

# Crystal structure of bis(3-carboxy-1-methylpyridinium) octabromide

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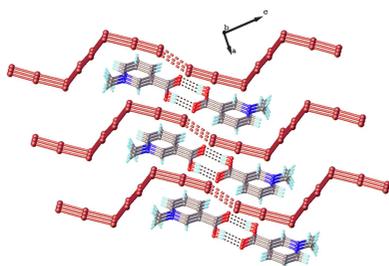
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The crystal structure of the title salt, bis(3-carboxy-1-methylpyridinium) octabromide,  $2C_7H_8NO_2^+ \cdot Br_8^{2-}$ , consists of 3-carboxy-1-methylpyridinium (*N*-methylnicotinic acid) cations, which are stacked between relatively rare  $[Br_8]^{2-}$  anions. The polybromide  $[Br_8]^{2-}$  anion has point group symmetry  $\bar{1}$  and can be described as being composed of two  $[Br_3]^-$  anions connected with a  $Br_2$  molecule in a *Z*-shaped manner. Contacts between neighboring octabromide anions ensure the creation of pseudo-polymeric chains propagating along [111]. The organic cations are located between anionic chains and are connected to each other through  $O-H \cdots O$  hydrogen bonds and to the  $[Br_8]^{2-}$  anions through  $\pi \cdots Br$  interactions that induce the creation of a supramolecular tri-periodic network. In addition, the presence of weak  $C-H \cdots Br$  contacts leads to the creation of layers, which align parallel to (11 $\bar{2}$ ).

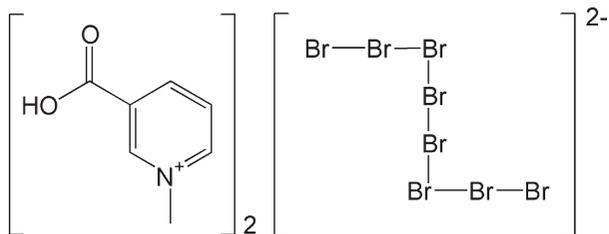
## 1. Chemical context

Polyhalide anions have been the subject of extensive studies within the past century, whereby polyiodides offer the greatest diversity of known compounds among all polyhalide anions. The first triiodide-containing crystal structure,  $(NH_4)[I_3]$ , was determined and characterized by Mooney in 1935 (Mooney, 1935). The known anions range from the smallest possible unit,  $[I_3]^-$ , through multiple discrete species of the types  $[I_{2n+1}]^-$ ,  $[I_{2n+2}]^{2-}$ ,  $[I_{2n+3}]^{3-}$  and other types from  $[I_3]^-$  to  $[I_{29}]^{3-}$  (Svensson & Kloo, 2003) to infinite polymeric structures (Madhu *et al.*, 2016). A significantly smaller number of polyhalide anions is known for lighter halogens. This fact is mostly associated with the higher volatility of bromine, chlorine and fluorine in comparison with iodine, and thus their tendency to loss of halogen. However, several polybromide mono- ( $[Br_3]^-$ ,  $[Br_5]^-$ ,  $[Br_7]^-$ ,  $[Br_9]^-$ ,  $[Br_{11}]^-$ ) and dianions ( $[Br_4]^{2-}$ ,  $[Br_6]^{2-}$ ,  $[Br_8]^{2-}$ ,  $[Br_{10}]^{2-}$ ) are also known so far (Sonnenberg *et al.*, 2020).

One of the most common applications of polybromide anions is in halogenation reactions. They are typically accessible in stable solid bulk form or as liquids with no measurable vapor pressure, depending on the organic cation. Thus, they can be handled much more easily than elemental liquid bromine (Sonnenberg *et al.*, 2020). Polybromides, for example  $[HMIM][Br_9]$  where HMIM = 1-hexyl-3-methylimidazolium, have also been shown to form room-temperature ionic liquids, which can potentially be applied as a liquid electrode (Haller *et al.*, 2013). Moreover, the use of the tribromide anion in the  $[Br_3]^-/Br^-$  redox pair as a mediator in dye-sensitized solar cells has been reported to be an efficient alternative to the frequently used  $[I_3]^-/I^-$  system (Kakiage *et al.*, 2013). Poly-



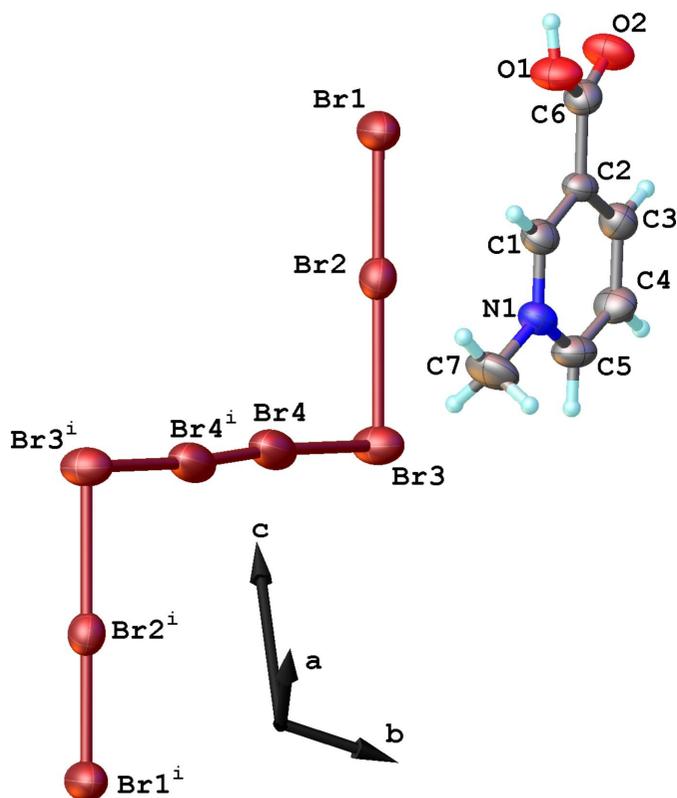
bromides have also been applied in zinc/bromine redox-flow batteries (Naresh *et al.*, 2022).



In the present communication, we report a new polybromide compound containing a Z-shaped octabromide anion,  $2(\text{C}_7\text{H}_8\text{NO}_2)^+ [\text{Br}_8]^{2-}$ , and report its synthesis, crystal structure and Hirshfeld surface analysis.

## 2. Structural commentary

The crystal structure of the title compound consists of 3-carboxy-1-methylpyridinium (or *N*-methylnicotinic acid) cations separated by  $[\text{Br}_8]^{2-}$  anions (Fig. 1). The polybromide  $[\text{Br}_8]^{2-}$  anion can be described as two  $[\text{Br}_3]^-$  moieties connected to a central  $\text{Br}_2$  molecule in a Z-shaped manner (Fig. 2). The title salt has point group symmetry  $\bar{1}$ , with the inversion center located at the midpoint of the central  $\text{Br}_2$  molecule. The Br–Br distance in the latter is 2.4002 (15) Å,



**Figure 1**  
A fragment of the crystal structure of title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i)  $-x, -y, -z$ .]

**Table 1**  
Hydrogen-bond geometry (Å, °).

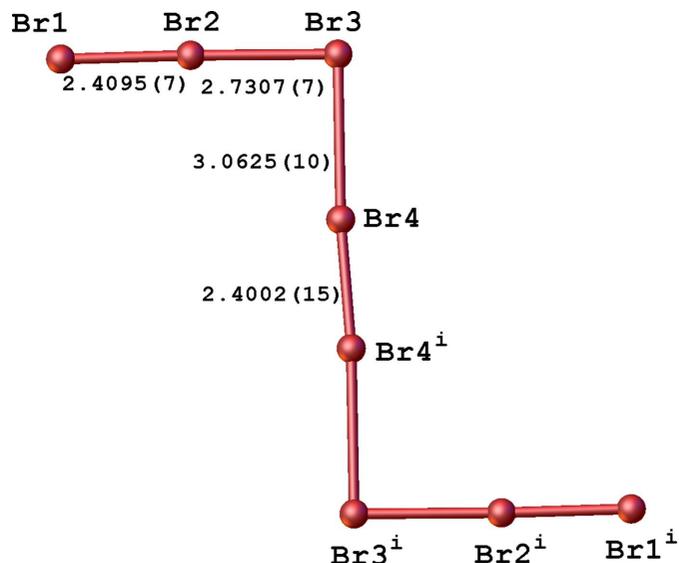
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1}\cdots\text{O2}^{\text{i}}$	0.80 (7)	1.89 (7)	2.668 (5)	164 (7)
$\text{C1}-\text{H1A}\cdots\text{Br3}^{\text{ii}}$	0.93	2.96	3.838 (5)	158
$\text{C5}-\text{H5}\cdots\text{Br4}^{\text{iii}}$	0.93	2.99	3.881 (5)	160
$\text{C7}-\text{H7A}\cdots\text{Br3}^{\text{ii}}$	0.96	2.92	3.857 (6)	166

Symmetry codes: (i)  $-x + 2, -y + 2, -z + 1$ ; (ii)  $x + 1, y, z$ ; (iii)  $-x, -y + 1, -z$ .

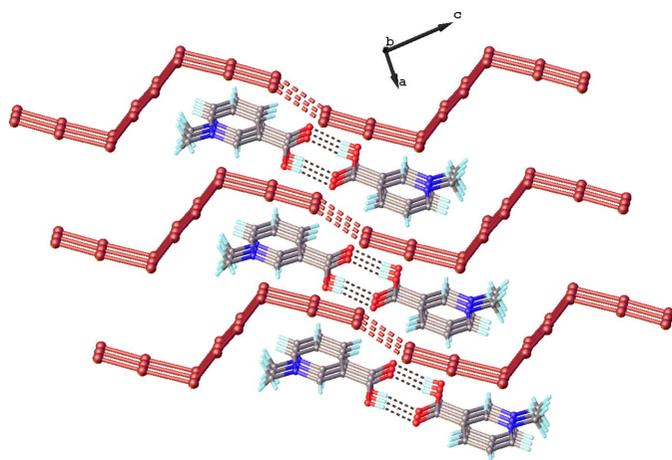
which is slightly higher than 2.308 Å observed in  $[(\text{Bz})(\text{Ph})_3\text{P}]_2^+[\text{Br}_8]^{2-}$  where  $(\text{Bz})(\text{Ph})_3\text{P}^+$  = benzyltriphenylphosphonium (Wolff *et al.*, 2011) and 2.354 Å in  $[\text{Q}^+]_2[\text{Br}_8]^{2-}$  where  $\text{Q}^+$  = quinuclidinium (Robertson *et al.*, 1997). The Br1–Br2–Br3 distances in the  $[\text{Br}_3]^-$  moiety of the title compound are 2.4095 (7) Å and 2.7307 (7) Å (Fig. 2). For comparison, while in  $[\text{Q}^+]_2[\text{Br}_8]^{2-}$  these values are similar (2.432 and 2.663 Å), in  $[(\text{Bz})(\text{Ph})_3\text{P}]_2^+[\text{Br}_8]^{2-}$  these bond lengths are rather equalized (2.518 and 2.498 Å). The angle between the  $[\text{Br}_3]^-$  and  $\text{Br}_2$  fragment in the title compound is 90.37 (2)°, which lies in the range between 80° and 112° observed for the  $[\text{Br}_8]^{2-}$  anions in other octabromide compounds listed in the *Database survey*. The  $[\text{Br}_8]^{2-}$  anion in the title compound is planar with the mean deviation from the best plane through the eight atoms of 0.013 Å.

## 3. Supramolecular features

The  $\text{Br1}\cdots\text{Br1}(-x + 1, -y + 1, -z + 1)$  distance between neighboring  $[\text{Br}_8]^{2-}$  anions is 3.1813 (12) Å, which is smaller than the sum of van der Waal radii of 3.7 Å. This interaction contributes to the formation of infinite supramolecular chains propagating along [111] (Fig. 3). The organic cations are located between anionic chains and are connected with  $[\text{Br}_8]^{2-}$  through  $\pi\cdots\text{Br}$  interactions [with a centroid  $\cdots\text{Br}$  distance of 3.5577 (18) Å] into a supramolecular tri-periodic framework



**Figure 2**  
A fragment of the title compound showing the Z-shaped octabromide anion; numbers are bond lengths (in Å).



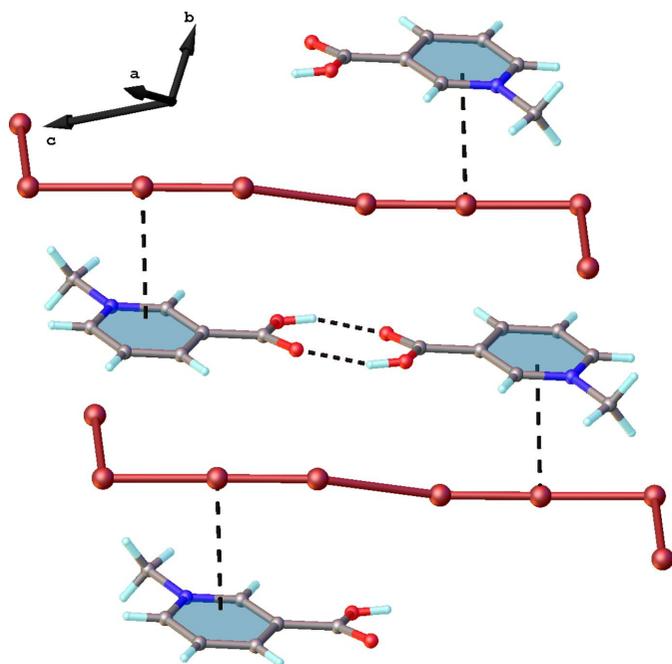
**Figure 3**  
The crystal structure of the title compound in a view along the *b* axis showing infinite chains of anions. Hydrogen bonds between organic cations are shown as black dashed lines. Br...Br contacts between  $[\text{Br}_8]^{2-}$  anions are shown as red dashed lines.

(Fig. 4). Neighboring cations of *N*-methylnicotinic acid are hydrogen-bonded with each other (Fig. 3, Table 1). In addition, the organic cations show weak C—H...Br contacts with the polybromide anions (Table 1) that lead to the creation of layers extending parallel to  $(11\bar{2})$ .

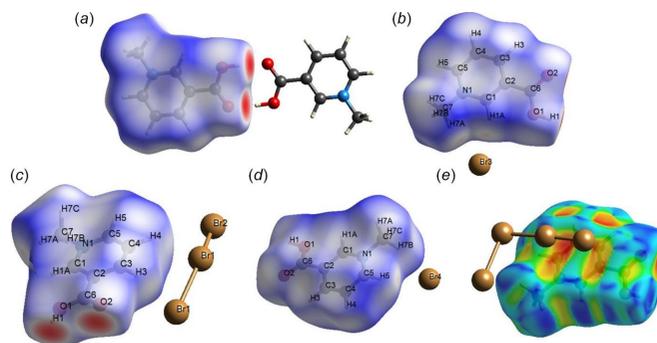
#### 4. Hirshfeld surface analysis

Hirshfeld surface analysis and two-dimensional fingerprint plots of the title compound were generated using *Crystal Explorer* (Spackman *et al.*, 2021).

The graphical representation of the Hirshfeld surface of the 3-carboxy-1-methylpyridinium cation reveals the presence of a

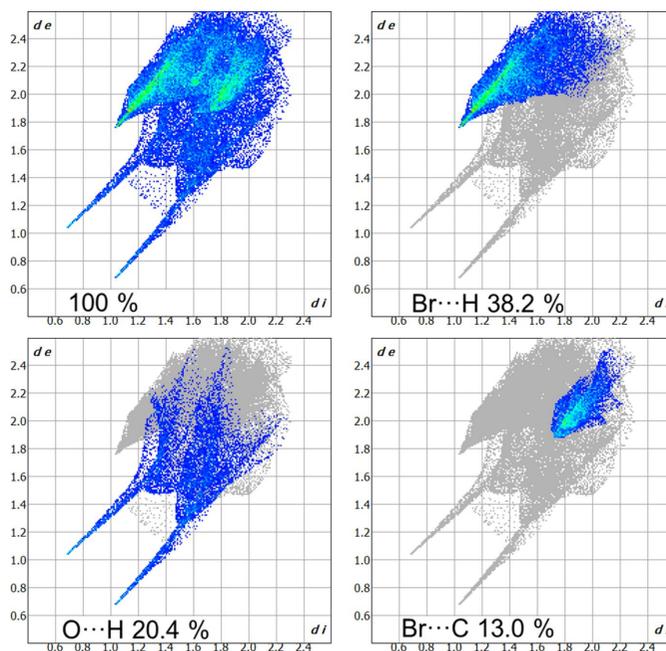


**Figure 4**  
The  $\pi$ ...anion interactions in the title compound.

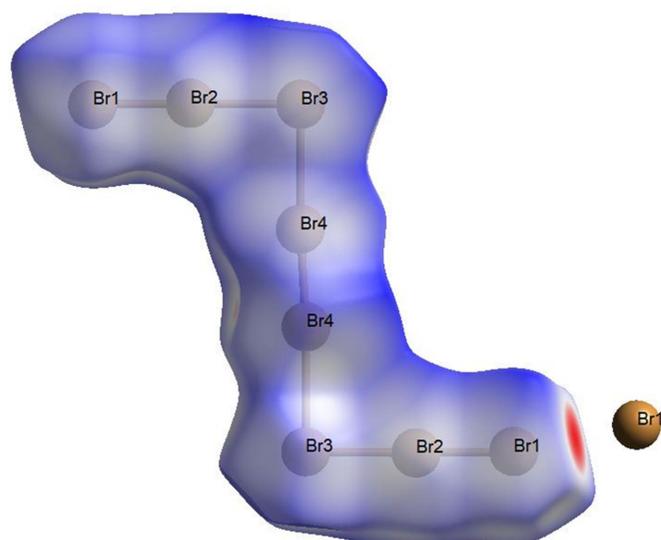


**Figure 5**  
Hirshfeld surface of the 3-carboxy-1-methylpyridinium cation plotted over  $d_{\text{norm}}$  (*a–d*) or shape index (*e*). The neighboring atoms are shown in ball-and-stick mode for clarity. The surface regions with the strongest intermolecular interactions are shown in red.

rather strong O—H...O hydrogen bond with a neighboring organic cation, as shown in bright red ( $d_{\text{norm}}$  plot, Fig. 5*a*), and the presence of weak C—H...Br contacts between the organic cation and the octabromide anion ( $d_{\text{norm}}$  plot, Fig. 5*b–d*) as well as  $\pi$ ...Br interactions between the 3-carboxy-1-methylpyridinium and the fragment of polybromide anions located above the aromatic ring (shape-index plot, Fig. 5*e*). The contributions of selected weak interactions to the crystal packing are shown as two-dimensional Hirshfeld surface fingerprint plots in Fig. 6. The strongest contribution is from Br...H interactions (38.2%) with the next major contributions from O...H (20.4%) and Br...C (13.0%).



**Figure 6**  
Hirshfeld surface fingerprint plot for 3-carboxy-1-methylpyridinium showing overall (100%), Br...H, O...H and Br...C contributions. The  $d_e$  and  $d_i$  values are the distances to the closest external and internal atoms, respectively, from a given point to the Hirshfeld surface.

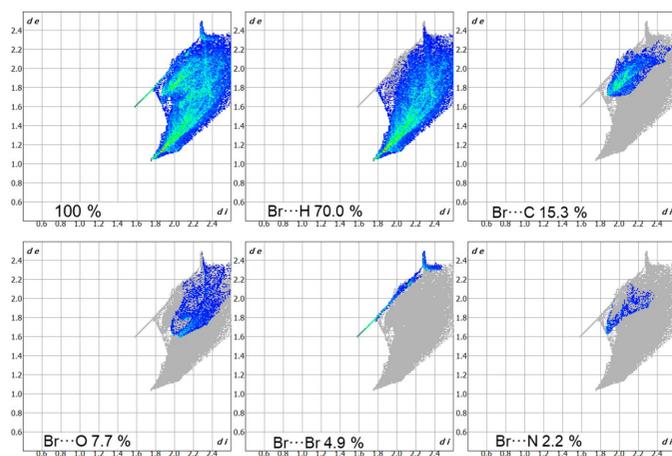


**Figure 7**  
Hirshfeld surface of the octabromide anion plotted over  $d_{\text{norm}}$ . The surface regions with the strongest intermolecular interactions are shown in red.

The graphical representation of the Hirshfeld surface of the octabromide anion is given in Fig. 7 ( $d_{\text{norm}}$  plot). The most prominent interaction is observed with a neighboring  $[\text{Br}_8]^{2-}$  anion and is shown in red. Observed contacts with the organic cation are significantly weaker and are shown in colors from light pink to white. The fingerprint plots for the octabromide anion are given in Fig. 8. Here the highest contributions are observed for  $\text{Br}\cdots\text{H}$  (70.0%) and  $\text{Br}\cdots\text{C}$  (15.3%) contacts. Other types of interaction make significantly smaller contribution to the crystal packing, *viz.*  $\text{Br}\cdots\text{O}$  (7.7%),  $\text{Br}\cdots\text{Br}$  (4.9%) and  $\text{Br}\cdots\text{N}$  (2.2%).

## 5. Database survey

A search of the tribromide moiety in the Cambridge Crystal Database (CSD version 5.43, last update March 2022; Groom



**Figure 8**  
Hirshfeld surface fingerprint plot for octabromide anion showing overall (100%),  $\text{Br}\cdots\text{H}$ ,  $\text{Br}\cdots\text{C}$ ,  $\text{Br}\cdots\text{O}$ ,  $\text{Br}\cdots\text{Br}$  and  $\text{Br}\cdots\text{N}$  contributions.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$2\text{C}_7\text{H}_8\text{NO}_2^+\cdot\text{Br}_8^{2-}$
$M_r$	915.52
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
$a, b, c$ (Å)	6.8537 (5), 7.0873 (6), 14.5145 (6)
$\alpha, \beta, \gamma$ (°)	95.746 (5), 91.156 (4), 115.002 (7)
$V$ (Å <sup>3</sup> )	634.23 (8)
$Z$	1
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	12.67
Crystal size (mm)	0.17 × 0.11 × 0.06
Data collection	
Diffractometer	Xcalibur, Eos
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2021)
$T_{\text{min}}, T_{\text{max}}$	0.458, 1.000
No. of measured, independent and observed [ $I \geq 2\sigma(I)$ ] reflections	9457, 3008, 1848
$R_{\text{int}}$	0.048
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.689
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.047, 0.075, 1.02
No. of reflections	3008
No. of parameters	132
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.38, -1.32

Computer programs: *CrysAlis PRO* (Rigaku OD, 2021), *SHELXT* (Sheldrick, 2015), *OLEX2.refine* (Bourhis *et al.*, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

*et al.*, 2016) revealed 327 crystal structures, while only 28 of them containing four Br atoms connected in a row. The closest analogues to the title compound containing Z-shaped octabromide anions were found to be REKBAK (Robertson *et al.*, 1997), ICOVUS (Fromm *et al.*, 2006), RAQGIB (Wolff *et al.*, 2011) and PAQSAE (Sonnenberg *et al.*, 2017).

## 6. Synthesis and crystallization

0.5 mmol of *N*-methylnicotinamide was mixed with 2 ml of HBr (48%<sub>w</sub>) and left to evaporate. After three days, red crystals appeared in the mixture. They were separated and kept in the mother solution prior to the diffraction measurement.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Aromatic H atoms were positioned geometrically and refined with riding coordinates [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ]. Methyl H atoms were positioned geometrically and were allowed to ride on C atoms and rotate around the N–C bond [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ ]. The H atom of the carboxyl group was found from a difference-Fourier map and was refined with a fixed distance of  $d(\text{O}–\text{H}) = 0.85$  Å and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

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## supporting information

*Acta Cryst.* (2023). E79, 977-981 [https://doi.org/10.1107/S2056989023008460]

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## Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2021); cell refinement: *CrysAlis PRO* (Rigaku OD, 2021); data reduction: *CrysAlis PRO* (Rigaku OD, 2021); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015); program(s) used to refine structure: *olex2.refine* (Bourhis *et al.*, 2015); molecular graphics: *Olex2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *Olex2* (Dolomanov *et al.*, 2009).

## Bis(3-carboxy-1-methylpyridinium) octabromide

## Crystal data

$2\text{C}_7\text{H}_8\text{NO}_2^+ \cdot \text{Br}_8^{2-}$   
 $M_r = 915.52$   
 Triclinic,  $P\bar{1}$   
 $a = 6.8537$  (5) Å  
 $b = 7.0873$  (6) Å  
 $c = 14.5145$  (6) Å  
 $\alpha = 95.746$  (5)°  
 $\beta = 91.156$  (4)°  
 $\gamma = 115.002$  (7)°  
 $V = 634.23$  (8) Å<sup>3</sup>

$Z = 1$   
 $F(000) = 424.594$   
 $D_x = 2.397$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 2335 reflections  
 $\theta = 3.2\text{--}23.7^\circ$   
 $\mu = 12.67$  mm<sup>-1</sup>  
 $T = 293$  K  
 Block, light red  
 $0.17 \times 0.11 \times 0.06$  mm

## Data collection

Xcalibur, Eos  
 diffractometer  
 Detector resolution: 16.1593 pixels mm<sup>-1</sup>  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (CrysAlisPro; Rigaku OD, 2021)  
 $T_{\min} = 0.458$ ,  $T_{\max} = 1.000$   
 9457 measured reflections

3008 independent reflections  
 1848 reflections with  $I \geq 2\sigma(I)$   
 $R_{\text{int}} = 0.048$   
 $\theta_{\max} = 29.3^\circ$ ,  $\theta_{\min} = 2.8^\circ$   
 $h = -8 \rightarrow 9$   
 $k = -9 \rightarrow 9$   
 $l = -19 \rightarrow 19$

## Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.075$   
 $S = 1.02$   
 3008 reflections  
 132 parameters  
 1 restraint  
 13 constraints

H atoms treated by a mixture of independent  
 and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0186P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = -0.001$   
 $\Delta\rho_{\max} = 1.38$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.32$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL,  
 $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.0112 (5)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br2	0.06745 (8)	0.45917 (8)	0.30515 (3)	0.05120 (19)
Br3	-0.18168 (9)	0.43980 (10)	0.15210 (3)	0.0628 (2)
Br1	0.29688 (10)	0.47662 (9)	0.43679 (4)	0.0673 (2)
Br4	-0.04755 (10)	0.12253 (10)	0.04613 (3)	0.0781 (3)
O1	0.9137 (6)	0.8874 (6)	0.3821 (2)	0.0564 (10)
O2	0.7895 (5)	1.0613 (5)	0.4839 (2)	0.0540 (10)
N1	0.4595 (6)	0.8218 (6)	0.1811 (2)	0.0420 (10)
C2	0.6297 (7)	0.9597 (7)	0.3314 (3)	0.0348 (12)
C6	0.7873 (8)	0.9736 (8)	0.4062 (3)	0.0430 (13)
C1	0.6035 (7)	0.8341 (7)	0.2488 (3)	0.0423 (13)
H1a	0.6851 (7)	0.7580 (7)	0.2398 (3)	0.0507 (15)*
C4	0.3646 (8)	1.0582 (8)	0.2730 (3)	0.0477 (13)
H4	0.2828 (8)	1.1345 (8)	0.2802 (3)	0.0572 (16)*
C5	0.3421 (8)	0.9306 (8)	0.1928 (3)	0.0497 (14)
H5	0.2430 (8)	0.9193 (8)	0.1454 (3)	0.0597 (17)*
C3	0.5093 (8)	1.0726 (8)	0.3430 (3)	0.0444 (13)
H3	0.5259 (8)	1.1585 (8)	0.3981 (3)	0.0533 (16)*
C7	0.4279 (8)	0.6816 (8)	0.0942 (3)	0.0660 (17)
H7a	0.508 (4)	0.600 (4)	0.1002 (9)	0.099 (3)*
H7b	0.2774 (10)	0.589 (4)	0.0823 (13)	0.099 (3)*
H7c	0.477 (5)	0.7640 (9)	0.0437 (5)	0.099 (3)*
H1	0.992 (7)	0.879 (9)	0.426 (3)	0.099 (3)*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br2	0.0515 (4)	0.0417 (3)	0.0592 (3)	0.0185 (3)	0.0015 (2)	0.0076 (2)
Br3	0.0686 (4)	0.0771 (5)	0.0512 (3)	0.0412 (3)	-0.0081 (3)	0.0013 (3)
Br1	0.0787 (5)	0.0529 (4)	0.0661 (4)	0.0265 (3)	-0.0223 (3)	0.0019 (3)
Br4	0.0779 (5)	0.0717 (5)	0.0592 (4)	0.0069 (4)	-0.0200 (3)	0.0140 (3)
O1	0.057 (3)	0.077 (3)	0.047 (2)	0.042 (2)	-0.0104 (17)	-0.0010 (19)
O2	0.057 (2)	0.072 (3)	0.0359 (18)	0.036 (2)	-0.0069 (15)	-0.0123 (17)
N1	0.039 (3)	0.046 (3)	0.036 (2)	0.015 (2)	-0.0041 (18)	-0.0001 (19)
C2	0.029 (3)	0.040 (3)	0.032 (2)	0.012 (2)	-0.0030 (19)	0.006 (2)
C6	0.038 (3)	0.045 (3)	0.049 (3)	0.021 (3)	-0.002 (2)	0.005 (3)
C1	0.035 (3)	0.045 (3)	0.043 (3)	0.014 (2)	-0.002 (2)	0.004 (2)
C4	0.049 (3)	0.053 (3)	0.051 (3)	0.032 (3)	-0.002 (2)	0.004 (3)
C5	0.045 (3)	0.063 (4)	0.041 (3)	0.024 (3)	-0.007 (2)	0.009 (3)
C3	0.048 (3)	0.044 (3)	0.039 (3)	0.019 (3)	0.001 (2)	0.002 (2)
C7	0.074 (4)	0.078 (4)	0.041 (3)	0.034 (3)	-0.018 (3)	-0.020 (3)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Br2—Br3	2.7307 (7)	C2—C1	1.380 (6)
Br2—Br1	2.4095 (7)	C2—C3	1.373 (6)

Br3—Br4	3.0625 (10)	C1—H1a	0.9300
Br1—Br1 <sup>i</sup>	3.1813 (12)	C4—H4	0.9300
Br4—Br4 <sup>ii</sup>	2.4002 (15)	C4—C5	1.365 (6)
O1—C6	1.290 (6)	C4—C3	1.370 (6)
O1—H1	0.845 (19)	C5—H5	0.9300
O2—C6	1.228 (5)	C3—H3	0.9300
N1—C1	1.348 (5)	C7—H7a	0.9600
N1—C5	1.332 (6)	C7—H7b	0.9600
N1—C7	1.476 (5)	C7—H7c	0.9600
C2—C6	1.483 (6)		
Br1—Br2—Br3	178.04 (3)	H1a—C1—C2	120.0 (3)
Br4—Br3—Br2	90.37 (2)	C5—C4—H4	120.4 (3)
Br1 <sup>i</sup> —Br1—Br2	162.42 (4)	C3—C4—H4	120.4 (3)
Br4 <sup>ii</sup> —Br4—Br3	176.22 (3)	C3—C4—C5	119.2 (5)
H1—O1—C6	116 (4)	C4—C5—N1	121.2 (4)
C5—N1—C1	120.7 (4)	H5—C5—N1	119.4 (3)
C7—N1—C1	119.4 (4)	H5—C5—C4	119.4 (3)
C7—N1—C5	119.8 (4)	C4—C3—C2	119.8 (4)
C1—C2—C6	120.3 (5)	H3—C3—C2	120.1 (3)
C3—C2—C6	120.6 (4)	H3—C3—C4	120.1 (3)
C3—C2—C1	119.2 (4)	H7a—C7—N1	109.5
O2—C6—O1	125.2 (4)	H7b—C7—N1	109.5
C2—C6—O1	114.6 (4)	H7b—C7—H7a	109.5
C2—C6—O2	120.1 (5)	H7c—C7—N1	109.5
C2—C1—N1	120.0 (5)	H7c—C7—H7a	109.5
H1a—C1—N1	120.0 (3)	H7c—C7—H7b	109.5
O1—C6—C2—C1	9.9 (5)	N1—C1—C2—C6	179.8 (4)
O1—C6—C2—C3	-169.6 (4)	N1—C1—C2—C3	-0.6 (5)
O2—C6—C2—C1	-169.9 (4)	N1—C5—C4—C3	-0.7 (6)
O2—C6—C2—C3	10.6 (5)	C2—C3—C4—C5	0.3 (5)

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

#### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ O2 <sup>iii</sup>	0.80 (7)	1.89 (7)	2.668 (5)	164 (7)
C1—H1A $\cdots$ Br3 <sup>iv</sup>	0.93	2.96	3.838 (5)	158
C5—H5 $\cdots$ Br4 <sup>v</sup>	0.93	2.99	3.881 (5)	160
C7—H7A $\cdots$ Br3 <sup>iv</sup>	0.96	2.92	3.857 (6)	166

Symmetry codes: (iii)  $-x+2, -y+2, -z+1$ ; (iv)  $x+1, y, z$ ; (v)  $-x, -y+1, -z$ .