

Diphenylboron chelate of an 3-hydroxy-
N-(2-hydroxyalkyl)hydroxamic acidWolfgang Kliegel,^a Ute
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Key indicators

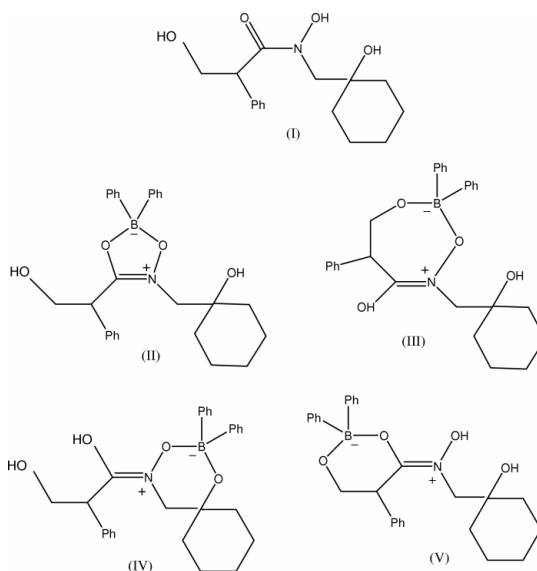
Single-crystal X-ray study
T = 294 K
Mean $\sigma(C-C) = 0.007 \text{ \AA}$
R factor = 0.051
wR factor = 0.054
Data-to-parameter ratio = 18.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.4-[(1-Hydroxycyclohexyl)methyl]-5-(2-hydroxy-1-phenyl-ethyl)-2,2-diphenyl-1,3-dioxo-4-azonia-2-borata-4-cyclopentene benzene hemisolvate, $C_{28}H_{32}BNO_4 \cdot 0.5C_6H_6$, contains a five-membered BONCO heterocycle with a *B*-envelope conformation, formed by the hydroxamate portion of the molecule. Bond lengths and angles are similar to those in related compounds. The crystal structure contains a molecule of benzene lying on a crystallographic inversion centre. The heterocycle molecules are linked by pairs of $O-H \cdots O$ hydrogen bonds and possible $O-H \cdots \pi$ -interactions.

Received 26 September 2002

Accepted 3 October 2002

Online 11 October 2002

Comment

In the course of our research on the formation of boron complexes with functionally modified hydroxamic acids (Kliegel *et al.*, 1996, 2001, 2002, and references therein), the tetradentate ligand (I), obtained from (\pm)tropic acid and 1-(*N*-hydroxyaminomethyl)cyclohexanol, was reacted with diphenylborinic acid (anhydride).The resulting crystalline compound shows the elemental composition of a 1:1 Ph_2B complex of (I), and IR and 1H NMR spectroscopic features of the supposed molecular structure (II), possessing a five-membered BONCO chelate ring. However, a seven-membered isomeric structure, (III), which can be envisioned on the grounds of the established molecular structures of similar seven-membered boron chelates (Kliegel *et al.*, 1988, 2000), could not be excluded unambiguously. Evidence against (III) is the 1H NMR upfield shift of two OH proton signals, which suggests two alcoholic hydroxy groups; the hydroxyl proton of the lactim form of a hydroxamic acid

moiety, as in (III), should appear at a lower field. Furthermore two six-membered chelate structures, (IV) and (V), had to be considered. The BONCCO ring system, as in (IV), is well known (Kliegel *et al.*, 2000, and reference No. 3 therein), and was also established by an X-ray structure analysis (Ebeling *et al.*, 1989), and a BOCCCO chelate ring, as in (V), has been proved for the six-membered diphenylboron chelates of salicylaldehyde derivatives (Kliegel *et al.*, 1993, 1997). As discussed above for (III), a low-field hydroxyl proton signal of the $\text{N}=\text{C}-\text{OH}$ or the $\text{C}=\text{N}-\text{OH}$ form of the hydroxamic acid moiety could be expected in the ^1H NMR spectrum of (IV) or (V), but is not found. Thus, the hydroxamatoboron complex (II) seems most likely. The X-ray analysis confirms structure (II), with a five-membered BONCO chelate ring.

The crystal structure contains compound (II) (four molecules per cell) and benzene solvent (two molecules per cell), which occupies an inversion centre at $\frac{1}{2}, \frac{1}{2}, 0$; the solvent exhibits large thermal motion, and rather poor dimensions. Compound (II) has an asymmetric centre (at C9), but the material is a racemate, since it was synthesized from racemic starting material (the *S* isomer is depicted in Fig. 1). The detailed structure of the chelate ring system in (II) is very similar to that found in related hydroxamatoboron chelates (Kliegel *et al.*, 1996, 2001, 2002, and references therein), the BONCO ring having a slight *B*-envelope conformation [dihedral angle magnitudes 1.5 (3)–6.9 (3)°]. The short C1–N1 bond distance of 1.297 (3) Å corresponds to a high amount of double-bond character, with a π -bond order of around 0.8, similar to the hydroxamatoboron complex reported recently (Kliegel *et al.*, 2002). Comparable to the latter is also the retention of about 50% of the double-bond character of the C1–O2 carbonyl bond of the hydroxamate moiety. The two O–B bonds show a difference of 0.030 Å between the longer (C)O–B bond [1.569 (5) Å] and the shorter (N)O–B bond [1.539 (4) Å]; this difference lies in the normal range 0.001–0.035 Å found in other hydroxamatoboron complexes (Kliegel *et al.*, 1996, 2001).

R and *S* molecules of (II) are linked about a centre of inversion at 0,0,0 by a pair of O3–H3...O4 hydrogen bonds (Table 2). Atom H4, bonded to O4, does not participate in hydrogen bonding; there may be some O4–H4... π interaction between the molecules related by the inversion centre, since there are contacts between the O4–H4 group and atoms C17 and C18 of the C17-phenyl ring, with O...C = 3.347 (4) Å, and H...C = 2.48 and 2.54 (4) Å.

Experimental

Preparation of *N*,3-dihydroxy-*N*-[(1-hydroxycyclohexyl)methyl]-2-phenylpropionic amide, (I): (\pm)-3-hydroxy-2-phenylpropionic acid (tropic acid, 4.99 g, 30 mmol) and 1-(*N*-hydroxyaminomethyl)cyclohexanol (Kliegel & Becker, 1977) (4.36 g, 30 mmol) were dissolved in 30 ml of 2-propanol by slight heating. A solution of *N,N'*-dicyclohexylcarbodiimide (6.19 g, 30 mmol) in 30 ml CH_2Cl_2 was added dropwise under stirring. After storing at room temperature for 12 h, the precipitated *N,N'*-dicyclohexylurea was filtered off, and the solution was evaporated *in vacuo*. After addition of 90 ml 2M NaOH, the solution was extracted with 2 × 50 ml of CH_2Cl_2 . The aqueous

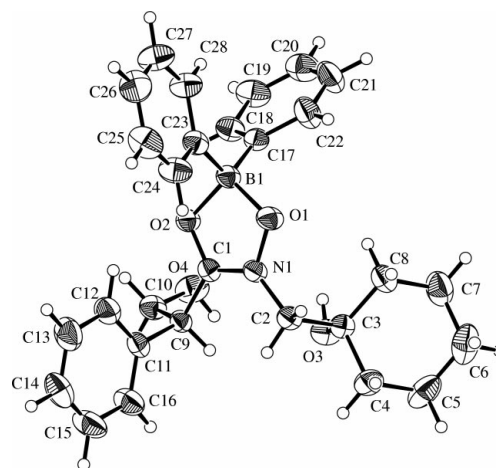


Figure 1
View of a molecule of (II) (*S* isomer, 33% probability ellipsoids).

phase was acidified (aqueous HCl) and extracted with 5 × 60 ml of ether. The combined ether solutions were washed with a saturated aqueous solution of NaHCO_3 and dried over Na_2SO_4 . The ether was distilled off partially, and crystallization commenced after cooling and addition of petroleum ether. Yield: 4.51 g (51%) of colourless crystals, m.p. 393–395 K (from ether/petroleum ether). IR (KBr): 3550, 3520–2500 (curtain, O–H), 1620 cm^{-1} (C=O). ^1H NMR (400 MHz, CDCl_3 -TMS), δ (p.p.m.): 1.19–1.83 [*m*, $(\text{CH}_2)_5$], 2.06 (*s*, broad, exchangeable, N–C–C–OH), 3.02 (*s*, broad, exchangeable, C–C–C–OH), 3.35–4.44 (*m*, N- CH_2 , O- CH_2CH), 7.25–7.33 (*m*, 5 aromatic H), 8.11 (*s*, exchangeable, N–OH). Analysis calculated for $\text{C}_{16}\text{H}_{23}\text{NO}_4$: C 65.51, H 7.90, N 4.77%; found: C 65.53, H 8.04, N 4.65%.

Preparation of 4-[(1-hydroxycyclohexyl)methyl]-5-(2-hydroxy-1-phenylethyl)-2,2-diphenyl-1,3-dioxia-4-azonia-2-borata-4-cyclopentene, (II): (I) (1.47 g, 5 mmol) and oxybis(diphenylborane) (diphenylborinic acid anhydride, 0.87 g, 2.5 mmol) were dissolved in a small amount of absolute ethanol with slight heating. Cooling of the solution and/or addition of petroleum ether yielded 1.90 g (83%) of colourless crystals, m.p. 406–407 K (from ethanol). IR (KBr): 3510, 3420 (O–H), 1615 cm^{-1} (C=N/C=O). ^1H NMR (400 MHz, CDCl_3 -TMS), δ (p.p.m.): 1.20–1.66 [*m*, $(\text{CH}_2)_5$], 2.37 (*s*, exchangeable, N–C–C–OH), 3.10 (*s*, exchangeable, C–C–C–OH), 3.73 (*s*, N- CH_2), 3.78–4.28 (*m*, O- CH_2CH), 7.20–7.39 (13 aromatic H), 7.53 and 7.55 (*d* and *d*, $J = 1$ Hz, 2 aromatic H). Analysis calculated for $\text{C}_{28}\text{H}_{32}\text{BNO}_4$: C 73.53, H 7.05, N 3.06%; found: C 73.60, H 7.05, N 3.01%. The compound gives a blue colour reaction with diphenylcarbazone in methanolic solution, indicating the presence of a diphenylboron moiety (Neu, 1960; Friese & Umland, 1978). Single crystals suitable for X-ray crystallography were obtained by slow crystallization from ethanol and a small amount of petroleum ether/benzene, m.p. 404–405 K.

Crystal data

$\text{C}_{28}\text{H}_{32}\text{BNO}_4 \cdot 0.5\text{C}_6\text{H}_6$
 $M_r = 496.42$
Monoclinic, $P2_1/c$
 $a = 12.310$ (1) Å
 $b = 22.089$ (2) Å
 $c = 10.965$ (1) Å
 $\beta = 108.26$ (1)°
 $V = 2831.4$ (5) Å³
 $Z = 4$

$D_x = 1.164$ Mg m⁻³
Mo K α radiation
Cell parameters from 25 reflections
 $\theta = 15.1$ – 18.9°
 $\mu = 0.08$ mm⁻¹
 $T = 294$ K
Prism, colourless
0.45 × 0.25 × 0.25 mm

Data collection

Enraf–Nonius CAD-4
diffractometer
 ω -2 θ scans
Absorption correction: ψ scan (local
program; Rettig, 1978)
 $T_{\min} = 0.96$, $T_{\max} = 0.98$
6443 measured reflections
6443 independent reflections

2467 reflections with $I > 3\sigma(I)$
 $\theta_{\max} = 27.5^\circ$
 $h = 0 \rightarrow 15$
 $k = 0 \rightarrow 28$
 $l = -14 \rightarrow 13$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F
 $R = 0.051$
 $wR = 0.054$
 $S = 1.96$
6443 reflections
342 parameters

H atoms treated by a mixture of
independent and constrained
refinement
 $w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$
 $(\Delta/\sigma)_{\max} = 0.04$
 $\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1–N1	1.383 (4)	C13–C14	1.357 (7)
O1–B1	1.539 (4)	C14–C15	1.352 (6)
O2–C1	1.288 (4)	C15–C16	1.382 (6)
O2–B1	1.569 (5)	C17–C18	1.385 (5)
O3–C3	1.424 (3)	C17–C22	1.391 (5)
O4–C10	1.413 (4)	C17–B1	1.600 (5)
N1–C1	1.297 (3)	C18–C19	1.387 (6)
N1–C2	1.456 (4)	C19–C20	1.352 (7)
C1–C9	1.500 (4)	C20–C21	1.368 (8)
C2–C3	1.523 (4)	C21–C22	1.391 (7)
C3–C4	1.527 (4)	C23–C24	1.382 (5)
C3–C8	1.523 (5)	C23–C28	1.384 (5)
C4–C5	1.521 (5)	C23–B1	1.593 (4)
C5–C6	1.510 (7)	C24–C25	1.375 (5)
C6–C7	1.515 (7)	C25–C26	1.357 (7)
C7–C8	1.508 (4)	C26–C27	1.364 (7)
C9–C10	1.536 (3)	C27–C28	1.380 (5)
C9–C11	1.513 (4)	C29–C30	1.38 (2)
C11–C12	1.383 (4)	C29–C31 ¹	1.46 (2)
C11–C16	1.377 (5)	C30–C31	1.21 (2)
C12–C13	1.383 (5)		
N1–O1–B1	106.2 (2)	C13–C14–C15	119.5 (4)
C1–O2–B1	108.6 (2)	C14–C15–C16	120.8 (5)
O1–N1–C1	112.3 (2)	C11–C16–C15	120.6 (3)
O1–N1–C2	116.7 (2)	C18–C17–C22	116.3 (4)
C1–N1–C2	130.9 (3)	C18–C17–B1	122.6 (3)
O2–C1–N1	114.0 (3)	C22–C17–B1	120.9 (3)
O2–C1–C9	121.6 (2)	C17–C18–C19	122.2 (4)
N1–C1–C9	124.3 (3)	C18–C19–C20	120.0 (4)
N1–C2–C3	113.6 (3)	C19–C20–C21	120.1 (5)
O3–C3–C2	108.5 (2)	C20–C21–C22	120.0 (4)
O3–C3–C4	105.5 (2)	C17–C22–C21	121.5 (4)
O3–C3–C8	111.6 (3)	C24–C23–C28	116.2 (3)
C2–C3–C4	108.4 (3)	C24–C23–B1	120.2 (3)
C2–C3–C8	112.0 (3)	C28–C23–B1	123.6 (3)
C4–C3–C8	110.5 (2)	C23–C24–C25	121.6 (3)
C3–C4–C5	111.5 (3)	C24–C25–C26	121.1 (4)
C4–C5–C6	112.2 (3)	C25–C26–C27	118.9 (4)
C5–C6–C7	110.2 (3)	C26–C27–C28	120.2 (4)
C6–C7–C8	111.3 (3)	C23–C28–C27	122.0 (4)
C3–C8–C7	113.3 (3)	C30–C29–C31 ¹	115 (1)
C1–C9–C10	110.4 (3)	C29–C30–C31	117 (1)
C1–C9–C11	111.2 (2)	C29 ¹ –C31–C30	119 (1)
C10–C9–C11	110.5 (2)	O1–B1–O2	98.2 (2)
O4–C10–C9	112.0 (2)	O1–B1–C17	112.7 (2)
C9–C11–C12	122.3 (3)	O1–B1–C23	110.2 (3)
C9–C11–C16	119.8 (3)	O2–B1–C17	108.3 (3)
C12–C11–C16	118.0 (3)	O2–B1–C23	110.1 (3)
C11–C12–C13	120.3 (4)	C17–B1–C23	115.8 (3)
C12–C13–C14	120.7 (3)		

Symmetry code: (i) $1 - x, 1 - y, -z$.

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3–H3 \cdots O4 ⁱ	0.83 (4)	1.99 (4)	2.794 (4)	161 (3)

Symmetry code: (i) $-x, -y, -z$.

O-bound H atoms were refined freely; other H atoms were made to ride on their attached atoms.

Data collection: *CAD-4 Diffractometer Control Software* (Enraf–Nonius, 1978); cell refinement: *CAD-4 Diffractometer Control Software*; data reduction: local programs (Rettig, 1978); program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980); program(s) used to refine structure: *ORFLS* (Busing *et al.*, 1962); software used to prepare material for publication: *TEXSAN* (Molecular Structure Corporation, 1989).

We thank the Natural Sciences and Engineering Research Council of Canada and the Fonds der Chemische Industrie, Frankfurt am Main, for financial support.

References

- Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
- Ebeling, E., Kliegel, W., Rettig, S. J. & Trotter, J. (1989). *Can. J. Chem.* **67**, 933–940.
- Enraf–Nonius (1978). *CAD-4 Diffractometer Control Software*. Enraf–Nonius, Delft, The Netherlands.
- Friese, B. & Umland, F. (1978). *Anal. Chim. Acta*, **96**, 303–310.
- Kliegel, W. & Becker, H. (1977). *Chem. Ber.* **110**, 2067–2089.
- Kliegel, W., Drückler, K., Rettig, S. J. & Trotter, J. (1993). *Can. J. Chem.* **71**, 919–923.
- Kliegel, W., Lubkowitz, G., Pokriefke, J. O., Rettig, S. J. & Trotter, J. (2000). *Can. J. Chem.* **78**, 1325–1344.
- Kliegel, W., Metge, J., Patrick, B. O., Rettig, S. J. & Trotter, J. (2001). *Acta Cryst. E57*, o1120–o1122.
- Kliegel, W., Metge, J., Rettig, S. J. & Trotter, J. (1997). *Can. J. Chem.* **75**, 1203–1214.
- Kliegel, W., Schumacher, U., Patrick, B. O., Rettig, S. J. & Trotter, J. (2002). *Acta Cryst. E58*, o1095–o1097.
- Kliegel, W., Schumacher, U., Rettig, S. J. & Trotter, J. (1996). *Can. J. Chem.* **74**, 445–452.
- Kliegel, W., Tajerbashi, M., Rettig, S. J. & Trotter, J. (1988). *Can. J. Chem.* **66**, 2621–2630.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80*. Universities of York, England, and Louvain, Belgium.
- Molecular Structure Corporation (1989). *TEXSAN*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Neu, R. (1960). *Z. Anal. Chem.* **176**, 343–346.
- Rettig, S. J. (1978). *Data reduction program*. University of British Columbia, Canada.