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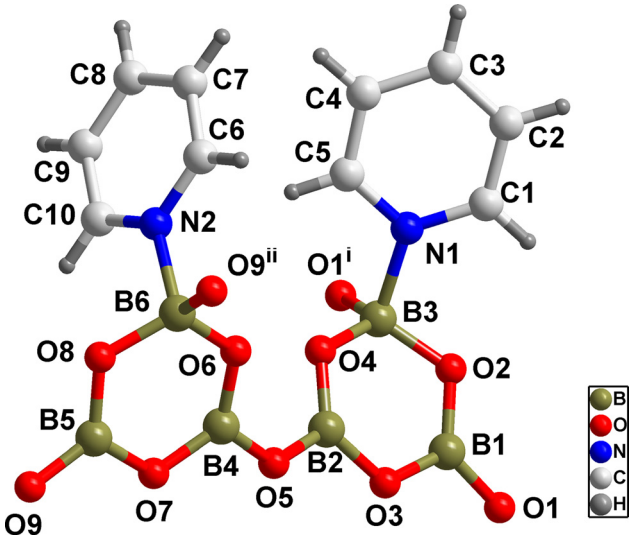
The crystal structure of poly[6,6′-oxybis(4-(pyridin-1-ium-1-yl)-1,3,5,2,4,6-trioxatriborinan-2-olate)], $[B_6O_9](C_5H_5N)_2$



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Abstract

$[B_6O_9](C_5H_5N)_2$, monoclinic, $P2_1/c$ (no. 14), a = 15.0450(11) Å, b = 5.8526(4) Å, c = 17.9672(13) Å, β = 92.768(2)°, V = 1580.2(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0367, $wR_{ref}(F^2)$ = 0.0855, T = 296 K.

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The asymmetric unit (labeled atoms) of the title crystal structure is shown in the figure (symmetry codes: (i) $1 - x$, $-0.5 + y$, $0.5 - z$; (ii) $2 - x$, $0.5 + y$, $0.5 - z$). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Block, colorless
Size:	0.08 × 0.05 × 0.03 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.13 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	18,679, 3928, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2926
$N(param)_{refined}$:	244
Programs:	Bruker programs [1], SHELX [2, 3]

Source of material

A mixture of H_3BO_3 (0.618 g, 10 mmol) and $Li(CF_3SO_3)_2$ (0.156 g, 1 mmol) was added into pyridine (2.5 mL) and water (0.5 mL). After stirring for 15 min, the resulting mixture was sealed in a 25 mL Teflon lined stainless steel autoclave, heated at 190 °C for 8 days, and then slowly cooled to room temperature. The colorless block crystals $[B_6O_9](C_5H_5N)_2$ were obtained by accident.

Experimental details

The structure was solved by direct methods and refined using the SHELXL programs [2, 3]. The hydrogen atoms were restrained. Their U_{iso} values were set to $1.2U_{eq}$ of the parent atoms.

Comment

As an important part of inorganic materials, borates have a wide range of properties due to their structural diversity [4–6]. After decades of exploration and research, only a few borates have been proved to be nonlinear optical (NLO) materials. However, most of these borates consist of isolated, layered, or framework oxoboron anions formed by organic templates. Borates with inorganic-organic hybrid

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

	x	*y*	*z*	U_{iso}^*/U_{eq}
B1	0.54358 (11)	1.0869 (3)	0.20770 (9)	0.0198 (3)
B2	0.67370 (11)	0.8546 (3)	0.22184 (9)	0.0217 (3)
B3	0.57315 (10)	0.8800 (3)	0.32264 (8)	0.0189 (3)
B4	0.82736 (11)	0.6952 (3)	0.22010 (9)	0.0224 (4)
B5	0.94858 (11)	0.4421 (3)	0.20314 (9)	0.0219 (3)
B6	0.93956 (11)	0.6481 (3)	0.32059 (8)	0.0210 (3)
O1	0.48868 (7)	1.20232 (19)	0.16008 (5)	0.0258 (2)
O2	0.53154 (6)	1.06594 (19)	0.28180 (5)	0.0231 (2)
O3	0.61697 (7)	0.9850 (2)	0.17693 (5)	0.0271 (3)
O4	0.65405 (6)	0.79780 (18)	0.29153 (5)	0.0228 (2)
O5	0.74920 (7)	0.7824 (2)	0.18931 (6)	0.0323 (3)
O6	0.85838 (7)	0.74982 (18)	0.28914 (5)	0.0238 (2)
O7	0.87287 (7)	0.5526 (2)	0.17429 (5)	0.0281 (3)
O8	0.97356 (7)	0.46507 (19)	0.27645 (5)	0.0248 (2)
O9	0.99339 (7)	0.3106 (2)	0.15590 (5)	0.0270 (3)
N1	0.60319 (8)	0.9724 (2)	0.40625 (6)	0.0195 (3)
N2	0.90917 (8)	0.5324 (2)	0.39877 (7)	0.0225 (3)
C1	0.57680 (10)	1.1730 (3)	0.43321 (8)	0.0268 (3)
H1A	0.546800	1.275876	0.401562	0.032*
C2	0.59329 (11)	1.2301 (3)	0.50725 (9)	0.0332 (4)
H2A	0.574694	1.370290	0.525265	0.040*
C3	0.63743 (11)	1.0777 (3)	0.55392 (8)	0.0336 (4)
H3A	0.648335	1.112773	0.604016	0.040*
C4	0.66542 (11)	0.8721 (3)	0.52578 (8)	0.0325 (4)
H4A	0.695680	0.766969	0.556446	0.039*
C5	0.64776 (10)	0.8253 (3)	0.45155 (8)	0.0265 (3)
H5A	0.667255	0.687786	0.432178	0.032*
C6	0.91371 (11)	0.6523 (3)	0.46208 (8)	0.0308 (4)
H6A	0.939625	0.796576	0.462184	0.037*
C7	0.88139 (12)	0.5698 (4)	0.52709 (9)	0.0442 (5)
H7A	0.885302	0.656857	0.570418	0.053*
C8	0.84326 (13)	0.3568 (4)	0.52701 (11)	0.0511 (6)
H8A	0.821129	0.296833	0.570330	0.061*
C9	0.83835 (14)	0.2342 (4)	0.46211 (12)	0.0521 (5)
H9A	0.812402	0.089957	0.460920	0.063*
C10	0.87192 (12)	0.3249 (3)	0.39851 (10)	0.0381 (4)
H10A	0.868613	0.240334	0.354635	0.046*

frameworks containing coordinative B–N bonds are unusual [7, 8].

The asymmetric unit of the title compound consists of two six-membered rings each comprising one triangular BO_3 and two tetrahedral BO_3N groups. The average B–O distances around three- and four-coordinate boron atoms are 1.368(2) and 1.442(2) Å, respectively. The B–N distance in BO_3N tetrahedra is 1.640–1.644(2) Å, which are comparable with those found in other borates with coordinative B–N bond [7–9].

The structure of the title compound is different from those of previous reports on $[B_6O_9](en)_2@(H_2en)Cl_2$ [7] and $[B_6O_9](en)_2$ [9] (en = ethylenediamine). The title structure is built up from extended neutral $[B_6O_9]$ layers linked by pyridine molecules through coordinative B–N bonds. However, since ethylenediamine is a bidentate ligand, each $[B_6O_9]$ layer connects with neighboring layers by ethylenediamine through coordinative B–N bonds, resulting in a 3D supramolecular framework.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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