Supporting Information

$Na_3B_6O_{10}(HCOO)$: An Ultraviolet Nonlinear Optical Sodium Borate-Formate

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Experimental Section

Table S1. X-ray crystallographic data for **1**.

Empirical formula	$B_6CHNa_3O_{12}$
M_r	338.85
crystal system	Orthorhombic
space group	$P2_12_12_1$
a (Å)	7.6375(8)
b (Å)	9.9345(9)
c (Å)	12.7231(13)
V (Å^3)	965.36(17)
Z	4
D_c (g cm^{-3})	2.331
μ (mm^{-1})	0.327
F(000)	664
crystal size (mm)	0.25× 0.20 ×0.12
index ranges	2.60-27.48
GOF	1.086
collected reflcns	8227
unique reflcns (R_{int})	2193 (0.0630)
observed reflcns [$I > 2\sigma(I)$]	1743
refined parameters	199
Flack parameter	0.8(7)
R_1[a]/wR_2[b] [$I > 2\sigma(I)$]	0.0432/ 0.0859
R_1[a]/wR_2[b] (all data)	0.0636/ 0.0964
largest difference peak/hole	0.272 /-0.344

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S2. Selected bond lengths (Å) for compound **1**[a].

Bond	Distance (Å)	Bond	Distance (Å)
Na(1)-O(11)	2.313(4)	B(1)-O(2)	1.378(4)
Na(1)-O(2A)	2.335(3)	B(2)-O(4)	1.451(4)
Na(1)-O(3B)	2.389(3)	B(2)-O(5)	1.454(4)
Na(1)-O(8C)	2.506(2)	B(2)-O(2)	1.458(4)
Na(1)-O(9)	2.586(3)	B(2)-O(6)	1.510(4)
Na(1)-O(10)	2.800(3)	B(3)-O(10I)	1.429(4)
Na(2)-O(12D)	2.335(3)	B(3)-O(7)	1.446(4)
Na(2)-O(5B)	2.406(3)	B(3)-O(3)	1.471(4)
Na(2)-O(10)	2.411(3)	B(3)-O(6)	1.517(4)
Na(2)-O(7)	2.518(2)	B(4)-O(5J)	1.349(4)
Na(2)-O(4E)	2.755(3)	B(4)-O(8)	1.366(4)
Na(2)-O(1F)	2.845(3)	B(4)-O(4)	1.373(4)
Na(3)-O(7G)	2.440(3)	B(5)-O(1A)	1.443(4)
Na(3)-O(2)	2.448(3)	B(5)-O(9)	1.455(4)
Na(3)-O(12B)	2.466(3)	B(5)-O(8)	1.463(4)
Na(3)-O(3G)	2.488(3)	B(5)-O(6)	1.529(3)
Na(3)-O(11H)	2.544(4)	B(6)-O(10)	1.352(4)
Na(3)-O(4)	2.553(3)	B(6)-O(9)	1.366(4)
Na(3)-O(12H)	2.774(3)	B(6)-O(7)	1.374(4)
B(1)-O(1)	1.352(3)	C-O(12)	1.214(4)
B(1)-O(3)	1.367(4)	C-O(11)	1.237(5)

[a] Symmetry codes: A: $-x + 1/2, -y + 1, z - 1/2$; B: $x - 1/2, -y + 1/2, -z + 1$; C: $-x, y - 1/2, -z + 1/2$; D: $-x + 1/2, -y, z + 1/2$; E: $x, y - 1, z$; F: $-x, y - 1/2, -z + 3/2$; G: $-x, y + 1/2, -z + 3/2$; H: $-x + 1/2, -y + 1, z + 1/2$; I: $x + 1/2, -y + 1/2, -z + 1$; J: $x - 1/2, -y + 3/2, -z + 1$.

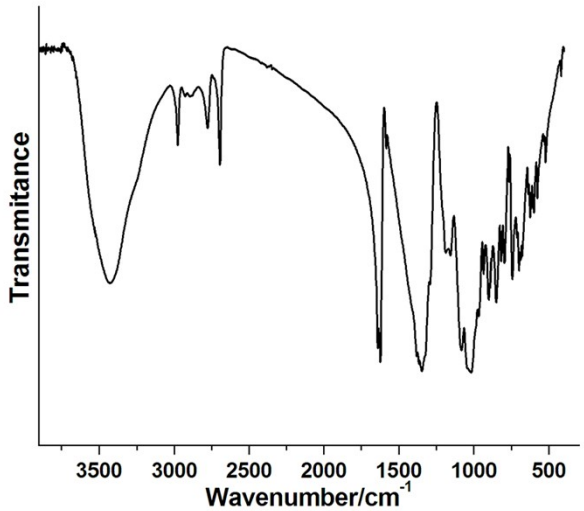

Figure S1. IR spectra of **1**.

In the IR spectra of **1**, the strong band around 1626 cm^{-1} is corresponding to the stretching vibrations of the COO^{-}. The characteristic bands around 1349 cm^{-1} are due to B–O asymmetric stretching of BO_3

units and the asymmetrical stretching of carboxylate groups. The bands around 1022 cm^{-1} are associated with BO_4 units. Since the deformation vibration of COO^- and the bending vibrations of the BO_3 group overlap in the low frequency vibrations, it is difficult to clearly distinguish the weak absorption bands at 851/744/694/524 cm^{-1}. These assignments are similar to the reported results.[1-2]

(1) F. He, Q. Wang, M. Liu, L. Huang, D. Gao, J. Bi and G. Zou, Hydrogen Bonding Assisted Construction of Graphite-like Deep-UV Optical Materials with Two Types of Parallel π-Conjugated Units, *Cryst. Growth Des.*, 2018, **18**, 4756−4765.

(2) Y. Guo, D. Zhang, T. Zheng, L. Huang, D. Gao, J. Bi and G. Zou, Noncentrosymmetric $Rb_3(COOH)_3(H_3BO_3)_2$ vs Centrosymmetric $Cs_3(COOH)_3(H_3BO_3)_2$, *Cryst. Growth Des.*, 2021, **21**, 5976−5982.

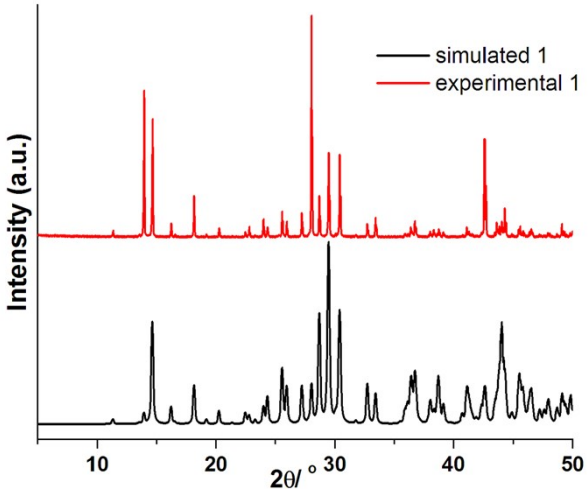

Figure S2. The experimental and simulated PXRD patterns of **1**.

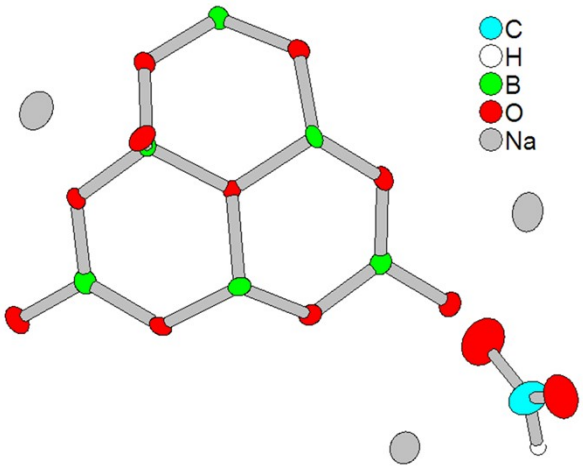

Figure S3. The asymmetric unit of **1**.

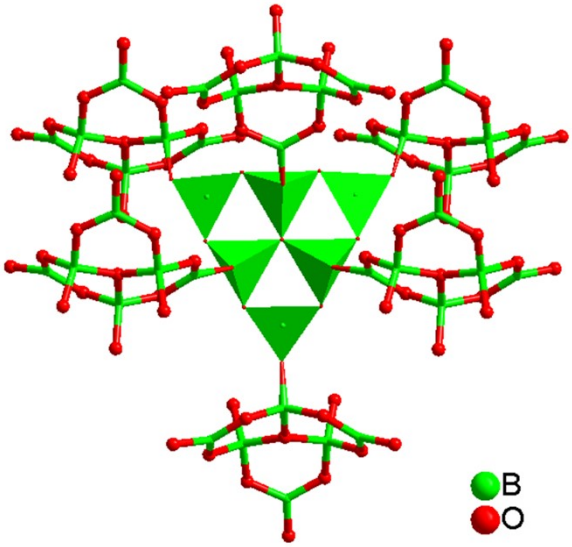

Figure S4. View of the linkage of the $(B_6O_{13})^{8-}$ cluster units in **1**.

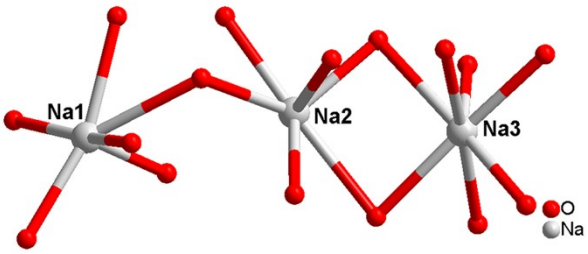

Figure S5. The coordination environments of Na^+ ions.

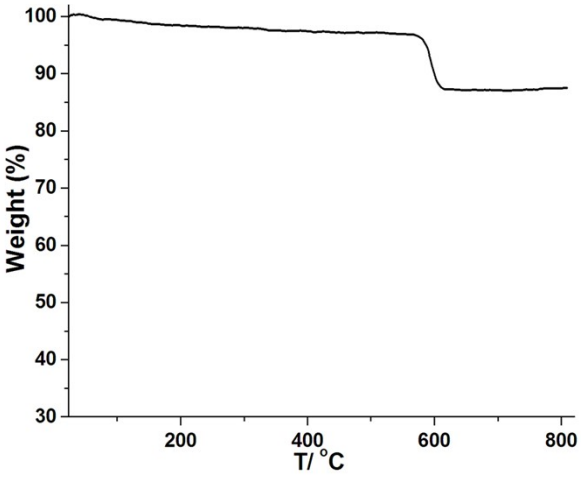

Figure S6. TG curve of compound **1** under air atmosphere (10 ºC/min).

The curve shows that a gradual weight loss of 12.8% (calcd: 13.3%) was observed in the temperature range 100-610 ºC, and assigned to the decomposition of $HCOO^-$ units.