Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

N-[2-(*H*ydroxymethoxyboryl)benzyl]-4,7-phenanthrolinium bromide methanol solvate

Marilyn M. Olmstead,[a]* Jeff T. Suri[b] and Bakthan Singaram[b]

[a]Department of Chemistry, University of California, Davis, CA 95616, USA, and [b]Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, USA

Correspondence e-mail:
olmstead@indigo.ucdavis.edu

Received 3 December 2003
Accepted 19 January 2004
Online 30 January 2004

The structure of the phenanthroline-derived boronic acid viologen, $C_{20}H_{18}BN_2O_2^+\cdot Br^-\cdot CH_3OH$, as a methanol solvate, was determined as part of a fluorescence quenching study. There is $-\pi$ stacking of the phenanthroline rings and hydrogen bonding involving Br^- ions.

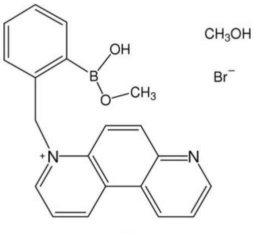
Key indicators

Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.005 Å
R factor = 0.042
wR factor = 0.096
Data-to-parameter ratio = 13.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The compound *N*-[2-(hydroxymethoxyboryl)benzyl]-4,7-phenanthrolinium bromide methanol solvate, (I), is of interest as a saccharide sensor because the fluorescence quenching of a pyranine–(I) complex is suppressed in the presence of monosaccharides (Camara *et al.*, 2002; Suri *et al.*, 2003). Another compound in this study, *N*,*N*′-bisbenzyl-4,7-phenanthrolinium dibromide methanol solvate, containing a dication, was reported in the previous paper (Olmstead *et al.*, 2004).



(I)

As shown in Fig. 1, the phenanthroline group is *N*-benzylated. The benzyl group was derivatized as a boronic acid, but this became a monomethyl ester during the process of crystallization from methanol. The boronic ester is hydrogen bonded to a solvent methanol molecule, which in turn is hydrogen bonded to the Br^- ion. The r.m.s. deviation of the phenanthroline plane is 0.020 Å. This plane makes an angle of 89.43 (9)° with the C14–C19 benzene ring plane. There is a minor twist [2.07 (8)°] between the end six-membered rings of the phenanthroline group.

The packing features centrosymmetrically related phenanthroline rings. These are arranged in columns in the structure, while the bromide, methanol and benzyl groups are arranged between them. These stacking arrangements are shown in Figs. 2 and 3. The distances between the ring centroids (DC), those between the planes through the rings (DP) and the lateral shifts (SH) are, for C1–C4/C8/C9 and C1–C4/C8/C9 at $(-x, 1-y, -z)$, DC = 3.691 (5) Å, DP = 3.397 (4) Å and SH = 1.444 (17) Å; and for C1–C4/C8/C9 and C4/N2/C5–C8 at $(-x, 1-y, -z)$, DC = 3.538 (6) Å, DP = 3.398 (4) Å and SH = 0.984 (23) Å. The closest intermolecular contact for the Br^- ion (excluding the hydrogen bond to methanol) is that involving the H atom *para* to the N atom bearing the positive charge, the second closest being that involving the H atom

DOI: 10.1107/S1600536804001369

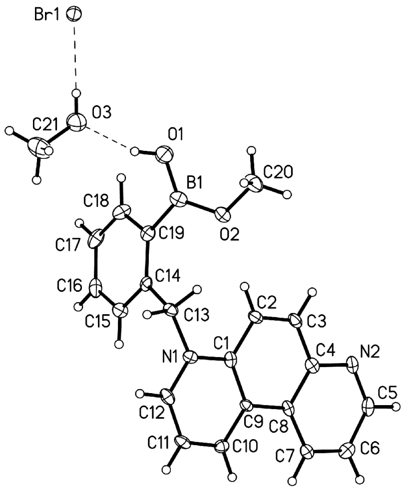


Figure 1
A view of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. Hydrogen bonds are indicated by dashed lines.

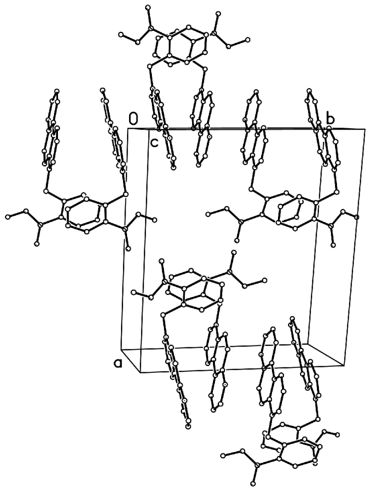


Figure 2
The packing of the cation only, as viewed down the *c* axis. The phenanthroline moiety is arranged in stacks of centrosymmetric pairs.

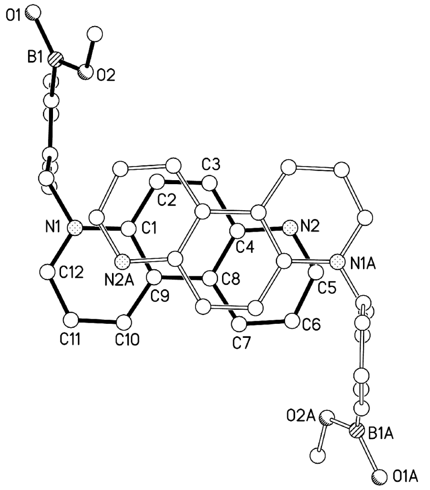


Figure 3
A portion of the structure, showing the pairwise π–π interaction between the phenanthroline moieties of centrosymmetrically related neighbors.

ortho to the same N atom. In addition, there are two weak hydrogen bonds of the types C—H···O and C—H···N. These distances are given in Table 1.

Experimental

The compound was synthesized as described in the Supporting Information of Suri *et al.* (2002). Crystals were obtained following recrystallization from methanol.

Crystal data

$C_{20}H_{18}BN_2O_2^{+}\cdot Br^{-}CH_4O$
$M_r = 441.13$
Monoclinic, $P2_1/c$
$a = 16.376\ (3)$ Å
$b = 13.894\ (3)$ Å
$c = 9.0289\ (15)$ Å
$\beta = 103.723\ (4)^\circ$
$V = 1995.7\ (7)$ Å^3
$Z = 4$
$D_x = 1.468$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 545 reflections
$\theta = 2.5$–$25.^\circ$
$\mu = 2.08$ mm^{-1}
$T = 90\ (2)$ K
Plate, colorless
0.18 × 0.11 × 0.05 mm

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{\min} = 0.705$, $T_{\max} = 0.903$
11 491 measured reflections
3618 independent reflections
2624 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 25.3^\circ$
$h = -19 \rightarrow 19$
$k = -16 \rightarrow 16$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.096$
$S = 1.12$
3618 reflections
261 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.63$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*A*···O3	0.83 (5)	1.84 (5)	2.674 (4)	178 (5)
O3—H3*A*···Br1	0.97 (5)	2.22 (5)	3.187 (3)	177 (4)
C12—H12···Br1$^{\rm i}$	0.95	2.86	3.425 (4)	119
C10—H10···Br1$^{\rm ii}$	0.95	2.75	3.604 (4)	150
C13—H13*A*···O2	0.99	2.22	3.017 (5)	137
C11—H11···N2$^{\rm iii}$	0.95	2.38	3.320 (5)	172

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x - 1, y, z$; (iii) $x, y, 1 + z$.

H atoms attached to C atom were refined as riding on their parent atoms, with C—H distances of 0.95 Å (0.98 Å for methyl H atoms). The methanol H atoms and boronic acid H atoms were located in a difference Fourier map and their positions were refined. All $U_{\rm iso}$(H) values were set to $1.2U_{\rm eq}$ of the bonded atoms ($1.5U_{\rm eq}$ for methyl H atoms).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

JTS and BS thank the BioSTAR Project and the Industry–University Cooperative Research Program with Glumetric for their continued financial support.

References

Bruker (2002). *SMART* (Version 5.054) and *SAINT* (Version 6.22). Bruker AXS Inc., Madison, Wisconsin, USA.

Camara, J. N., Suri, J. T., Cappuccio, F. E., Wessling, R. A. & Singaram, B. (2002). *Tetrahedron Lett.* **43**, 1139–1141.

Olmstead, M. M., Suri, J. T., & Singaram, B. (2004). *Acta Cryst.* E**60**, o275–o277.

Sheldrick, G. M. (1994). *SHELXTL*. Version 5.1. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (2001). *SADABS*. Version 2.03. University of Göttingen, Germany.

Suri, J. T., Cordes, D. B., Cappuccio, F. E., Wessling, R. A. & Singaram, B. (2003). *Langmuir*, **19**, 5145–5152.