relatively large, 137.3(3)°, however not unexpected, since similar values have been reported also for other complexes containing a B–O–B bond, e.g., 131.4(3)° for **2** [1e,21].

The conformation of the seven-membered heterocyclic ring in **1** can be described as distorted chair, whereby the plane of the chair is formed by atoms O2, B1 C6 and C7. Atoms B2 and O3 deviate less from this plane than atom N1, $\Delta d = 0.49$, 0.52 and −0.73 Å, respectively.

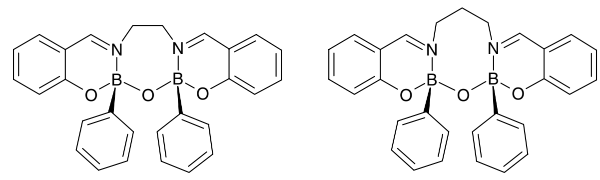
Considering that with the related ligand salaminolH_2 a dimeric complex of type **III** (Scheme 2) has been obtained instead of the monomeric dinuclear species **1** (type **II**), the question arises, why different products are formed? Comparing the molecular models of the two possible products, neither a steric repulsion nor an angular strain that might disfavor the dimeric structure can be found. Therefore, we suppose that both structures might be possible, nevertheless, the dimeric product, being the kinetic product [1e], cannot be isolated under the reaction conditions applied in here, because the products formed from acacenH_2 are more soluble and no precipitation occurs during the reaction. For the salicylaldehyde derivative the dimeric product precipitates during the reaction.

3.2. Preparation and characterization of acacen[B(Ph)–O–B(Ph)] ***3*** *and acacpen[B(Ph)–O–B(Ph)]* ***4***

AcacenH_2 and acacpenH_2 are known ligands and have been prepared as reported [8]. On reaction of acacenH_2 and acacpenH_2 with phenylboronic acid in a 1:2 stoichiometry the dinuclear complexes **3** and **4** are obtained in yields of 41% and 68%, respectively (Scheme 7). Interestingly, both complexes are well soluble in a series of solvents like chloroform, ethyl acetate, acetone and DMSO, while the analogous salen and salpen derivatives have very low solubility. The products have been identified by elemental analysis, IR and NMR (^{1}H, ^{13}C, ^{11}B) spectroscopy, mass spectrometry and additionally by X-ray crystallography in the case of complex **4**.

As in the case of complex **1** the distribution of the π-electron density in the ligand changes upon coordination to the boron atoms, $\Delta\delta(^{13}C) = 19.1$ ppm for C2, $\Delta\delta = 4.3$ ppm for C-4 in the case of **3** and $\Delta\delta(^{13}C) = 19.4$ ppm for C2, $\Delta\delta = 3.6$ ppm for C-4 in the case of **4**. For both complexes the formation of a central heterocycle containing two boron atoms involved in a $N \rightarrow B$ bond is confirmed by (i) the appearance of AB systems for the NCH_2 methylene hydrogen atoms in the ^{1}H NMR spectra, with signals at $\delta = 3.2$ and 3.5 ppm, (ii) the integration of the ^{1}H NMR spectra indicating the presence of two B-phenyl groups per ligand, and (iii) a signal in the ^{11}B NMR spectrum characteristic for a tetracoordinate boron atom at $\delta = 4$ ppm for **3** and $\delta = 5$ ppm for **4**.

On the basis of the available spectroscopic data it is not possible to determine the correct conformation of the seven- and eight-membered heterocyclic rings in **3** and **4**, and neither the configuration of the boron atoms. For the analogous salen[B(Ph)–O–B(Ph)] and salpen[B(Ph)–O–B(Ph)] complexes **5** and **6** it has been reported previously that the B-phenyl groups may be in *cis*- or *trans*-orientation, giving in the first case a boat and in the second case a chair conformation. Due to the fact that both isomers possess molecular symmetry – a mirror plane in the *cis*-isomer and a C_2 axis in the *trans*-isomer – a differentiation by NMR spectroscopy was not possible. Nevertheless, based on X-ray crystallographic studies it has been proposed that **5** and **6** have *cis*-configuration [3].



5 **6**

In order to evaluate, which isomer is thermodynamically more favored in the case of complexes **3** and **4**, we optimized the molecular structures by computational methods using HF/6-31G(d, p) (*PC GAMESS* software [15]). In previous studies it has been shown that this basis set is adequate for the calculation of boron compounds having a coordinative $N \rightarrow B$ bond [22]. The calculated molecular structures of the *cis*- and *trans*-isomers of **3** and **4** are shown in Fig. 2, confirming that the heterocyclic rings in the *cis*-isomers possess a boat-conformation and in the *trans*-isomers a chair or a twisted conformation. The calculated energy differences indicate that in both cases the *cis*-isomer is slightly more stable than the *trans*-isomer, $\Delta\Delta H_f = 1.78$ kcal/mol for **3** and $\Delta\Delta H_f = 4.32$ kcal/mol for **4**. These results agree with the structural studies realized for the corresponding salen and salpen derivatives [3].

Fortunately, crystals suitable for X-ray crystallography could be grown for complex **4**, so that in this case the computational results can be supported by the experimentally determined molecular structure. The most relevant crystallographic data are summarized in

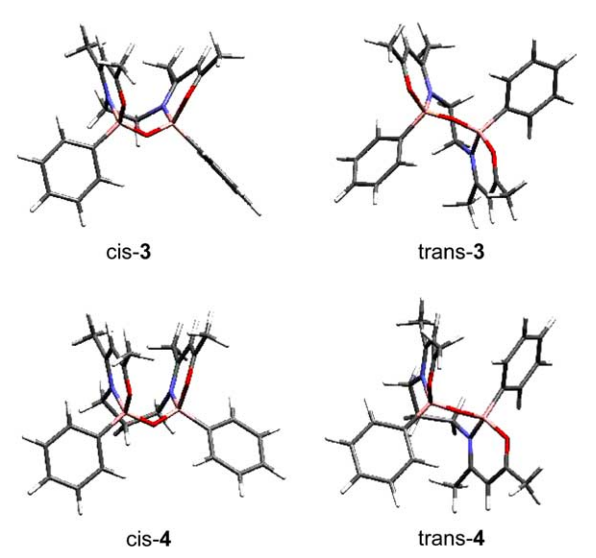
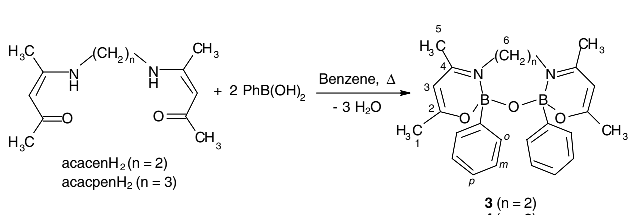


Fig. 2. Calculated molecular structures of compounds **3** and **4** (*cis* and *trans*-isomers).



Scheme 7. Preparation of complexes **3** and **4**.

Table 3
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for compounds **3** and **4** (theoretical data for compounds **3** and **4**, X-ray data for compound **4**)

	cis-**3**, *trans*-**3**[a,b] (calculated data)	*cis*-**4**, *trans*-**4**[a,b] (calculated data)	**4**[c] (X-ray data)
Bond lengths			
B1–N1	1.621/1.619	1.643/1.648	1.624(6)
B1–O1	1.529/1.522	1.547/1.532	1.530(5)
B1–O3	1.389/1.392	1.386/1.401	1.397(5)
B1–C14	1.635/1.633	1.608/1.624	1.613(6)
N1–C3	1.298/1.304	1.322/1.303	1.297(5)
N1–C6	1.479/1.475	1.492/1.465	1.479(5)
O1–C1	1.278/1.267	1.288/1.265	1.300(5)
C1–C2	1.388/1.373	1.360/1.373	1.363(6)
C2–C3	1.421/1.422	1.405/1.422	1.410(6)
C6–C7	1.561/1.538	1.554/1.541	1.516(6)
Bond angles			
O1–B1–N1	104.9/107.2	107.1/105.6	105.4(3)
O1–B1–O3	111.2/106.5	108.3/105.6	112.0(3)
O1–B1–C14	107.8/104.9	106.5/105.4	107.5(3)
O3–B1–C14	111.1/117.1	115.1/116.4	113.1(3)
O3–B1–N1	110.3/111.0	112.6/111.0	110.7(3)
N1–B1–C14	111.4/110.6	106.9/111.9	107.9(3)
B1–O1–C1	124.3/126.3	125.3/124.1	125.1(3)
B1–N1–C3	123.5/121.7	120.9/119.9	124.0(4)
B1–N1–C6	114.0/118.8	116.2/117.8	114.3(3)
B1–O3–B2	131.6/133.0	126.4/141.3	130.9(3)
O1–C1–C2	123.9/122.4	121.7/121.8	122.1(4)
C1–C2–C3	121.2/120.6	123.1/121.1	121.8(4)
C2–C3–N1	120.9/121.7	121.0/121.2	119.8(4)
C3–N1–C6	122.5/118.9	122.5/120.8	121.5(4)
N1–C6–C7	112.7/118.3	112.5/116.7	115.1(4)
C6–C7–C8	–/–	114.4/115.9	116.0(4)
Torsion angles			
B1–N1–C6–C7	84.7/6.8	65.7/−85.0	−107.1(4) −102.8(4)
N1–C6–C7–C8/N2	−25.2/−63.2	47.7/98.8	65.0(5) 59.4(5)
C6–C7–N2–B2	59.8/19.4	–/–	–/–
C6–C7–C8–N2	–/–	−67.9/−64.9	−60.8(5) −67.9(5)
C7–N2–B2–O3	54.0/54.6	–/–	–/–
C7–C8–N2–B2	–/–	−40.8/−27.8	105.4(4) 106.6(4)
N2–B2–O3–B1	39.8/−47.1	45.1/−33.9	−56.4(5) −70.8(5)
C8–N2–B2–O3	–/–	67.2/90.1	−60.6(5) −43.9(5)
B2–O3–B1–N1	−56.4/−29.7	−61.3/−48.0	62.1(5) 56.9(5)
O3–B1–N1–C6	−30.9/58.4	−53.6/81.1	52.5(4) 63.5(4)
O1–C1–C2–C3	7.2, −2.8 −4.3, −5.0	2.7, −0.7 2.3, 4.0	−5.7(6), 0.9(7) −0.7(7), 5.1(7)
C1–C2–C3–N1	−11.7, 2.2 2.2, 4.2	−4.2, −0.4 −5.6, −9.4	2.8(6), −0.4(7) −4.7(7), −5.6(7)
C2–C3–N1–B1	−6.6, 4.1 −0.6, −1.8	−4.9, 1.5 9.2, −6.0	9.2(6), 4.7(6) 1.8(6), −8.7(6)
C3–N1–B1–O1	24.8, −8.6 0.7, 0.1	13.0, −1.4 23.3, 22.4	−15.9(5), −8.1(5) 4.8(5), 20.2(5)
N1–B1–O1–C1	−29.4, 8.3 −2.9, −0.9	−15.1, 0.4 −27.8, −29.3	13.1(5), 8.6(5) −10.3(5), −21.2(5)

Table 3 (*continued*)

	cis-**3**, *trans*-**3**[a,b] (calculated data)	*cis*-**4**, *trans*-**4**[a,b] (calculated data)	**4**[c] (X-ray data)
B1–O1–C1–C2	16.4, −3.6	8.5/0.5	−4.0(6), −6.0(6)
	4.9, 3.4	17.3/18.3	9.1(6), 10.9(6)

[a] Mean values except for the torsion angles (see note b).

[b] The two values in each line correspond to the torsion angles of one isomer (first line *cis*-isomer, second line *trans*-isomer).

[c] Mean values for the two molecules in the asymmetric unit (in the case of the torsion angles each of the singular values is listed: the values in the same line correspond to analogous angles in the same molecule).

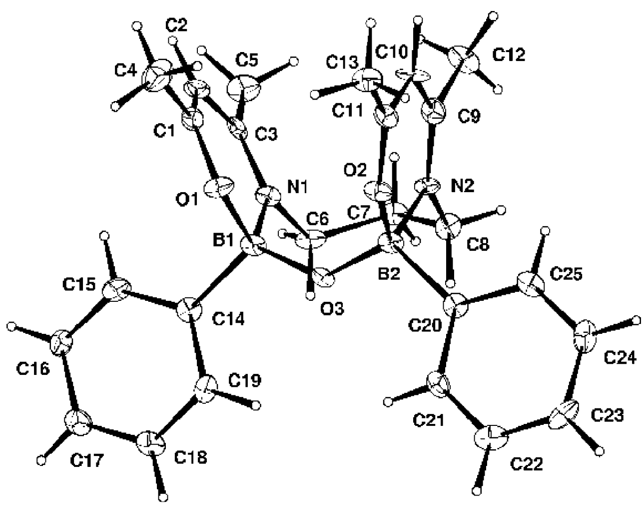


Fig. 3. Perspective view of the molecular structure of compound **4**. Ellipsoids are shown at the 50% probability level.

Table 1. Selected bond lengths, bond angles and torsion angles are listed in Table 3.

As can be seen from the molecular structure shown in Fig. 3, the central eight-membered heterocycle has a distorted boat-conformation with the B-phenyl groups having *cis*-orientation. Nevertheless, while in the corresponding salpen[B(PH)–O–B(Ph)] complex **6**, the salicylidene groups have an almost parallel orientation in **4** a mutual displacement of the acetylacetimine groups is observed, thus causing that the boat is more distorted (see torsion angles in Table 3). This mutual displacement of the acetylacetimine moieties most probably results from the transannular steric repulsion between the methyl groups. Moreover, the conformation of the eight-membered heterocyclic ring in **4** is significantly different for the two independent molecules present in the asymmetric unit of the crystal lattice. Comparing the torsion angles in Table 3, the most significant variations are related to twists around the C6–C7, C7–C8, N1–B1, N2–B2, B1–O3 and B2–O3 bonds. Apparently, also the torsion angles in the six-membered heterocycles are affected by these distortions, since there are large variations comparing the corresponding angles for the two heterocycles present in one and the same molecule as well as between the two independent molecules in the asymmetric unit (Table 3). While the torsion angles in the almost planar, six-membered C_3BNO heterocycle in complex **1** show only variations between −2.3(5)° and 4.0(5)°, in the analogous heterocycles of **4** there are variations between −21.2(5)° and +20.2(5)°.

The bond angles in the eight-membered heterocycle of **4** vary from 110.7(3)° to 130.9(3)° and are similar to the ones found for complex **6**, with the exception that the B–N–C and B–O–B bond angles are smaller, 114.3(3)° ↔ 118.9(2)° for B–N–CH_2 and 130.9(3)° ↔ 134.6(2)° for B–O–B.

While in comparison to the molecular structure of complex **1** the bond lengths in the acetylacetimine fragment are practically the same in complex **4**, characteristic changes in the bond lengths around the boron atom are occurring, i. e. the N → B and B1–O1 bonds are longer, 1.625(6) ↔ 1.574(4) Å and 1.527(5) ↔ 1.508(4) Å, respectively, and the B1–O2 bond is shorter, 1.397(4) ↔ 1.435(4) Å. Significant variations in the bond angles are not observed, but the B–O–B bond angle is smaller in comparison to **1**, 130.9(3)° ↔ 137.3(3)°.

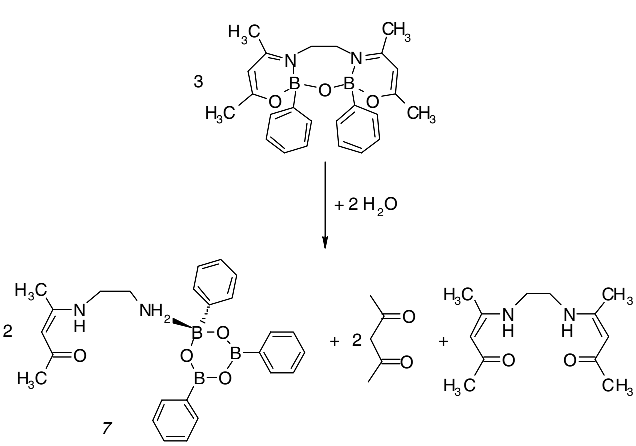
A comparison of the theoretical and experimental geometric data of complex *cis*-**4** in Table 3 shows a reasonably well agreement with respect to bond lengths and bond angles. In the case of the bond lengths, mayor differences are only observed for the N → B, 1.643 ↔ 1.624(6) Å, and the C6–C7 bonds, 1.554 ↔ 1.516(6) Å. In the case of the bond angles, the largest differences occur for O1–B1–O3, B1–N1–C3 and B1–O3–B2 with differences of 3.7, 3.1 and 4.5°. The variations are larger for the torsion angles, especially for the BNCC and NCCC bonds, however, due to the fact that there also significant variations between the torsion angles in the two independent molecules present in the asymmetric unit of the crystal lattice, it can be supposed that the conformation of the eight-membered heterocyclic ring presents some flexibility.

The preference of the *cis*-configuration over the *trans*-configuration in complexes **3** and **4** can be explained by the fact that the angular and conformational strains are less in the boat conformer when compared to the chair conformer. This can be recognized comparing the bond angles in each pair of corresponding isomers (Table 3). For complex **3** the O3–B1–N1, B1–N1–C6, N1–C6–C7 and B1–O3–B2 bond angles have larger deviations from the ideal tetrahedral angle in the case of the *trans*-isomer. The same tendency is observed for the isomers of complex **4**, where the calculated B1–O3–B2 bond angle in *trans*-**4** reaches a value of 141.3°.

3.3. Preparation and characterization of the 1,3,5-triphenylboroxine derivative 7

In an attempt to grow crystals of complex **3** suitable for an X-ray crystallographic study, in several occasions a crystalline material containing the 1,3,5-triphenylboroxine derivative **7** and the acacenH_2 ligand in a 2:1 proportion was obtained. The composition of these crystals was analyzed by elemental analysis, NMR (^{1}H, ^{13}C, ^{11}B) spectroscopy and X-ray diffraction. A possible path for the hydrolysis of **3** is shown in Scheme 8, where it is proposed that three equivalents of the ligand are partially hydrolyzed by two equivalents of water to give two equivalents of the triboroxine derivative **7**, two equivalents of 2,4-pentanedione and one equivalent of acacenH_2. Apparently, between two equivalents of **7** and one equivalent of the ligand a crystal lattice of sufficient stability is formed to displace the reaction equilibrium in this direction. Such 1,3,5-triphenylboroxine adducts are well-known [23]. The ^{1}H, ^{13}C and ^{11}B NMR data of **7** indicate that the boroxine adduct is dissociated in solution or that there exists a fast dynamic exchange equilibrium between the 4-(2-aminoethyleneamino)-pent-3-en-2-one and the B_3O_3 heterocycle. Such equilibria have been already reported for related systems [23d,23f].

The most relevant crystallographic data are summarized in Table 1. Selected bond lengths, bond angles and torsion angles are listed in Table 4. The molecular structure shown in Fig. 4 proves the existence of the N → B coordinative bond in the solid-state, 1.626(4) Å. The molecular geometry of the 1,3,5-triphenylboroxine adduct is similar to that observed for a series of related adducts with amines as Lewis basic ligands [23d]. This



Scheme 8. Possible mechanism for the hydrolysis of complex **7** in the presence of water.

Table 4
Selected bond lengths (Å), bond angles (°) and torsion angles (°) for compound **7** (mean values)

Bond lengths			
B1–N1	1.626(4)	B3–C7	1.566(4)
B1–O1	1.470(4)	N1–C19	1.492(3)
B1–O3	1.474(4)	C19–C20	1.506(4)
B1–C1	1.604(4)	N2–C20	1.448(4)
B2–O1	1.341(4)	N2–C21	1.340(4)
B2–O2	1.386(4)	C21–C23	1.382(4)
B2–C13	1.569(5)	C23–C24	1.407(4)
B3–O2	1.390(4)	O4–C24	1.270(4)
B3–O3	1.342(4)		
Bond angles			
O1–B1–N1	104.1(2)	O1–B2–O2	121.3(3)
O1–B1–O3	113.1(3)	O2–B3–O3	120.5(3)
O1–B1–C1	112.7(3)	B1–O1–B2	121.9(3)
O3–B1–C1	112.5(3)	B1–O3–B3	122.5(3)
O3–B1–N1	104.2(2)	B2–O2–B3	120.1(3)
N1–B1–C1	109.7(2)		
Torsion angles			
N1–C19–C20–N2	66.9(3)		

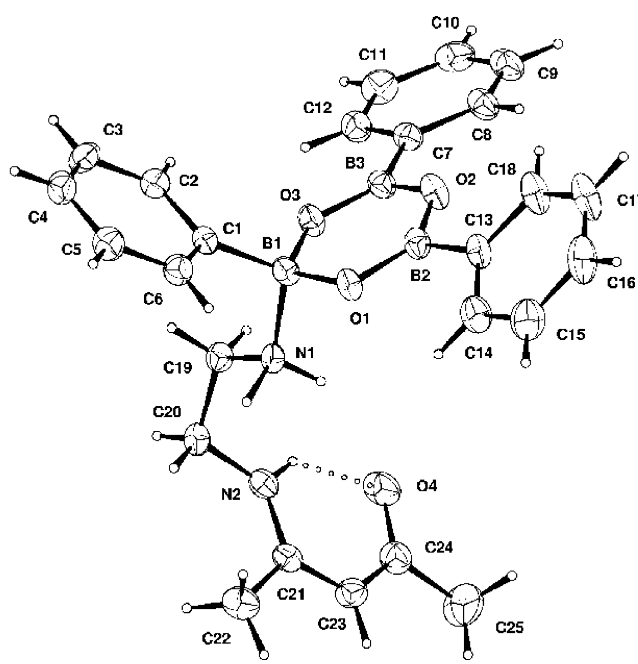


Fig. 4. Perspective view of the molecular structure of compound **7**. Ellipsoids are shown at the 20% probability level.

X-ray structure gives also evidence for the predomination of the cetamine tautomeric form for the ligands used in this contribution, since the positions of the acetylacetimine hydrogen atoms in the uncoordinated chelate rings could be localized by a difference Fourier map (N–H ··· O = 1.98 Å, N ··· O = 2.67 Å). The C24–O4, C23–C24, C21–C23 and C21–N2 bond lengths of 1.270(3), 1.406(4), 1.382(4) and 1.340(4) Å, respectively, support this observation. Similar values are found for the uncoordinated acacenH_2 molecules present in the crystal lattice.

4. Conclusions

This contribution has shown that the 2,4-pentanedione derived ligands acacaminolH_2, acacenH_2 and acacpenH_2 react with phenylboronic acid in a similar way as the corresponding salicylaldehyde derivatives salaminolH_2, salenH_2 and salpenH_2. However, the products prepared in here are much more soluble than the salicylaldehyde derivatives. Furthermore, the presence of two methyl groups in the six-membered chelate ring enhances the steric bulk of this part of the ligand, causing changes in the molecular composition or the molecular structure of the product: with acacaminolH_2 a dinuclear monomeric instead of a dimeric complex was obtained, while in the case of acacenH_2 and acacpenH_2 a significant distortion of the boat conformation of the central heterocyclic ring was predicted by computational methods and confirmed experimentally for one of the complexes.

Acknowledgements

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