

catena-Poly[bis(4-methylbenzylammonium) [[dibromidocadmate(II)]-di- μ -bromido]]

Ramkumar Aarthi,^a Aravazhi Amalan Thiruvalluvar^{b*} and Chidambaram Ramachandra Raja^a

^aDepartment of Physics, Government Arts College (Autonomous), Kumbakonam 612 002, Tamilnadu, India, and

^bPrincipal, Kunthavai Naacchiyaar Government Arts College for Women (Autonomous), Thanjavur 613 007, Tamilnadu, India. *Correspondence e-mail: thiruvalluvar.a@gmail.com

Received 14 May 2018

Accepted 25 May 2018

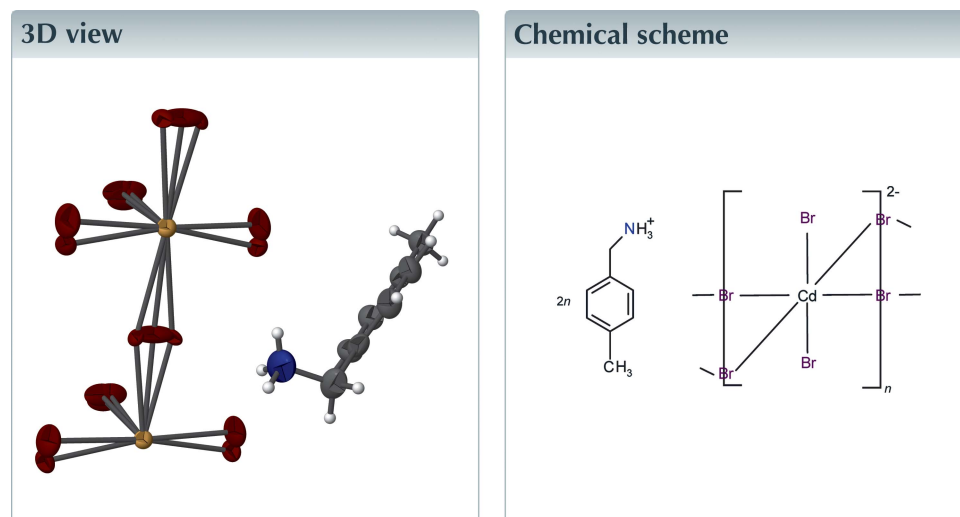
Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; centrosymmetric organic–inorganic hybrid material; C—H \cdots Br and N—H \cdots Br hydrogen bondings; C—H \cdots π interactions; disorder.

CCDC reference: 1845375

Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the centrosymmetric organic–inorganic hybrid salt, $\{(C_8H_{12}N)_2[CdBr_4]\}_n$, comprises of one 4-methylbenzylammonium cation and one half of a disordered $[CdBr_4]^{2-}$ anion that is completed by application of mirror symmetry. The resulting $CdBr_6$ octahedra share edges to form ${}^\infty[CdBr_{4/2}Br_{2/2}]^{2-}$ layers parallel to the *ac* plane. Cations and anions are connected by N—H \cdots Br and C—H \cdots Br hydrogen bonds. No π – π stacking interactions are observed between the benzene rings, but C—H \cdots π interactions towards them are found.



Structure description

Non-linear optical materials are suitable candidates for photonics and optoelectronic industries. Applications such as frequency conversion, optical switching *etc.*, can be well provided using these materials (Marcy *et al.*, 1992). Organic non-linear optical crystals with conjugated π electrons usually show a higher non-linear optical response in comparison with inorganic crystals. However, due to weak intermolecular interactions, organic crystals frequently have a lower mechanical and thermal stability, which does not allow them to be used in high-power laser applications. On the other hand, inorganic crystals have better mechanical and thermal stability, but they are not efficient in producing large non-linear optical effects due to the presence of ionic or covalent bonds (Jiang & Fang, 1999). To overcome the disadvantage of organic and inorganic crystals in this respect, organic–inorganic hybrid crystals may be used by combining their beneficial properties. Moreover, these organic–inorganic hybrid crystals often possess greater third order non-linear optical properties. Herein we report the synthesis and crystal structure

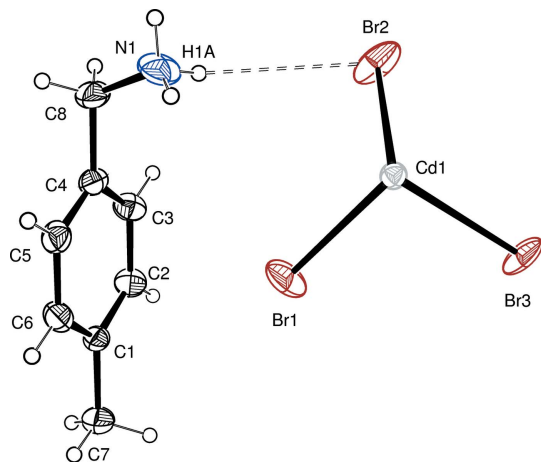


Figure 1
A view of the asymmetric unit showing the atom numbering and displacement ellipsoids drawn at the 30% probability level. Only the major part of the disordered anion is displayed. Dashed lines indicate hydrogen-bonding interaction.

of a new organic–inorganic hybrid compound, bis(4-methylbenzylammonium) tetrabromidocadmate.

The asymmetric unit of the title compound consists of one half of a tetrabromidocadmate anion, $[\text{CdBr}_4]^{2-}$, and one 4-methylbenzylammonium cation, $(\text{C}_8\text{H}_{12}\text{N})^+$, as shown in Fig. 1. The cadmium cation is located on a mirror plane (Wyckoff position 4c) and its resulting coordination environ-

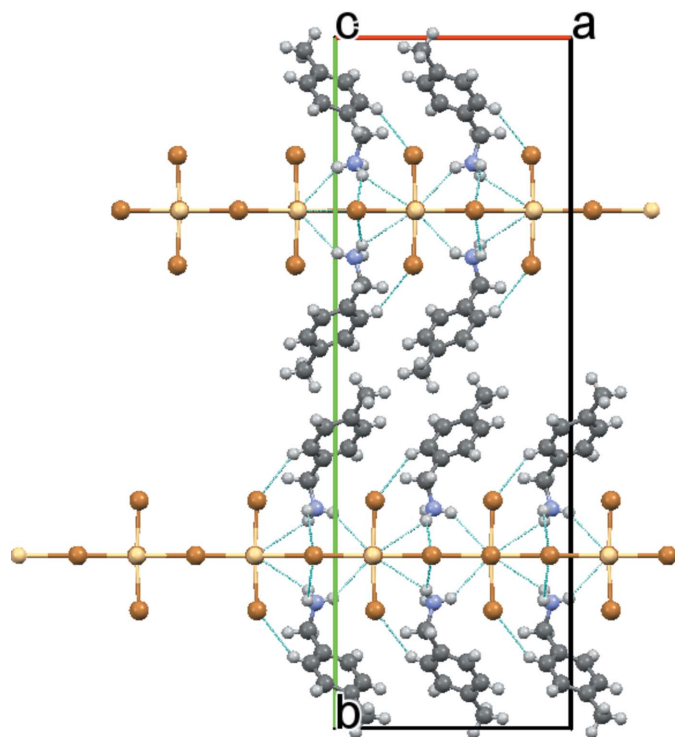


Figure 2
Packing diagram of the title compound viewed down the *c* axis, showing the alternate stacking of organic and inorganic layers. Dashed lines indicate the hydrogen-bonding network.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

*Cg*1 is the centroid of the C1–C6 benzene ring.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C8–H8B...Br1 ^{ri}	0.97	3.03	3.707 (8)	128
N1–H1B...Br3 ⁱ	0.85 (2)	2.79 (4)	3.521 (7)	145 (5)
N1–H1B...Br1 ^{i'}	0.85 (2)	3.11 (4)	3.597 (7)	119 (3)
N1–H1B...Br3 ^{ri}	0.85 (2)	2.83 (4)	3.59 (2)	150 (5)
N1–H1B...Br3 ^{rii}	0.85 (2)	3.01 (4)	3.74 (2)	147 (5)
N1–H1C...Br2 ^z	0.86 (2)	2.84 (3)	3.604 (6)	149 (4)
N1–H1C...Br3 ⁱⁱⁱ	0.86 (2)	3.05 (4)	3.647 (7)	129 (4)
N1–H1C...Br2 ^{zi}	0.86 (2)	2.63 (3)	3.371 (12)	145 (4)
N1–H1C...Br3 ⁱⁱⁱⁱⁱ	0.86 (2)	2.82 (4)	3.43 (2)	130 (4)
N1–H1C...Br3 ^{riiii}	0.86 (2)	2.97 (5)	3.59 (3)	132 (4)
N1–H1A...Br1 ⁱⁱⁱ	0.85 (2)	3.06 (3)	3.825 (8)	150 (4)
N1–H1A...Br2	0.85 (2)	2.96 (5)	3.579 (7)	131 (5)
N1–H1A...Br2 ^{z'}	0.85 (2)	2.57 (5)	3.239 (13)	136 (5)
C7–H7C... <i>Cg</i> 1 ^v	0.96	2.95	3.824 (5)	152

Symmetry codes: (i) $x, y, z + 1$; (ii) $x, -y + \frac{1}{2}, z + 1$; (iii) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + 1, -y + 1, -z + 1$.

ment is distorted octahedral. The three unique bromine ligands are disordered around the mirror plane. Individual CdBr_6 octahedra share four corners to form polymeric ${}^\infty[\text{CdBr}_{4/2}\text{Br}_{2/2}]^{2-}$ layers extending parallel to the *ac* plane (Fig. 2).

The 4-methylbenzylammonium cations are sandwiched between the tetrabromidocadmate layers (Fig. 2). They are linked among themselves by weak (methyl)C–H... π interactions (Fig. 3, Table 1). The crystal packing is assured by a

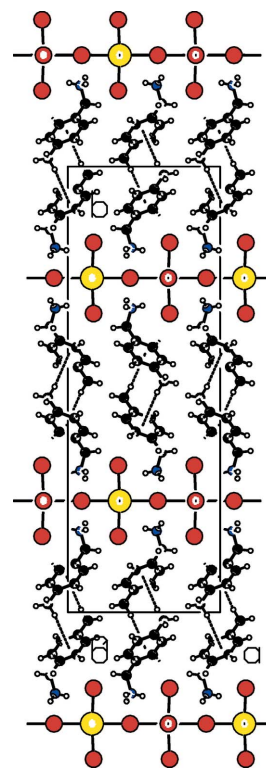


Figure 3
Partial packing showing the *C*7–*H*7C... π interaction involving the C1–C6 benzene ring.

Table 2
Experimental details.

Crystal data	
Chemical formula	(C ₈ H ₁₂ N) ₂ [CdBr ₄]
<i>M</i> _r	676.41
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.2127 (5), 32.8269 (15), 5.6279 (3)
<i>V</i> (Å ³)	2071.51 (17)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	8.77
Crystal size (mm)	0.15 × 0.10 × 0.10
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2004)
<i>T</i> _{min} , <i>T</i> _{max}	0.389, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	37568, 2984, 1970
<i>R</i> _{int}	0.069
(sin θ/λ) _{max} (Å ⁻¹)	0.697
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.037, 0.088, 1.05
No. of reflections	2984
No. of parameters	142
No. of restraints	24
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.81, -1.00

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *PLATON* (Spek, 2009), *Mercury* (Macrae *et al.*, 2008) and *pubCIF* (Westrip, 2010).

complex hydrogen-bonding system, involving the positively charged ammonium groups and to a minor extent the methylene group as donor groups, and the bromide ligands of the anionic layers as acceptor groups (Table 1). Bond lengths and angles within the cation have their usual values as reported for the isotopic compound bis(4-methylbenzylammonium) tetrachloridocadmiate (Kefi *et al.*, 2011). However, the anion in the latter shows no disorder.

Synthesis and crystallization

Bis(4-methylbenzylammonium) tetrabromidocadmiate(II) single crystals were grown by the solution growth solvent

evaporation method. A mixture of 4-methylbenzylamine (2 mmol, 1.27 ml) and cadmium bromide (CdBr₂) (1 mmol, 1.36 g) was dissolved in diluted hydrobromic acid (HBr) (10 ml, 1 *M*). The resultant solution was stirred using a magnetic stirrer for 3 h and kept in a constant temperature bath at 311 K. After 15 d colourless single crystals of the title compound were harvested.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The anionic structure shows disorder of all bromine atoms relative to the mirror plane, with occupancies of 0.720 (11) for the major part and 0.280 (11) for the minor part (denoted by primed characters). Similarity restraints (SIMU) were used to model the disorder.

Acknowledgements

The authors are thankful to the Sophisticated Analytical Instrument Facility (SAIF), IITM, Chennai 600 036, Tamilnadu, India for the single-crystal X-ray diffraction data.

Funding information

Funding for this research was provided by: Council of Scientific and Industrial Research (CSIR), New Delhi, India [grant No. 03(1301)13/EMR II to CR].

References

- Bruker (2004). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Jiang, M. & Fang, Q. (1999). *Adv. Mater.* **11**, 1147–1151.
- Kefi, R., Zeller, M., Lefebvre, F. & Ben Nasr, C. (2011). *Int. J. Inorg. Chem.* Article ID, 274073, 1–7.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Marcy, H. O., Warren, L. F., Webb, M. S., Ebbers, C. A., Velsko, S. P., Kennedy, G. C. & Catella, G. C. (1992). *Appl. Opt.* **31**, 5051–5060.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2018). 3, x180780 [https://doi.org/10.1107/S2414314618007800]

catena-Poly[bis(4-methylbenzylammonium) [[dibromidocadmate(II)]-di- μ -bromido]]

Ramkumar Aarthi, Aravazhi Amalan Thiruvalluvar and Chidambaram Ramachandra Raja

catena-Poly[bis(4-methylbenzylammonium) [[dibromidocadmate(II)]-di- μ -bromido]]

Crystal data

(C₈H₁₂N)₂[CdBr₄]

$M_r = 676.41$

Orthorhombic, *Pnma*

$a = 11.2127$ (5) Å

$b = 32.8269$ (15) Å

$c = 5.6279$ (3) Å

$V = 2071.51$ (17) Å³

$Z = 4$

$F(000) = 1288$

$D_x = 2.169$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6170 reflections

$\theta = 2.5$ – 27.5°

$\mu = 8.77$ mm⁻¹

$T = 296$ K

Block, colourless

0.15 × 0.10 × 0.10 mm

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and φ scan

Absorption correction: multi-scan
(SADABS; Bruker, 2004)

$T_{\min} = 0.389$, $T_{\max} = 0.746$

37568 measured reflections

2984 independent reflections

1970 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.069$

$\theta_{\max} = 29.7^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -14 \rightarrow 15$

$k = -45 \rightarrow 45$

$l = -7 \rightarrow 7$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.088$

$S = 1.05$

2984 reflections

142 parameters

24 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0277P)^2 + 5.1831P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.81$ e Å⁻³

$\Delta\rho_{\min} = -1.00$ e Å⁻³

Extinction correction: SHELXL2018

(Sheldrick, 2015b),

$Fc^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0082 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.4324 (4)	0.44964 (12)	0.3872 (7)	0.0372 (9)	
C2	0.5437 (4)	0.43565 (14)	0.3195 (8)	0.0456 (10)	
H2	0.579347	0.446011	0.183098	0.055*	
C3	0.6027 (4)	0.40631 (14)	0.4526 (9)	0.0472 (11)	
H3	0.677009	0.396989	0.403256	0.057*	
C4	0.5526 (4)	0.39089 (12)	0.6566 (8)	0.0412 (10)	
C5	0.4428 (5)	0.40513 (14)	0.7255 (8)	0.0472 (11)	
H5	0.407920	0.395140	0.863571	0.057*	
C6	0.3835 (4)	0.43407 (14)	0.5926 (8)	0.0459 (11)	
H6	0.309133	0.443235	0.642622	0.055*	
C7	0.3682 (5)	0.48134 (15)	0.2413 (8)	0.0520 (11)	
H7A	0.290710	0.486181	0.307885	0.078*	
H7B	0.359938	0.471808	0.080859	0.078*	
H7C	0.413262	0.506217	0.242179	0.078*	
C8	0.6147 (5)	0.35857 (15)	0.8012 (9)	0.0597 (14)	
H8A	0.700247	0.361869	0.783922	0.072*	
H8B	0.595227	0.362480	0.967529	0.072*	
Cd1	0.34125 (3)	0.250000	0.23592 (6)	0.02551 (12)	
Br1	0.3312 (5)	0.32949 (4)	0.2275 (4)	0.0651 (6)	0.720 (11)
Br2	0.5909 (3)	0.250000	0.2364 (9)	0.0747 (17)	0.720 (11)
Br3	0.3399 (6)	0.250000	−0.2602 (13)	0.0559 (8)	0.720 (11)
Br1'	0.3826 (6)	0.32979 (8)	0.2391 (5)	0.0347 (11)	0.280 (11)
Br2'	0.5958 (6)	0.2653 (3)	0.247 (2)	0.0274 (13)	0.140 (6)
Br3'	0.3238 (17)	0.2539 (8)	−0.275 (4)	0.0559 (8)	0.140 (6)
N1	0.5829 (5)	0.31794 (13)	0.7335 (10)	0.0681 (13)	
H1B	0.5098 (18)	0.3121 (17)	0.719 (8)	0.082*	
H1C	0.614 (4)	0.3004 (15)	0.828 (7)	0.082*	
H1A	0.617 (4)	0.3150 (18)	0.599 (5)	0.082*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.044 (2)	0.030 (2)	0.038 (2)	0.0022 (17)	−0.0081 (18)	0.0000 (17)
C2	0.048 (3)	0.041 (2)	0.048 (2)	−0.002 (2)	0.002 (2)	0.0096 (19)
C3	0.039 (2)	0.043 (3)	0.059 (3)	0.001 (2)	−0.001 (2)	0.004 (2)
C4	0.051 (2)	0.027 (2)	0.045 (2)	−0.0041 (19)	−0.017 (2)	0.0010 (17)
C5	0.064 (3)	0.042 (2)	0.035 (2)	0.002 (2)	0.002 (2)	0.0024 (19)
C6	0.051 (3)	0.040 (3)	0.047 (3)	0.008 (2)	0.003 (2)	−0.002 (2)
C7	0.057 (3)	0.045 (2)	0.053 (3)	0.010 (2)	−0.009 (2)	0.006 (2)

C8	0.083 (4)	0.037 (2)	0.059 (3)	0.007 (2)	-0.030 (3)	0.005 (2)
Cd1	0.02616 (19)	0.02671 (18)	0.02367 (19)	0.000	0.00016 (16)	0.000
Br1	0.074 (2)	0.0250 (4)	0.0961 (8)	0.0072 (5)	0.0031 (9)	0.0004 (4)
Br2	0.0194 (7)	0.158 (5)	0.0468 (9)	0.000	-0.0007 (7)	0.000
Br3	0.0405 (19)	0.110 (2)	0.0168 (10)	0.000	-0.0038 (11)	0.000
Br1'	0.0312 (19)	0.0227 (8)	0.0502 (14)	-0.0024 (8)	-0.0081 (11)	-0.0006 (8)
Br2'	0.0191 (19)	0.019 (2)	0.044 (3)	0.0048 (17)	-0.001 (2)	0.008 (3)
Br3'	0.0405 (19)	0.110 (2)	0.0168 (10)	0.000	-0.0038 (11)	0.000
N1	0.078 (3)	0.031 (2)	0.095 (4)	0.003 (2)	-0.018 (3)	0.011 (3)

Geometric parameters (Å, °)

C1—C6	1.378 (6)	Cd1—Br1	2.6124 (11)
C1—C2	1.383 (6)	Cd1—Br1 ⁱ	2.6125 (11)
C1—C7	1.508 (6)	Cd1—Br1'	2.660 (2)
C2—C3	1.388 (6)	Cd1—Br1 ⁱⁱ	2.660 (2)
C2—H2	0.9300	Cd1—Br3 ⁱⁱⁱ	2.77 (2)
C3—C4	1.374 (6)	Cd1—Br3 ⁱⁱⁱⁱ	2.77 (2)
C3—H3	0.9300	Cd1—Br3	2.792 (8)
C4—C5	1.373 (7)	Cd1—Br2	2.799 (3)
C4—C8	1.507 (6)	Cd1—Br2 ^{iv}	2.800 (7)
C5—C6	1.380 (6)	Cd1—Br2 ^v	2.800 (7)
C5—H5	0.9300	Cd1—Br2 ^v	2.812 (3)
C6—H6	0.9300	Cd1—Br3 ⁱⁱ	2.836 (8)
C7—H7A	0.9600	Br2'—Br2 ⁱⁱ	1.008 (19)
C7—H7B	0.9600	Br3'—Br3 ⁱⁱ	0.26 (6)
C7—H7C	0.9600	N1—H1B	0.846 (18)
C8—N1	1.432 (6)	N1—H1C	0.857 (18)
C8—H8A	0.9700	N1—H1A	0.853 (18)
C8—H8B	0.9700		
C6—C1—C2	117.8 (4)	Br1 ⁱ —Cd1—Br3 ⁱⁱⁱ	88.2 (6)
C6—C1—C7	121.6 (4)	Br1—Cd1—Br3	88.95 (5)
C2—C1—C7	120.6 (4)	Br1 ⁱ —Cd1—Br3	88.95 (5)
C1—C2—C3	120.8 (4)	Br1—Cd1—Br2	92.47 (13)
C1—C2—H2	119.6	Br1 ⁱ —Cd1—Br2	92.47 (13)
C3—C2—H2	119.6	Br3—Cd1—Br2	90.36 (17)
C4—C3—C2	120.8 (4)	Br1—Cd1—Br2 ^{iv}	97.9 (3)
C4—C3—H3	119.6	Br1 ⁱ —Cd1—Br2 ^{iv}	77.20 (18)
C2—C3—H3	119.6	Br3—Cd1—Br2 ^{iv}	91.6 (3)
C5—C4—C3	118.5 (4)	Br2—Cd1—Br2 ^{iv}	169.44 (19)
C5—C4—C8	120.1 (5)	Br1—Cd1—Br2 ^{iv}	77.20 (18)
C3—C4—C8	121.4 (5)	Br1 ⁱ —Cd1—Br2 ^v	97.9 (3)
C4—C5—C6	120.9 (4)	Br3—Cd1—Br2 ^v	91.6 (3)
C4—C5—H5	119.5	Br2—Cd1—Br2 ^v	169.44 (19)
C6—C5—H5	119.5	Br1—Cd1—Br2 ^v	87.59 (12)
C1—C6—C5	121.2 (4)	Br1 ⁱ —Cd1—Br2 ^v	87.59 (12)
C1—C6—H6	119.4	Br3—Cd1—Br2 ^v	92.87 (17)

C5—C6—H6	119.4	Br2—Cd1—Br2 ^v	176.769 (15)
C1—C7—H7A	109.5	Br1—Cd1—Br3 ⁱⁱ	91.03 (5)
C1—C7—H7B	109.5	Br1 ⁱ —Cd1—Br3 ⁱⁱ	91.03 (5)
H7A—C7—H7B	109.5	Br3—Cd1—Br3 ⁱⁱ	179.4 (3)
C1—C7—H7C	109.5	Br2—Cd1—Br3 ⁱⁱ	90.26 (17)
H7A—C7—H7C	109.5	Br2 ^v —Cd1—Br3 ⁱⁱ	86.51 (17)
H7B—C7—H7C	109.5	Cd1—Br2—Cd1 ^{vi}	176.9 (2)
N1—C8—C4	113.4 (4)	Cd1—Br3—Cd1 ^{vii}	179.4 (3)
N1—C8—H8A	108.9	Br2 ⁱ —Br2'—Cd1	79.99 (18)
C4—C8—H8A	108.9	Cd1 ^{vi} —Br2'—Cd1	159.6 (4)
N1—C8—H8B	108.9	Br3 ⁱ —Br3'—Cd1	87.5 (5)
C4—C8—H8B	108.9	Cd1 ^{vii} —Br3'—Cd1	170.5 (8)
H8A—C8—H8B	107.7	C8—N1—H1B	119 (4)
Br1—Cd1—Br1 ⁱ	174.6 (3)	C8—N1—H1C	111 (4)
Br1—Cd1—Br1 ⁱⁱ	172.4 (3)	H1B—N1—H1C	108 (3)
Br1 ⁱ —Cd1—Br1 ⁱⁱ	12.59 (4)	C8—N1—H1A	103 (4)
Br1—Cd1—Br3 ⁱⁱⁱ	88.2 (6)	H1B—N1—H1A	109 (3)
Br1 ⁱ —Cd1—Br3 ⁱⁱⁱ	93.5 (6)	H1C—N1—H1A	107 (3)
Br1—Cd1—Br3 ⁱⁱⁱ	93.5 (6)		
C6—C1—C2—C3	1.2 (7)	C8—C4—C5—C6	-178.6 (4)
C7—C1—C2—C3	-179.7 (4)	C2—C1—C6—C5	-0.7 (7)
C1—C2—C3—C4	-0.9 (7)	C7—C1—C6—C5	-179.9 (4)
C2—C3—C4—C5	0.1 (7)	C4—C5—C6—C1	-0.1 (7)
C2—C3—C4—C8	179.1 (4)	C5—C4—C8—N1	87.8 (6)
C3—C4—C5—C6	0.4 (7)	C3—C4—C8—N1	-91.2 (6)

Symmetry codes: (i) $x, -y+1/2, z$; (ii) $x, y, z+1$; (iii) $x, -y+1/2, z+1$; (iv) $x-1/2, -y+1/2, -z+1/2$; (v) $x-1/2, y, -z+1/2$; (vi) $x+1/2, y, -z+1/2$; (vii) $x, y, z-1$.

Hydrogen-bond geometry (\AA , $^\circ$)

Cg1 is the centroid of the C1–C6 benzene ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C8—H8B \cdots Br1 ⁱⁱⁱ	0.97	3.03	3.707 (8)	128
N1—H1B \cdots Br3 ⁱⁱ	0.85 (2)	2.79 (4)	3.521 (7)	145 (5)
N1—H1B \cdots Br1'	0.85 (2)	3.11 (4)	3.597 (7)	119 (3)
N1—H1B \cdots Br3 ⁱⁱⁱ	0.85 (2)	2.83 (4)	3.59 (2)	150 (5)
N1—H1B \cdots Br3 ⁱⁱⁱ	0.85 (2)	3.01 (4)	3.74 (2)	147 (5)
N1—H1C \cdots Br2 ⁱⁱ	0.86 (2)	2.84 (3)	3.604 (6)	149 (4)
N1—H1C \cdots Br3 ^{vi}	0.86 (2)	3.05 (4)	3.647 (7)	129 (4)
N1—H1C \cdots Br2 ⁱⁱ	0.86 (2)	2.63 (3)	3.371 (12)	145 (4)
N1—H1C \cdots Br3 ^{vi}	0.86 (2)	2.82 (4)	3.43 (2)	130 (4)
N1—H1C \cdots Br3 ^{viii}	0.86 (2)	2.97 (5)	3.59 (3)	132 (4)
N1—H1A \cdots Br1 ^{vi}	0.85 (2)	3.06 (3)	3.825 (8)	150 (4)
N1—H1A \cdots Br2	0.85 (2)	2.96 (5)	3.579 (7)	131 (5)
N1—H1A \cdots Br2'	0.85 (2)	2.57 (5)	3.239 (13)	136 (5)
C7—H7C \cdots Cg1 ^{ix}	0.96	2.95	3.824 (5)	152

Symmetry codes: (ii) $x, y, z+1$; (iii) $x, -y+1/2, z+1$; (vi) $x+1/2, y, -z+1/2$; (viii) $x+1/2, -y+1/2, -z+1/2$; (ix) $-x+1, -y+1, -z+1$.