

## Poly[triaqua- $\mu_4$ -pyridine-3,5-dicarboxylato-barium(II)]

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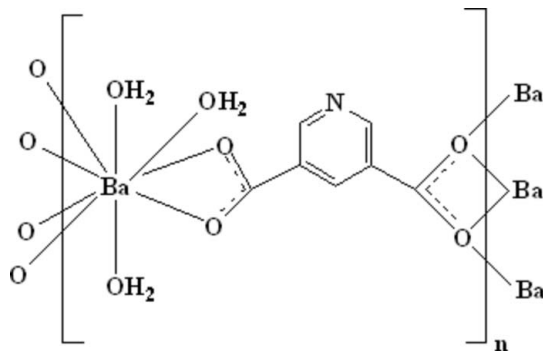
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Key indicators: single-crystal X-ray study;  $T = 100$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.020;  $wR$  factor = 0.048; data-to-parameter ratio = 18.2.

The reaction of the proton-transfer compound (pdaH<sub>2</sub>)(py-3,5-dc)·H<sub>2</sub>O (pda = propane-1,3-diamine and py-3,5-dcH<sub>2</sub> = pyridine-3,5-dicarboxylic acid) with Ba(NO<sub>3</sub>)<sub>2</sub> leads to the formation of the title polymeric compound, [Ba(C<sub>7</sub>H<sub>3</sub>NO<sub>4</sub>)(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub>. The Ba<sup>II</sup> atom is nine-coordinated by six carboxylate O atoms from the (py-3,5-dc)<sup>2-</sup> ligands, and three O atoms from the coordinated water molecules. The coordination polyhedron around the Ba<sup>II</sup> atom is best described as tricapped trigonal-prismatic. In the crystal structure, intermolecular interactions, such as X—H···O hydrogen bonds ( $X = \text{O}$  and C) and  $\pi$ – $\pi$  stacking [centroid–centroid distances between pyridine rings of 3.6191 (13) and 3.6192 (13) Å] play an important role in stabilizing the supramolecular structure.

### Related literature

For related literature, see: Aghabozorg *et al.* (2006, 2007, 2008); Dorazco-Gonzalez *et al.* (2006); Starosta *et al.* (2002a,b).



### Experimental

#### Crystal data

[Ba(C<sub>7</sub>H<sub>3</sub>NO<sub>4</sub>)(H<sub>2</sub>O)<sub>3</sub>]  
 $M_r = 356.49$   
Monoclinic,  $P2_1/c$   
 $a = 7.5922$  (4) Å  
 $b = 18.5576$  (10) Å  
 $c = 7.1832$  (4) Å  
 $\beta = 90.499$  (5)°  
 $V = 1012.02$  (9) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 3.95$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
0.25 × 0.25 × 0.20 mm

#### Data collection

Bruker SMART APEXII CCD  
area-detector diffractometer  
Absorption correction: multi-scan  
(APEX2; Bruker, 2005)  
 $T_{\min} = 0.386$ ,  $T_{\max} = 0.455$   
10713 measured reflections  
2664 independent reflections  
2575 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.035$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$   
 $wR(F^2) = 0.048$   
 $S = 1.00$   
2664 reflections  
146 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\max} = 1.18$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.66$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA···O1 <sup>i</sup>	0.84	2.13	2.924 (2)	158
O1W—H1WB···O1 <sup>ii</sup>	0.84	1.89	2.730 (2)	176
O2W—H2WA···O2 <sup>iii</sup>	0.81	1.96	2.761 (2)	172
O2W—H2WB···N1 <sup>iv</sup>	0.83	2.06	2.873 (3)	165
O3W—H3WA···N1 <sup>v</sup>	0.85	2.48	3.284 (3)	159
O3W—H3WB···O1W <sup>vi</sup>	0.85	2.02	2.851 (3)	165
C3—H3···O2W <sup>vii</sup>	0.93	2.47	3.362 (3)	161

Symmetry codes: (i)  $x, y, z + 1$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $x, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (iv)  $x - 1, y, z + 1$ ; (v)  $x - 1, y, z$ ; (vi)  $-x, -y + 1, -z + 1$ ; (vii)  $x, -y + \frac{3}{2}, z - \frac{1}{2}$ .

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2; data reduction: APEX2; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2029).

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**supplementary materials**

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## Poly[triaqua- $\mu_4$ -pyridine-3,5-dicarboxylato-barium(II)]

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### Comment

Recent interest of our researching group has focused on the synthesis and characterization of novel metal complexes of proton transfer compounds obtained using dipicolinic acid (Aghabozorg *et al.*, 2007). A convenient path to obtain polymeric structures is to use a multifunctional ligand to link metal ions to form an infinite arrangement (Starosta *et al.*, 2002a,b); Dorazco-Gonzalez *et al.*, 2006). The reaction of the proton transfer compound (pdaH<sub>2</sub>)(py-3,5-dc).H<sub>2</sub>O [pda = propane-1,3-diamine and py-3,5-dcH<sub>2</sub> = pyridine-3,5-dicarboxylic acid (Aghabozorg *et al.*, 2006)] with Ba(NO<sub>3</sub>)<sub>2</sub>, in aqueous solution with a 1:2 molar ratio, lead to the formation of the title polymeric compound, (I).

The monomeric units in the polymer (I) consist of one Ba<sup>II</sup> atom, one (py-3,5-dc)<sup>2-</sup> dianion and three aqua (H<sub>2</sub>O) ligands. The Ba<sup>II</sup> atom is nine-coordinate with six carboxylate oxygen atoms from the bridging (py-3,5-dc)<sup>2-</sup> ligands and three oxygen atoms from the coordinated water molecules (Figs. 1 and 2). The summation of bond angles O2W—Ba1—O3<sup>ii</sup>, O3<sup>ii</sup>—Ba1—O1 and O2W—Ba1—O1 is 360.94° hence, the Ba1 atom is located in the center of the plane (O1,O2,O3W<sup>ii</sup>). Atoms O2, O3W and O3<sup>i</sup> form a triangle, and atoms O1W, O4<sup>ii</sup>, O4<sup>iii</sup> form another triangle. So a prism, consisting of six O-atoms and three caps (O2W, O3<sup>iii</sup> and O1) on the faces around the Ba(II) atom is formed. The coordination polyhedron around the Ba<sup>II</sup> atom is hence, best described as a tricapped trigonal prism (Fig. 3).

In the molecular structure of (I) atoms O1 and O2, from one of the carboxylate groups, have only one Ba—O bond, while atoms O3 and O4 from three neighboring carboxylate groups have two Ba—O bonds. The bond distances between barium and the oxygen atoms are in the range 2.7399 (18)–2.8669 (16) Å.

In the crystal structure of (I) there are several O—H...O hydrogen bonds [in the range 2.730 (2)–2.924 (2) Å], and the pyridine N-atoms have N—H...O hydrogen bonds with neighboring coordinated water molecules [in the range 2.873 (3)–3.284 (3) Å]. C—H...O hydrogen bonds [with D...A distance 3.362 (3) Å], are also present (Table 1). There are  $\pi$ - $\pi$  stacking interactions between symmetry related pyridine (N1/C1—C5) rings with centroid...centroid distances of 3.6191 (13) and 3.6192 (13) Å (symmetry codes: (i) =  $x, -y + 3/2, z + 1/2$  and  $x$ ; (ii) =  $-y + 3/2, z - 1/2$ , respectively) (Fig.4).

All of these intermolecular interactions play an important role in forming the three dimensional polymeric system and stabilizing the structure.

### Experimental

The proton transfer compound (pdaH<sub>2</sub>)(py-3,5-dc), was prepared by the reaction of pyridine-3,5-dicarboxylic acid [py-3,5-dcH<sub>2</sub>], with propane-1,3-diamine [pda], (Aghabozorg *et al.*, 2006). Compound (I) was prepared by the reaction between Ba(NO<sub>3</sub>)<sub>2</sub> (292.5 mg, 0.5 mmol in water 25 ml) and the proton transfer compound (pdaH<sub>2</sub>)(py-3,5-dc) (241 mg, 1.0 mmol in water 25 ml), in a 1:2 molar ratio. Crystals were obtained by slow evaporation of the solvent at room temperature.

## Refinement

The water molecules H-atoms were located in difference Fourier maps and refined with distance O—H restrained to 0.85 (2) Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . The C-bound H-atoms were included in calculated positions and treated as riding atoms: C—H = 0.93 Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

## Figures

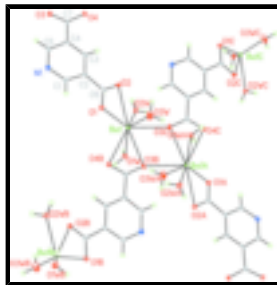


Fig. 1. The molecular structure of compound (I), with displacement ellipsoids drawn at the 50% probability level [A—C symmetry codes are: A =  $-x, 1 - y, 1 - z$ ; B =  $1 - x, -1/2 + y, 1/2 - z$ ; C =  $-1 + x, 3/2 - y, 1/2 + z$ ].

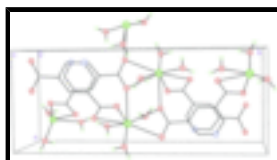


Fig. 2. A view, along the  $c$  axis, of the crystal packing of compound (I).

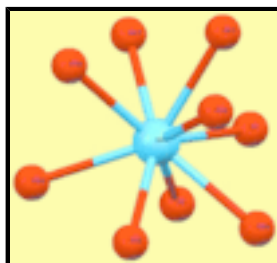


Fig. 3. A view of the distorted tricapped trigonal prism around the  $\text{Ba}^{\text{II}}$  atom [D:  $-1 + x, 3/2 - y, 1/2 + z$ ; E:  $x, 3/2 - y, -1/2 + z$ ; F:  $x, 3/2 - y, 1/2 + z$ ].

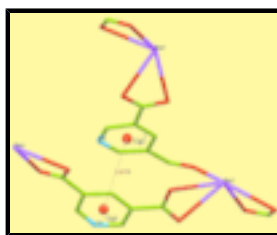


Fig. 4.  $\pi$ - $\pi$  Stacking interactions ( $\text{Cg1—Cg1}^i$ ) in compound (I). [ $\text{Cg1: N1/C1—C5}$ ; symmetry code: (i) =  $x, -y + 3/2, z + 1/2$ ].

## Poly[triaqua- $\mu_4$ -pyridine-3,5-dicarboxylato-barium(II)]

### Crystal data

[ $\text{Ba}(\text{C}_7\text{H}_3\text{NO}_4)(\text{H}_2\text{O})_3$ ]

$M_r = 356.49$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$F_{000} = 680$

$D_x = 2.340\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{Å}$

Cell parameters from 523 reflections

$a = 7.5922$ (4) Å	$\theta = 3\text{--}30^\circ$
$b = 18.5576$ (10) Å	$\mu = 3.95$ mm <sup>-1</sup>
$c = 7.1832$ (4) Å	$T = 100$ (2) K
$\beta = 90.499$ (5)°	Prism, colourless
$V = 1012.02$ (9) Å <sup>3</sup>	$0.25 \times 0.25 \times 0.20$ mm
$Z = 4$	

### Data collection

Bruker SMART APEX2 CCD area-detector diffractometer	2664 independent reflections
Radiation source: fine-focus sealed tube	2575 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.035$
Detector resolution: 0 pixels mm <sup>-1</sup>	$\theta_{\text{max}} = 29.0^\circ$
$T = 100$ (2) K	$\theta_{\text{min}} = 2.7^\circ$
$\varphi$ and $\omega$ scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan (APEX2; Bruker, 2005)	$k = -25 \rightarrow 25$
$T_{\text{min}} = 0.386$ , $T_{\text{max}} = 0.455$	$l = -9 \rightarrow 9$
10713 measured reflections	

### Refinement

Refinement on $F^2$	Hydrogen site location: mixed
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.019$	$w = 1/[\sigma^2(F_o^2) + (0.0132P)^2 + 2.3675P]$
$wR(F^2) = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{\text{max}} = 0.003$
2664 reflections	$\Delta\rho_{\text{max}} = 1.18$ e Å <sup>-3</sup>
146 parameters	$\Delta\rho_{\text{min}} = -0.66$ e Å <sup>-3</sup>
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXTL (Sheldrick, 1998), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0155 (5)

### Special details

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

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

## supplementary materials

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ba1	0.246077 (15)	0.566051 (6)	0.470978 (17)	0.00707 (6)
O1	0.4431 (2)	0.58907 (9)	0.1397 (2)	0.0115 (3)
O2	0.3179 (2)	0.68921 (8)	0.2430 (2)	0.0125 (3)
O3	0.8918 (2)	0.92324 (9)	0.0350 (3)	0.0153 (3)
O4	0.6006 (2)	0.92670 (8)	0.0586 (3)	0.0120 (3)
N1	0.8720 (3)	0.70081 (10)	-0.0669 (3)	0.0109 (3)
C1	0.7279 (3)	0.66597 (12)	-0.0073 (3)	0.0106 (4)
H1	0.7236	0.6162	-0.0206	0.013*
C2	0.5847 (3)	0.70043 (12)	0.0734 (3)	0.0083 (4)
C3	0.5887 (3)	0.77518 (11)	0.0851 (3)	0.0085 (4)
H3	0.4940	0.7999	0.1356	0.010*
C4	0.7341 (3)	0.81285 (12)	0.0214 (3)	0.0098 (4)
C5	0.8739 (3)	0.77268 (12)	-0.0512 (3)	0.0099 (4)
H5	0.9735	0.7973	-0.0908	0.012*
C6	0.4364 (3)	0.65684 (12)	0.1556 (3)	0.0090 (4)
C7	0.7438 (3)	0.89332 (12)	0.0389 (3)	0.0091 (4)
O1W	0.2873 (2)	0.50776 (9)	0.8310 (2)	0.0135 (3)
H1WA	0.3062	0.5376	0.9167	0.016*
H1WB	0.3736	0.4798	0.8421	0.016*
O2W	0.1920 (2)	0.67121 (9)	0.7367 (2)	0.0149 (3)
H2WA	0.2290	0.7117	0.7494	0.018*
H2WB	0.0948	0.6718	0.7890	0.018*
O3W	0.0471 (3)	0.56144 (11)	0.1471 (3)	0.0259 (4)
H3WA	0.0302	0.6021	0.0954	0.031*
H3WB	-0.0540	0.5424	0.1327	0.031*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ba1	0.00503 (8)	0.00616 (8)	0.01003 (9)	0.00006 (4)	-0.00019 (4)	0.00054 (4)
O1	0.0118 (8)	0.0072 (7)	0.0154 (8)	-0.0009 (6)	0.0004 (6)	-0.0004 (6)
O2	0.0120 (8)	0.0075 (7)	0.0179 (8)	0.0002 (6)	0.0034 (6)	0.0013 (6)
O3	0.0073 (8)	0.0101 (7)	0.0286 (10)	-0.0015 (6)	-0.0001 (7)	0.0019 (7)
O4	0.0078 (8)	0.0099 (7)	0.0182 (8)	0.0009 (6)	-0.0008 (6)	0.0001 (6)
N1	0.0102 (9)	0.0111 (8)	0.0114 (8)	0.0005 (7)	-0.0003 (7)	-0.0005 (7)
C1	0.0114 (10)	0.0101 (10)	0.0104 (9)	-0.0003 (8)	-0.0002 (8)	0.0000 (8)
C2	0.0087 (9)	0.0090 (9)	0.0072 (9)	-0.0017 (7)	-0.0019 (7)	0.0017 (7)
C3	0.0077 (9)	0.0088 (9)	0.0090 (9)	0.0012 (7)	-0.0017 (7)	0.0002 (7)
C4	0.0106 (10)	0.0071 (9)	0.0116 (10)	0.0012 (7)	-0.0031 (8)	0.0013 (7)
C5	0.0071 (9)	0.0120 (10)	0.0107 (9)	-0.0008 (7)	-0.0004 (7)	0.0008 (7)
C6	0.0088 (9)	0.0092 (9)	0.0087 (9)	-0.0014 (7)	-0.0026 (7)	0.0020 (7)
C7	0.0083 (10)	0.0084 (9)	0.0107 (9)	-0.0006 (7)	-0.0014 (7)	0.0017 (7)
O1W	0.0138 (8)	0.0129 (8)	0.0137 (8)	0.0029 (6)	-0.0017 (6)	-0.0005 (6)
O2W	0.0115 (8)	0.0094 (7)	0.0237 (9)	-0.0008 (6)	0.0048 (6)	-0.0048 (6)

O3W 0.0181 (10) 0.0359 (12) 0.0236 (10) -0.0038 (8) -0.0046 (8) 0.0020 (8)

*Geometric parameters (Å, °)*

Ba1—O3 <sup>i</sup>	2.7399 (18)	N1—C1	1.344 (3)
Ba1—O4 <sup>ii</sup>	2.7621 (17)	C1—C2	1.392 (3)
Ba1—O2W	2.7631 (17)	C1—H1	0.9300
Ba1—O3W	2.764 (2)	C2—C3	1.390 (3)
Ba1—O1W	2.8184 (17)	C2—C6	1.510 (3)
Ba1—O4 <sup>iii</sup>	2.8447 (16)	C3—C4	1.388 (3)
Ba1—O3 <sup>iii</sup>	2.8496 (17)	C3—H3	0.9300
Ba1—O1	2.8540 (17)	C4—C5	1.402 (3)
Ba1—O2	2.8669 (16)	C4—C7	1.500 (3)
Ba1—C6	3.181 (2)	C5—H5	0.9300
Ba1—C7 <sup>iii</sup>	3.207 (2)	C7—Ba1 <sup>v</sup>	3.207 (2)
Ba1—Ba1 <sup>iv</sup>	4.4914 (3)	O1W—H1WA	0.8399
O1—C6	1.264 (3)	O1W—H1WB	0.8385
O2—C6	1.255 (3)	O2W—H2WA	0.8061
O3—C7	1.254 (3)	O2W—H2WB	0.8314
O4—C7	1.260 (3)	O3W—H3WA	0.8500
N1—C5	1.338 (3)	O3W—H3WB	0.8508
O3 <sup>i</sup> —Ba1—O4 <sup>ii</sup>	156.10 (5)	O4 <sup>ii</sup> —Ba1—Ba1 <sup>iv</sup>	144.61 (3)
O3 <sup>i</sup> —Ba1—O2W	71.39 (5)	O2W—Ba1—Ba1 <sup>iv</sup>	101.11 (4)
O4 <sup>ii</sup> —Ba1—O2W	87.61 (5)	O3W—Ba1—Ba1 <sup>iv</sup>	67.19 (4)
O3 <sup>i</sup> —Ba1—O3W	67.27 (6)	O1W—Ba1—Ba1 <sup>iv</sup>	77.95 (4)
O4 <sup>ii</sup> —Ba1—O3W	135.86 (6)	O4 <sup>iii</sup> —Ba1—Ba1 <sup>iv</sup>	81.49 (3)
O2W—Ba1—O3W	121.34 (6)	O3 <sup>iii</sup> —Ba1—Ba1 <sup>iv</sup>	35.71 (4)
O3 <sup>i</sup> —Ba1—O1W	88.58 (5)	O1—Ba1—Ba1 <sup>iv</sup>	126.99 (3)
O4 <sup>ii</sup> —Ba1—O1W	73.10 (5)	O2—Ba1—Ba1 <sup>iv</sup>	130.60 (3)
O2W—Ba1—O1W	69.70 (5)	C6—Ba1—Ba1 <sup>iv</sup>	137.63 (4)
O3W—Ba1—O1W	144.69 (6)	C7 <sup>iii</sup> —Ba1—Ba1 <sup>iv</sup>	58.45 (4)
O3 <sup>i</sup> —Ba1—O4 <sup>iii</sup>	118.78 (5)	C6—O1—Ba1	92.98 (13)
O4 <sup>ii</sup> —Ba1—O4 <sup>iii</sup>	70.29 (5)	C6—O2—Ba1	92.58 (13)
O2W—Ba1—O4 <sup>iii</sup>	139.20 (5)	C7—O3—Ba1 <sup>vi</sup>	156.50 (16)
O3W—Ba1—O4 <sup>iii</sup>	97.46 (6)	C7—O3—Ba1 <sup>v</sup>	94.76 (14)
O1W—Ba1—O4 <sup>iii</sup>	71.18 (5)	Ba1 <sup>vi</sup> —O3—Ba1 <sup>v</sup>	106.92 (6)
O3 <sup>i</sup> —Ba1—O3 <sup>iii</sup>	73.08 (6)	C7—O4—Ba1 <sup>vii</sup>	146.93 (14)
O4 <sup>ii</sup> —Ba1—O3 <sup>iii</sup>	113.94 (5)	C7—O4—Ba1 <sup>v</sup>	94.85 (13)
O2W—Ba1—O3 <sup>iii</sup>	127.63 (5)	Ba1 <sup>vii</sup> —O4—Ba1 <sup>v</sup>	109.71 (5)
O3W—Ba1—O3 <sup>iii</sup>	76.14 (6)	C5—N1—C1	117.4 (2)
O1W—Ba1—O3 <sup>iii</sup>	72.23 (5)	N1—C1—C2	123.5 (2)
O4 <sup>iii</sup> —Ba1—O3 <sup>iii</sup>	45.89 (5)	N1—C1—H1	118.2
O3 <sup>i</sup> —Ba1—O1	130.66 (5)	C2—C1—H1	118.2

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O4 <sup>ii</sup> —Ba1—O1	70.49 (5)	C3—C2—C1	117.8 (2)
O2W—Ba1—O1	123.54 (5)	C3—C2—C6	121.8 (2)
O3W—Ba1—O1	65.75 (6)	C1—C2—C6	120.27 (19)
O1W—Ba1—O1	140.15 (5)	C4—C3—C2	120.0 (2)
O4 <sup>iii</sup> —Ba1—O1	81.72 (5)	C4—C3—H3	120.0
O3 <sup>iii</sup> —Ba1—O1	108.77 (5)	C2—C3—H3	120.0
O3 <sup>i</sup> —Ba1—O2	103.30 (5)	C3—C4—C5	117.5 (2)
O4 <sup>ii</sup> —Ba1—O2	84.35 (5)	C3—C4—C7	120.8 (2)
O2W—Ba1—O2	82.06 (5)	C5—C4—C7	121.6 (2)
O3W—Ba1—O2	69.46 (6)	N1—C5—C4	123.6 (2)
O1W—Ba1—O2	144.10 (5)	N1—C5—H5	118.2
O4 <sup>iii</sup> —Ba1—O2	127.01 (5)	C4—C5—H5	118.2
O3 <sup>iii</sup> —Ba1—O2	143.56 (5)	O2—C6—O1	123.4 (2)
O1—Ba1—O2	45.62 (5)	O2—C6—C2	118.63 (19)
O3 <sup>i</sup> —Ba1—C6	122.28 (5)	O1—C6—C2	117.9 (2)
O4 <sup>ii</sup> —Ba1—C6	71.86 (5)	O2—C6—Ba1	64.21 (11)
O2W—Ba1—C6	100.90 (5)	O1—C6—Ba1	63.64 (12)
O3W—Ba1—C6	70.44 (6)	C2—C6—Ba1	155.07 (14)
O1W—Ba1—C6	144.04 (5)	O3—C7—O4	124.0 (2)
O4 <sup>iii</sup> —Ba1—C6	103.86 (5)	O3—C7—C4	118.8 (2)
O3 <sup>iii</sup> —Ba1—C6	130.61 (6)	O4—C7—C4	117.20 (19)
O1—Ba1—C6	23.38 (5)	O3—C7—Ba1 <sup>v</sup>	62.31 (12)
O2—Ba1—C6	23.21 (5)	O4—C7—Ba1 <sup>v</sup>	62.10 (12)
O3 <sup>i</sup> —Ba1—C7 <sup>iii</sup>	95.74 (5)	C4—C7—Ba1 <sup>v</sup>	173.78 (14)
O4 <sup>ii</sup> —Ba1—C7 <sup>iii</sup>	91.73 (5)	Ba1—O1W—H1WA	115.9
O2W—Ba1—C7 <sup>iii</sup>	136.46 (5)	Ba1—O1W—H1WB	113.9
O3W—Ba1—C7 <sup>iii</sup>	87.91 (6)	H1WA—O1W—H1WB	102.1
O1W—Ba1—C7 <sup>iii</sup>	68.54 (5)	Ba1—O2W—H2WA	133.0
O4 <sup>iii</sup> —Ba1—C7 <sup>iii</sup>	23.05 (5)	Ba1—O2W—H2WB	117.3
O3 <sup>iii</sup> —Ba1—C7 <sup>iii</sup>	22.94 (5)	H2WA—O2W—H2WB	104.3
O1—Ba1—C7 <sup>iii</sup>	96.79 (5)	Ba1—O3W—H3WA	114.8
O2—Ba1—C7 <sup>iii</sup>	141.21 (5)	Ba1—O3W—H3WB	127.0
C6—Ba1—C7 <sup>iii</sup>	120.17 (6)	H3WA—O3W—H3WB	100.5
O3 <sup>i</sup> —Ba1—Ba1 <sup>iv</sup>	37.37 (3)		
O3 <sup>i</sup> —Ba1—O1—C6	77.70 (14)	O3W—Ba1—C6—O2	83.32 (13)
O4 <sup>ii</sup> —Ba1—O1—C6	-89.28 (13)	O1W—Ba1—C6—O2	-106.62 (14)
O2W—Ba1—O1—C6	-16.01 (14)	O4 <sup>iii</sup> —Ba1—C6—O2	176.43 (12)
O3W—Ba1—O1—C6	96.69 (13)	O3 <sup>iii</sup> —Ba1—C6—O2	133.56 (12)
O1W—Ba1—O1—C6	-114.31 (13)	O1—Ba1—C6—O2	157.3 (2)
O4 <sup>iii</sup> —Ba1—O1—C6	-161.22 (13)	C7 <sup>iii</sup> —Ba1—C6—O2	158.77 (12)
O3 <sup>iii</sup> —Ba1—O1—C6	161.19 (12)	Ba1 <sup>iv</sup> —Ba1—C6—O2	83.90 (13)
O2—Ba1—O1—C6	12.30 (12)	O3 <sup>i</sup> —Ba1—C6—O1	-118.76 (12)



C7 <sup>iii</sup> —Ba1—O1—C6	-178.70 (13)	O4 <sup>ii</sup> —Ba1—C6—O1	82.65 (13)
Ba1 <sup>iv</sup> —Ba1—O1—C6	126.05 (12)	O2W—Ba1—C6—O1	166.46 (12)
O3 <sup>i</sup> —Ba1—O2—C6	-147.25 (13)	O3W—Ba1—C6—O1	-73.95 (13)
O4 <sup>ii</sup> —Ba1—O2—C6	55.73 (13)	O1W—Ba1—C6—O1	96.11 (14)
O2W—Ba1—O2—C6	144.10 (13)	O4 <sup>iii</sup> —Ba1—C6—O1	19.16 (13)
O3W—Ba1—O2—C6	-88.09 (13)	O3 <sup>iii</sup> —Ba1—C6—O1	-23.71 (15)
O1W—Ba1—O2—C6	106.31 (14)	O2—Ba1—C6—O1	-157.3 (2)
O4 <sup>iii</sup> —Ba1—O2—C6	-4.34 (15)	C7 <sup>iii</sup> —Ba1—C6—O1	1.49 (14)
O3 <sup>iii</sup> —Ba1—O2—C6	-67.82 (15)	Ba1 <sup>iv</sup> —Ba1—C6—O1	-73.38 (14)
O1—Ba1—O2—C6	-12.38 (12)	O3 <sup>i</sup> —Ba1—C6—C2	141.4 (3)
C7 <sup>iii</sup> —Ba1—O2—C6	-29.99 (16)	O4 <sup>ii</sup> —Ba1—C6—C2	-17.2 (3)
Ba1 <sup>iv</sup> —Ba1—O2—C6	-118.05 (12)	O2W—Ba1—C6—C2	66.6 (4)
C5—N1—C1—C2	-1.8 (3)	O3W—Ba1—C6—C2	-173.8 (4)
N1—C1—C2—C3	2.9 (3)	O1W—Ba1—C6—C2	-3.7 (4)
N1—C1—C2—C6	-173.38 (19)	O4 <sup>iii</sup> —Ba1—C6—C2	-80.7 (3)
C1—C2—C3—C4	-1.5 (3)	O3 <sup>iii</sup> —Ba1—C6—C2	-123.6 (3)
C6—C2—C3—C4	174.74 (19)	O1—Ba1—C6—C2	-99.8 (4)
C2—C3—C4—C5	-0.8 (3)	O2—Ba1—C6—C2	102.9 (4)
C2—C3—C4—C7	-177.84 (19)	C7 <sup>iii</sup> —Ba1—C6—C2	-98.3 (3)
C1—N1—C5—C4	-0.7 (3)	Ba1 <sup>iv</sup> —Ba1—C6—C2	-173.2 (3)
C3—C4—C5—N1	2.0 (3)	Ba1 <sup>vi</sup> —O3—C7—O4	-165.2 (3)
C7—C4—C5—N1	179.0 (2)	Ba1 <sup>v</sup> —O3—C7—O4	-7.7 (2)
Ba1—O2—C6—O1	24.5 (2)	Ba1 <sup>vi</sup> —O3—C7—C4	15.6 (5)
Ba1—O2—C6—C2	-152.08 (16)	Ba1 <sup>v</sup> —O3—C7—C4	173.06 (17)
Ba1—O1—C6—O2	-24.6 (2)	Ba1 <sup>vi</sup> —O3—C7—Ba1 <sup>v</sup>	-157.5 (4)
Ba1—O1—C6—C2	151.98 (16)	Ba1 <sup>vii</sup> —O4—C7—O3	146.4 (2)
C3—C2—C6—O2	-2.9 (3)	Ba1 <sup>v</sup> —O4—C7—O3	7.7 (2)
C1—C2—C6—O2	173.2 (2)	Ba1 <sup>vii</sup> —O4—C7—C4	-34.4 (4)
C3—C2—C6—O1	-179.68 (19)	Ba1 <sup>v</sup> —O4—C7—C4	-173.03 (16)
C1—C2—C6—O1	-3.6 (3)	Ba1 <sup>vii</sup> —O4—C7—Ba1 <sup>v</sup>	138.6 (3)
C3—C2—C6—Ba1	-92.8 (4)	C3—C4—C7—O3	158.3 (2)
C1—C2—C6—Ba1	83.3 (4)	C5—C4—C7—O3	-18.7 (3)
O3 <sup>i</sup> —Ba1—C6—O2	38.51 (14)	C3—C4—C7—O4	-21.0 (3)
O4 <sup>ii</sup> —Ba1—C6—O2	-120.08 (13)	C5—C4—C7—O4	162.1 (2)
O2W—Ba1—C6—O2	-36.26 (13)		

Symmetry codes: (i)  $x-1, -y+3/2, z+1/2$ ; (ii)  $x, -y+3/2, z+1/2$ ; (iii)  $-x+1, y-1/2, -z+1/2$ ; (iv)  $-x, -y+1, -z+1$ ; (v)  $-x+1, y+1/2, -z+1/2$ ; (vi)  $x+1, -y+3/2, z-1/2$ ; (vii)  $x, -y+3/2, z-1/2$ .

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

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1W—H1WA $\cdots$ O1 <sup>viii</sup>	0.84	2.13	2.924 (2)	158
O1W—H1WB $\cdots$ O1 <sup>ix</sup>	0.84	1.89	2.730 (2)	176

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O2W—H2WA...O2 <sup>ii</sup>	0.81	1.96	2.761 (2)	172
O2W—H2WB...N1 <sup>x</sup>	0.83	2.06	2.873 (3)	165
O3W—H3WA...N1 <sup>xi</sup>	0.85	2.48	3.284 (3)	159
O3W—H3WB...O1W <sup>iv</sup>	0.85	2.02	2.851 (3)	165
C3—H3...O2W <sup>vii</sup>	0.93	2.47	3.362 (3)	161

Symmetry codes: (viii)  $x, y, z+1$ ; (ix)  $-x+1, -y+1, -z+1$ ; (ii)  $x, -y+3/2, z+1/2$ ; (x)  $x-1, y, z+1$ ; (xi)  $x-1, y, z$ ; (iv)  $-x, -y+1, -z+1$ ; (vii)  $x, -y+3/2, z-1/2$ .



Fig. 2

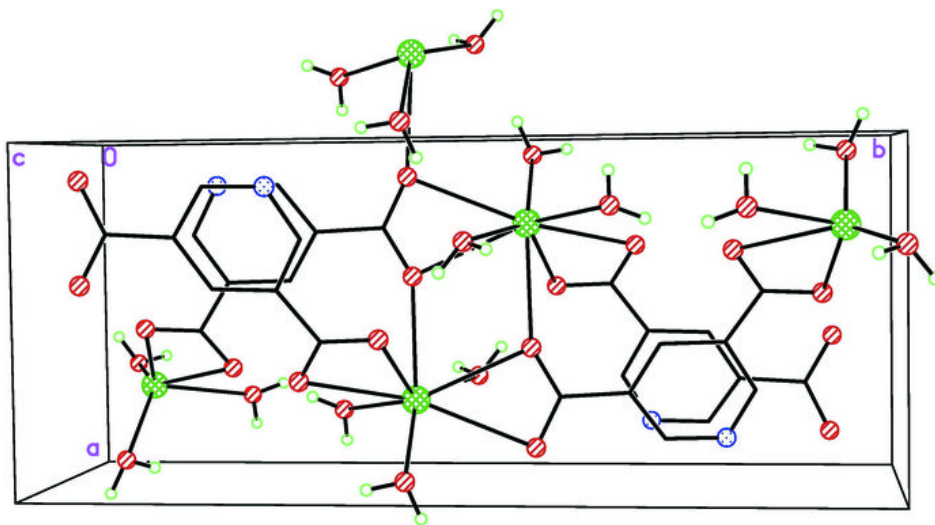


Fig. 3

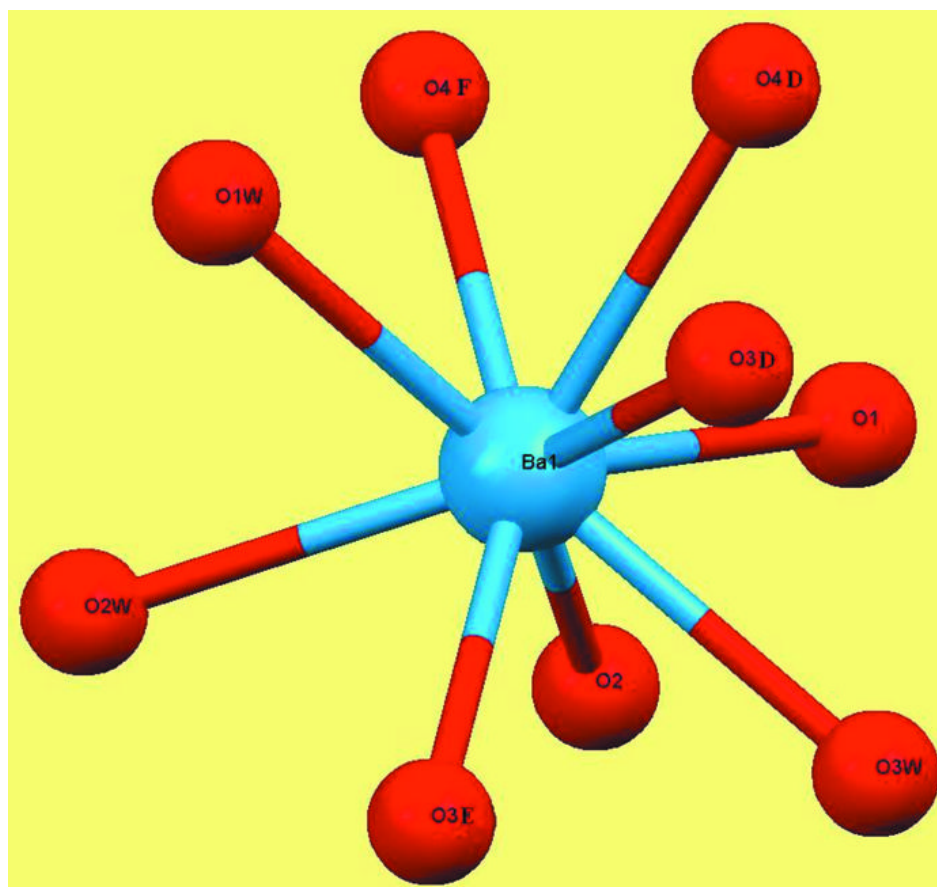


Fig. 4

