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## Rietveld refinement of a natural cobaltian mansfieldite from synchrotron data

Matteo Zoppi<sup>a\*</sup> and Giovanni Pratesi<sup>b</sup>

<sup>a</sup>Museo di Storia Naturale – Sezione di Mineralogia, Università di Firenze, via La Pira 4, 50121 Firenze, Italy, and <sup>b</sup>Dipartimento di Scienze della Terra, Università di Firenze, via La Pira 4, 50121 Firenze, Italy

Correspondence e-mail: matteo.zoppi@unifi.it

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Key indicators: powder synchrotron study;  $T = 298$  K; mean  $\sigma(\text{As}-\text{O}) = 0.004$  Å; disorder in main residue;  $R$  factor = 0.039;  $wR$  factor = 0.050; data-to-parameter ratio = 16.63.

A structural refinement of a natural sample of a Co-bearing mansfieldite,  $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$  [aluminium orthoarsenate(V) dihydrate], has been performed based on synchrotron powder diffraction data, with 5% of the octahedral Al sites replaced by Co. Mansfieldite is the aluminium analogue and an isotype of the mineral scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ), with which it forms a solid solution. The framework structure is based on  $\text{AsO}_4$  tetrahedra sharing their vertices with  $\text{AlO}_4(\text{H}_2\text{O})_2$  octahedra. Three of the four H atoms belonging to the two water molecules in *cis* positions take part in  $\text{O}-\text{H} \cdots \text{O}$  hydrogen bonding.

## Related literature

Mansfieldite ( $\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$ ) was first described by Allen *et al.* (1948) and the synthetic analogue was structurally characterised by Harrison (2000). For the structures of isotypic minerals and synthetic compounds, see: Botelho *et al.* (1994), Tang *et al.* (2001) (yanomamite,  $\text{InAsO}_4 \cdot 2\text{H}_2\text{O}$ ); Kniep *et al.* (1977) (variscite,  $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ); Hawthorne (1976), Kitahama *et al.* (1975), Xu *et al.* (2007) (scorodite,  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ); Taxer & Bartl (2004) (strengite,  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ); Loiseau *et al.* (1998) (synthetic  $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$ ); Mooney-Slater (1961) (synthetic  $\text{InPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{TIPO}_4 \cdot 2\text{H}_2\text{O}$ ).

## Experimental

## Crystal data

$\text{AlAsO}_4 \cdot 2\text{H}_2\text{O}$   
 $M_r = 203.53$   
 Orthorhombic, *Pbca*  
 $a = 8.79263$  (11) Å  
 $b = 9.79795$  (10) Å  
 $c = 10.08393$  (11) Å  
 $V = 868.73$  (2) Å<sup>3</sup>  
 $Z = 8$

Synchrotron radiation  
 $\lambda = 0.68780$  Å  
 $\mu = 7.25$  mm<sup>-1</sup>  
 $T = 298$  K  
 Specimen shape: flat sheet  
 $5.0 \times 5.0 \times 0.4$  mm  
 Particle morphology: powder, light pink

## Data collection

ESRF BM08 beamline  
 Specimen mounted in transmission mode  
 Scan method: fixed

Absorption correction: for a cylinder mounted on the  $\varphi$  axis  
 $T_{\min} = 0.072$ ,  $T_{\max} = 0.095$   
 $2\theta_{\min} = 6.0$ ,  $2\theta_{\max} = 53.0^\circ$   
 Increment in  $2\theta = 0.01^\circ$

## Refinement

$R_p = 0.039$   
 $R_{wp} = 0.050$   
 $R_{\text{exp}} = 0.039$   
 $R_B = 0.034$   
 $S = 1.31$   
 Excluded region(s): none

Profile function: CW pseudo-Voigt  
 60 parameters  
 No restraints  
 H-atom parameters not refined  
 Preferred orientation correction: Spherical harmonics ODF

Table 1

Selected bond lengths (Å).

|                       |           |         |           |
|-----------------------|-----------|---------|-----------|
| Al1—O1                | 1.908 (4) | Al1—O6w | 1.988 (4) |
| Al1—O2 <sup>i</sup>   | 1.906 (4) | As2—O1  | 1.676 (3) |
| Al1—O3 <sup>ii</sup>  | 1.850 (4) | As2—O2  | 1.654 (3) |
| Al1—O4 <sup>iii</sup> | 1.848 (4) | As2—O3  | 1.704 (4) |
| Al1—O5w               | 1.914 (4) | As2—O4  | 1.682 (4) |

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

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$                                | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|---|-------|--------------|--------------|----------------|
| $\text{O5w}-\text{H51} \cdots \text{O4}^i$    | 0.83  | 1.78         | 2.607 (5)    | 168 (1)        |
| $\text{O5w}-\text{H52} \cdots \text{O1}^{iv}$ | 0.71  | 2.03         | 2.614 (5)    | 161 (1)        |
| $\text{O6w}-\text{H62} \cdots \text{O3}$      | 0.93  | 1.71         | 2.587 (5)    | 156 (1)        |

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

Data collection: local image plate reading software; cell refinement: *GSAS* (Larson & Von Dreele, 2004) and *EXPGUI* (Toby, 2001); data reduction: *FIT2D* (Hammersley, 1997); program(s) used to solve structure: atomic coordinates from Harrison (2000); program(s) used to refine structure: *GSAS* and *EXPGUI*; molecular graphics: *VICS* (Izumi & Dilanian, 2005); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2209).

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## supporting information

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## Rietveld refinement of a natural cobaltian mansfieldite from synchrotron data

Matteo Zoppi and Giovanni Pratesi

### S1. Comment

The mineral mansfieldite belongs to the general group of hydrous arsenates, a structure subgroup of variscite ( $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ), and has been known since the discovery of Allen *et al.* (1948). It is of white to pale gray colour and has a vitreous luster. It often develops encrustations, crust-like or rounded aggregates on the matrix, and individual crystals are rarely observed. While the structural data of synthetic mansfieldite were reported recently by Harrison (2000), no data regarding natural samples have been provided in literature up to now, probably because of the rare occurrence of crystalline material suitable for structural investigations. Rietveld refinement of a natural sample of a Co-bearing mansfieldite has now been carried out using synchrotron powder diffraction data (Fig. 1).

Mansfieldite crystallizes in the *Pbca* space group and is isostructural with the arsenate minerals scorodite [ $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ] (Xu *et al.*, 2007; Hawthorne, 1976; Kitahama *et al.*, 1975), yanomamite [ $\text{InAsO}_4 \cdot 2\text{H}_2\text{O}$ ] (Tang *et al.*, 2001; Botelho *et al.*, 1994),  $\text{TlAsO}_4 \cdot 2\text{H}_2\text{O}$  (Mooney-Slater, 1961), and the phosphate minerals variscite [ $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ] (Kniep *et al.*, 1977), strengite [ $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ] (Taxer & Bartl, 2004),  $\text{InPO}_4 \cdot 2\text{H}_2\text{O}$  (Tang *et al.*, 2001; Mooney-Slater, 1961),  $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$  (Loiseau *et al.*, 1998) and  $\text{TlPO}_4 \cdot 2\text{H}_2\text{O}$  (Mooney-Slater, 1961). Correspondingly to the mentioned arsenates, the structure of mansfieldite is composed of  $\text{AsO}_4$  tetrahedra and  $\text{AlO}_4(\text{H}_2\text{O})_2$  octahedra, each tetrahedron being connected to four octahedra and each octahedron being connected to four tetrahedra, as shown in Fig. 2. The interatomic distances Al—O and As—O resulting from the refinement of the structure are reported in Table 1. The two water molecules are located in *cis* position, but the O atoms O5W and O6W do not participate in the linkage with the As— $\text{O}_4$  tetrahedra, while three of the hydrogen atoms (H1, H2 and H3) take part in D—H $\cdots$ A bonds that link O5W to O4, O5W to O1, and O6W to O3, respectively (Table 2). Such a structure framework displays channels along *b*. With respect to the synthetic mansfieldite (Harrison, 2000), the natural sample shows a slightly smaller unit cell volume, which is the effect of slightly smaller octahedral (9.110 *versus* 9.187 Å<sup>3</sup>) and tetrahedral (2.428 *versus* 2.450 Å<sup>3</sup>) volumes. Also the distortion index of both the polyhedra, 0.019 and 0.008 for the octahedral and tetrahedral site, respectively, is larger than that calculated for the synthetic material, *viz.* 0.014 and 0.002. A slight distortion of the structure is probably due to the small amount of incorporated Co and other elements present in the structure of the natural sample. Bond valence calculations show slightly overbonded values of 3.036 and 5.079 valence units for the cation in the octahedral site and in the tetrahedral site, respectively. The isotropic thermal parameters for O5W and O6W, 0.0182 (12) and 0.0164 (12) Å<sup>2</sup>, respectively, are slightly larger than those of the other oxygen atoms and reveal a certain degree of disorder of the water molecules along the channels, since they are not taking part in the metal-oxygen-metal chains of the structure.

### S2. Experimental

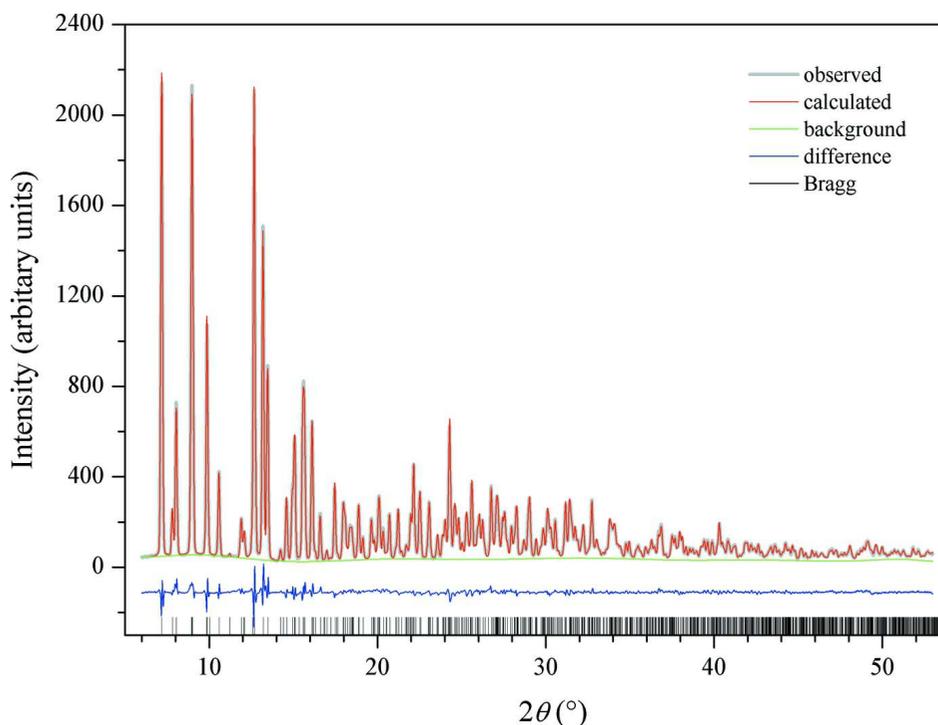
The specimen used in this study is from the locality of Mt. Cobalt, Cloncurry District, Queensland, Australia.

Preliminarily, some transparent single crystals were selected from massive, light purple coloured, mansfieldite associated with smolianinovite [ $(\text{Co}, \text{Ni}, \text{Mg}, \text{Ca})_3(\text{Fe}^{3+}, \text{Al})_2(\text{AsO}_4)_4 \cdot 11\text{H}_2\text{O}$ ]. The average elemental chemical composition, determined

using electron microprobe analyses, yielded the empirical chemical formula, calculated on a total of two cations per formula unit,  $(\text{Al}_{0.944}\text{Co}^{3+}_{0.046}\text{Cu}^{2+}_{0.005}\text{Fe}^{3+}_{0.003}\text{Zn}^{2+}_{0.002})_{\Sigma=1}(\text{As}_{0.972}\text{Al}_{0.022}\text{P}_{0.006})_{\Sigma=1}\text{O}_{3.975}\cdot 2\text{H}_2\text{O}$  resulting in the simplified formula  $\text{AlAsO}_4\cdot 2\text{H}_2\text{O}$ . The excess Al resulting from the calculation has been arbitrarily assigned to the tetrahedral site. X-ray data collections of some single crystals, with a CCD equipped diffractometer, revealed that all the samples were actually polycrystalline aggregates and showed irregular and broadened spots typical of materials with high mosaicity. Refinements from single-crystal X-ray diffraction data yielded, in the best case, a not satisfactorily  $R_F$  index of 6.54%. Fragments of pure mansfieldite were then ground and used for synchrotron X-ray data collection.

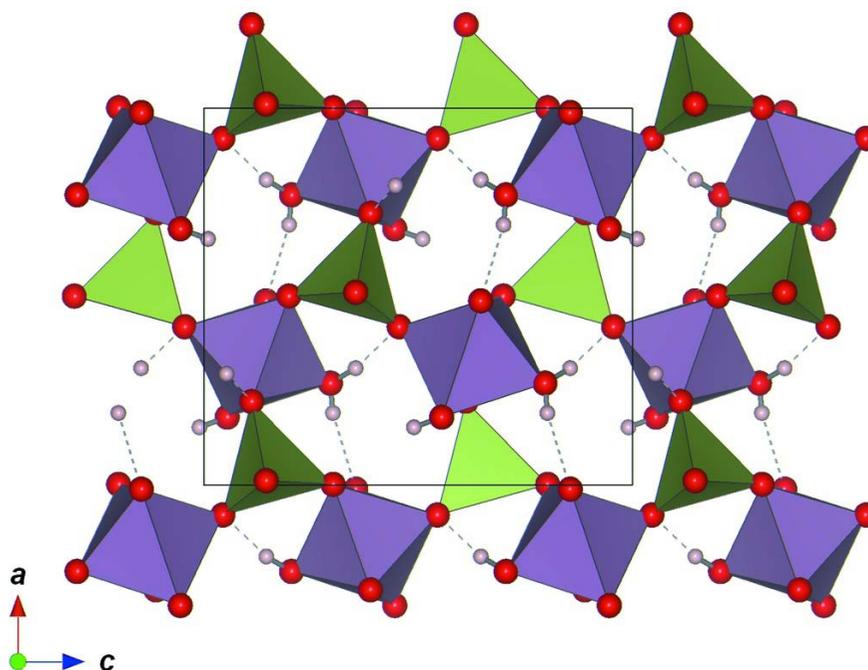
### S3. Refinement

Structural data were refined employing the Rietveld method and starting from the atomic coordinates provided by Harrison (2000), except for the H atom parameters that were not refined but included in the model. The site occupancies were assigned according to the composition of the idealised chemical formula  $(\text{Al}_{0.95}\text{Co}^{3+}_{0.05})\text{AsO}_4\cdot 2\text{H}_2\text{O}$ , with 5% Co at the octahedral Al sites.



**Figure 1**

The observed, calculated, background and difference X-ray diffraction profile for natural mansfieldite. Bragg reflection positions are shown at the bottom.

**Figure 2**

The crystal structure of mansfieldite, viewed along the  $b$  axis. The unit cell is outlined and the hydrogen bonds are represented by dashed lines.

### aluminium orthoarsenate(V) dihydrate

#### Crystal data

AlAsO<sub>4</sub>·2H<sub>2</sub>O  
 $M_r = 203.53$   
 Orthorhombic,  $Pbca$   
 Hall symbol: -P 2ac 2ab  
 $a = 8.79263$  (11) Å  
 $b = 9.79795$  (10) Å  
 $c = 10.08393$  (11) Å  
 $V = 868.73$  (2) Å<sup>3</sup>  
 $Z = 8$

$F(000) = 789$   
 $D_x = 3.112$  Mg m<sup>-3</sup>  
 Synchrotron radiation,  $\lambda = 0.68780$  Å  
 $\mu = 7.25$  mm<sup>-1</sup>  
 $T = 298$  K  
 Particle morphology: powder  
 light pink  
 flat sheet, 5.0 × 5.0 mm

#### Data collection

ESRF BM08 Beamline  
 diffractometer  
 Data collection mode: transmission  
 Scan method: Stationary detector

Absorption correction: for a cylinder mounted  
 on the  $\varphi$  axis  
 Debye-Scherrer, Term (=  $MU.r/wave$ ) = 2.4540.  
 Correction is not refined.  
 $T_{min} = 0.072$ ,  $T_{max} = 0.095$

#### Refinement

Refinement on  $I_{net}$   
 Least-squares matrix: full  
 $R_p = 0.039$   
 $R_{wp} = 0.050$

$R_{exp} = 0.039$   
 $R_{Bragg} = 0.034$   
 $R(F^2) = 0.03400$   
 $\chi^2 = 1.716$

? data points  
 Excluded region(s): none  
 Profile function: CW Pseudo-Voigt  
 60 parameters  
 no restraints  
 H-atom parameters not refined  
 $w = 1/[Y_i]$

$(\Delta/\sigma)_{\max} = 0.01$   
 Background function: GSAS Background  
 function number 1 with 14 terms. Shifted  
 Chebyshev function of 1st kind  
 Preferred orientation correction: Spherical  
 Harmonics ODF

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

|     | x           | y            | z            | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|-------------|--------------|--------------|----------------------------------|-----------|
| Al1 | 0.1478 (3)  | 0.18068 (16) | 0.12682 (18) | 0.0087 (5)*                      | 0.95      |
| Co1 | 0.1478 (3)  | 0.18068 (16) | 0.12682 (18) | 0.0087 (5)*                      | 0.05      |
| As2 | 0.03632 (9) | -0.13857 (6) | 0.15042 (6)  | 0.00875 (18)*                    |           |
| O1  | 0.0106 (4)  | 0.0308 (3)   | 0.1440 (3)   | 0.0055 (8)*                      |           |
| O2  | 0.0003 (5)  | -0.1986 (3)  | 0.3005 (3)   | 0.0077 (12)*                     |           |
| O3  | 0.2208 (5)  | -0.1729 (4)  | 0.1105 (3)   | 0.0086 (12)*                     |           |
| O4  | -0.0815 (5) | -0.2171 (3)  | 0.0434 (4)   | 0.0063 (11)*                     |           |
| O5w | 0.2296 (5)  | 0.1244 (4)   | 0.2939 (3)   | 0.0182 (12)*                     |           |
| O6w | 0.3186 (4)  | 0.0696 (4)   | 0.0559 (3)   | 0.0164 (12)*                     |           |
| H51 | 0.19        | 0.17         | 0.354        | 0.08*                            |           |
| H52 | 0.309       | 0.114        | 0.301        | 0.036*                           |           |
| H61 | 0.347       | 0.093        | -0.01        | 0.033*                           |           |
| H62 | 0.295       | -0.023       | 0.053        | 0.047*                           |           |

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

|   |               |                             |             |
|---|---------------|-----------------------------|-------------|
| Al1—O1                                  | 1.908 (4)     | As2—O4                      | 1.682 (4)   |
| Al1—O2 <sup>i</sup>                     | 1.906 (4)     | O5W—H51                     | 0.8295      |
| Al1—O3 <sup>ii</sup>                    | 1.850 (4)     | O5W—H52                     | 0.709       |
| Al1—O4 <sup>iii</sup>                   | 1.848 (4)     | O6W—H61                     | 0.746       |
| Al1—O5w                                 | 1.914 (4)     | O6W—H62                     | 0.931       |
| Al1—O6w                                 | 1.988 (4)     | O1—H52 <sup>iv</sup>        | 2.028       |
| As2—O1                                  | 1.676 (3)     | O3—H62                      | 1.709       |
| As2—O2                                  | 1.654 (3)     | O4—H51 <sup>v</sup>         | 1.790       |
| As2—O3                                  | 1.704 (4)     |                             |             |
| O1—Al1—O2 <sup>vi</sup>                 | 90.64 (19)    | O1—As2—O3                   | 108.35 (18) |
| O1—Al1—O3 <sup>ii</sup>                 | 179.4743 (18) | O1—As2—O4                   | 110.18 (18) |
| O1—Al1—O4 <sup>iii</sup>                | 91.93 (18)    | O2—As2—O3                   | 109.2 (2)   |
| O1—Al1—O5w                              | 86.31 (15)    | O2—As2—O4                   | 107.83 (19) |
| O1—Al1—O6w                              | 95.09 (18)    | O3—As2—O4                   | 110.13 (18) |
| O2 <sup>vi</sup> —Al1—O3 <sup>ii</sup>  | 88.84 (18)    | Al1—O1—As2                  | 132.9 (2)   |
| O2 <sup>vi</sup> —Al1—O4 <sup>iii</sup> | 91.28 (18)    | Al1 <sup>vii</sup> —O2—As2  | 134.7 (2)   |
| O2 <sup>vi</sup> —Al1—O5w               | 95.56 (17)    | Al1 <sup>viii</sup> —O3—As2 | 136.6 (2)   |
| O2 <sup>vi</sup> —Al1—O6w               | 173.9 (2)     | Al1 <sup>iii</sup> —O4—As2  | 134.6 (2)   |
| O3 <sup>ii</sup> —Al1—O4 <sup>iii</sup> | 87.99 (19)    | Al1—O5w—H51                 | 109.3 (3)   |
| O3 <sup>ii</sup> —Al1—O5w               | 93.84 (18)    | Al1—O5w—H52                 | 120.0 (3)   |
| O3 <sup>ii</sup> —Al1—O6w               | 85.4 (2)      | H51—O5w—H52                 | 114.6       |

|                            |             |             |           |
|----------------------------|-------------|-------------|-----------|
| O4 <sup>iii</sup> —A11—O5w | 172.94 (19) | A11—O6w—H61 | 113.9 (4) |
| O4 <sup>iii</sup> —A11—O6w | 90.54 (17)  | A11—O6w—H62 | 112.1 (3) |
| O5w—A11—O6w                | 82.82 (17)  | H61—O6w—H62 | 110.3     |
| O1—As2—O2                  | 111.20 (17) |             |           |

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

*Hydrogen-bond geometry (Å, °)*

| <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> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O5w—H51 $\cdots$ O4 <sup>i</sup>  | 0.83        | 1.78                | 2.607 (5)                  | 168 (1)                       |
| O5w—H52 $\cdots$ O1 <sup>ix</sup> | 0.71        | 2.03                | 2.614 (5)                  | 161 (1)                       |
| O6w—H62 $\cdots$ O3               | 0.93        | 1.71                | 2.587 (5)                  | 156 (1)                       |

Symmetry codes: (i)  $-x, y+1/2, -z+1/2$ ; (ix)  $x+3/2, y, -z+3/2$ .