

## A triclinic polymorph of dicadmium divanadate(V)

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Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(V-O) = 0.001$  Å;  $R$  factor = 0.016;  $wR$  factor = 0.037; data-to-parameter ratio = 21.3.

The title compound,  $Cd_2V_2O_7$ , was obtained under hydrothermal conditions. Different from the known monoclinic form, the new polymorph of  $Cd_2V_2O_7$  has triclinic symmetry and is isotypic with  $Ca_2V_2O_7$ . The building units of the crystal structure are two  $Cd^{2+}$  cations, with coordination numbers of six and seven, and two V atoms with a tetrahedral and a significantly distorted trigonal-pyramidal coordination environment, respectively. Two  $VO_5$  pyramids share an edge and each pyramid is connected to one  $VO_4$  tetrahedron *via* a corner atom, forming an isolated  $V_4O_{14}^{8-}$  anion. These anions are arranged in sheets parallel to  $(\bar{2}11)$  and are linked through the  $Cd^{2+}$  cations into a three-dimensional framework structure.

### Related literature

For  $Ca_2V_2O_7$ , isotypic with the title compound, see: Trunov *et al.* (1983). For the structure of the monoclinic polymorph of  $Cd_2V_2O_7$ , see: Au & Calvo (1967). For the thermal stability of the monoclinic polymorph, see: Krasnenko & Rotermel (2010). For applications of vanadates, see: Jin *et al.* (2013); Valverde *et al.* (2012). For bond-valence analysis, see: Brown & Altermatt (1985).

### Experimental

#### Crystal data

$Cd_2V_2O_7$	$\gamma = 80.145 (1)^\circ$
$M_r = 438.68$	$V = 281.45 (1) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 6.5974 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 6.8994 (2) \text{ \AA}$	$\mu = 10.65 \text{ mm}^{-1}$
$c = 6.9961 (2) \text{ \AA}$	$T = 296 \text{ K}$
$\alpha = 83.325 (1)^\circ$	$0.29 \times 0.17 \times 0.12 \text{ mm}$
$\beta = 63.898 (1)^\circ$	

#### Data collection

Bruker X8 APEX diffractometer	10113 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2009)	2134 independent reflections
$T_{\min} = 0.164$ , $T_{\max} = 0.376$	2077 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$	100 parameters
$wR(F^2) = 0.037$	$\Delta\rho_{\max} = 0.70 \text{ e \AA}^{-3}$
$S = 1.21$	$\Delta\rho_{\min} = -1.53 \text{ e \AA}^{-3}$
2134 reflections	

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and DIAMOND (Brandenburg, 2006); software used to prepare material for publication: publCIF (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2776).

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## supporting information

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## A triclinic polymorph of dicadmium divanadate(V)

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### S1. Comment

Vanadate-based compounds have received a great extent of interest and still remain promising functional materials. Their structural diversity, mainly associated with the ability of vanadium to form different anions like  $(VO_4)^{3-}$ ,  $(V_2O_7)^{4-}$ ,  $(V_4O_{12})^{4-}$ ,  $(V_{10}O_{28})^{6-}$ , is strongly required for catalysis applications (Jin *et al.*, 2013; Valverde *et al.*, 2012).

A bibliographic analysis revealed that pyrovanadates with the  $(V_2O_7)^{4-}$  anion can adopt different symmetries. For example,  $Cu_2V_2O_7$ ,  $Mn_2V_2O_7$  and  $Mg_2V_2O_7$  are polymorphic and exhibit both monoclinic and triclinic varieties, the Cu-member additionally an orthorhombic form. In the case of  $Co_2V_2O_7$ ,  $Ni_2V_2O_7$ , and  $Cd_2V_2O_7$  only one monoclinic form is yet known, for  $Zn_2V_2O_7$  two monoclinic forms are reported.  $Ca_2V_2O_7$  and  $Ba_2V_2O_7$  crystallize in the triclinic system,  $Sr_2V_2O_7$  is likewise polymorphic, with triclinic and tetragonal varieties. We report here on the crystal structure determination of a new form of  $Cd_2V_2O_7$  that was hydrothermally synthesized. In contrast to the known monoclinic polymorph (Au & Calvo, 1967) that is stable from ambient temperature to 1173 K (Krasnenko *et al.*, 2010), this new form has triclinic symmetry and is isotopic with  $Ca_2V_2O_7$  (Trunov *et al.*, 1983).

The structure of the title compound is built up from two types of vanadium sites and two types of cadmium sites, each with a different oxygen coordination as shown in Fig. 1. The coordination environment of V1 is tetrahedral with V1–O distances in the range 1.6882 (13) Å - 1.7708 (13) Å. V2 is surrounded by five oxygen atoms with four V2–O distances ranging from 1.6612 (14) Å to 1.8535 (13) Å and the fifth O atom at a longer distance V2–O1 = 2.0348 (13) Å, forming a distorted trigonal  $V_2O_5^{5-}$  pyramid. The bond valence sum calculation (Brown & Altermatt, 1985) for V1 and V2 are as expected, *viz.* 4.99 and 5.11 valence units, respectively. This result confirms the involvement of O1 in the V2 environment. The  $V_2O_5^{5-}$  pyramids build a dimeric unit  $(V_2)_2O_8^{6-}$  by sharing an edge. A corner atom (O1) of each of the pyramids is also part of a  $VO_4$  tetrahedron. This linkage leads to the formation of a centrosymmetric  $(V_4O_{14})^{8-}$  anion. This type of anion is rarely encountered in the crystal chemistry of pyrovanadates. Like in the monoclinic  $Cd_2V_2O_7$  variety (Au and Calvo, 1967),  $(V_2O_7)^{4-}$  groups made up from two corner-sharing  $VO_4$  tetrahedra are more commonly observed.

The two independent cadmium sites Cd1 and Cd2 are surrounded by six and seven oxygen atoms, respectively, in the form of distorted polyhedra. The Cd–O distance range from 2.2401 (13) Å to 2.5300 (13) Å for  $Cd1O_7$  and from 2.2449 (14) Å to 2.4562 (14) Å for  $Cd2O_6$ . As shown in Fig. 2, edge-sharing  $CdO_6$  and  $CdO_7$  polyhedra built up sheets parallel to  $(\bar{2}11)$  with 8-membered open rings. Two adjacent layers are linked by the  $(V_4O_{14})^{8-}$  groups into a three-dimensional framework (Fig. 3). In the monoclinic  $Cd_2V_2O_7$  polymorph, the  $CdO_6$  octahedra share edges and form sheets with six-membered rings that are linked by  $(V_2O_7)^{4-}$  groups.

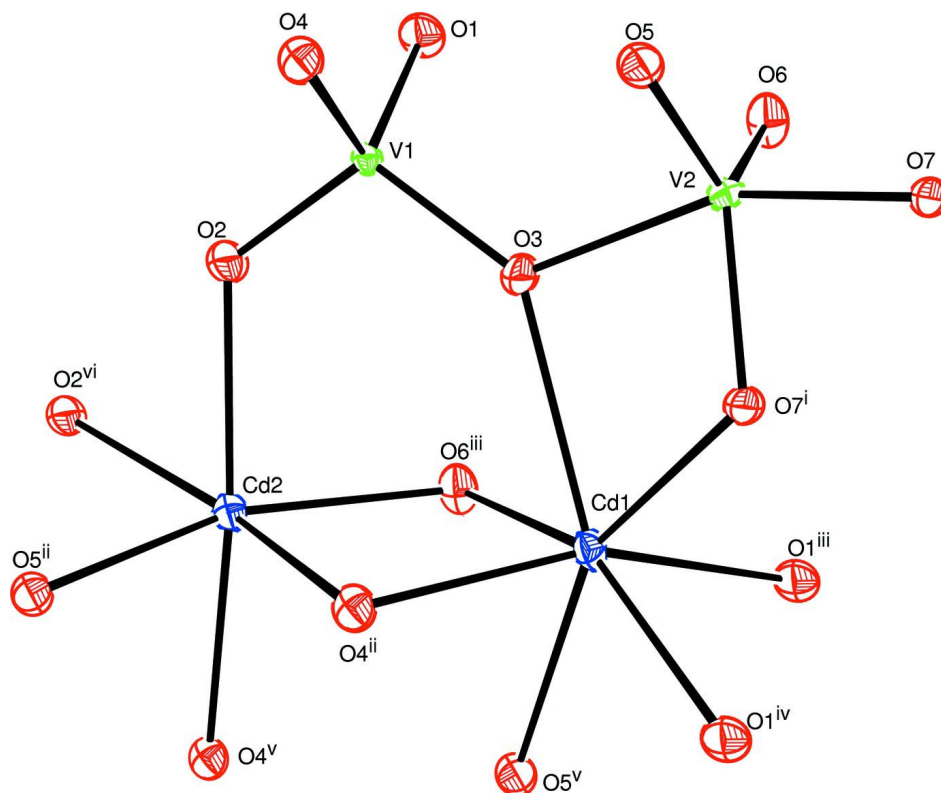
### S2. Experimental

Crystals of the title compound were isolated from the hydrothermal treatment of cadmium oxide, ammonium metavanadate and zinc oxide in a molar ratio Cd:V:Zn = 11:8:1. Zinc oxide, not present in the obtained crystals,

presumably acted as a mineralizing agent. The hydrothermal reaction was conducted in a 23 ml Teflon-lined autoclave, filled to 50% with distilled water and under autogeneous pressure at 493 K for four days. After being filtered off, washed with deionized water and air dried, the reaction product consists of colourless sheet-shaped crystals corresponding to the title compound.

### S3. Refinement

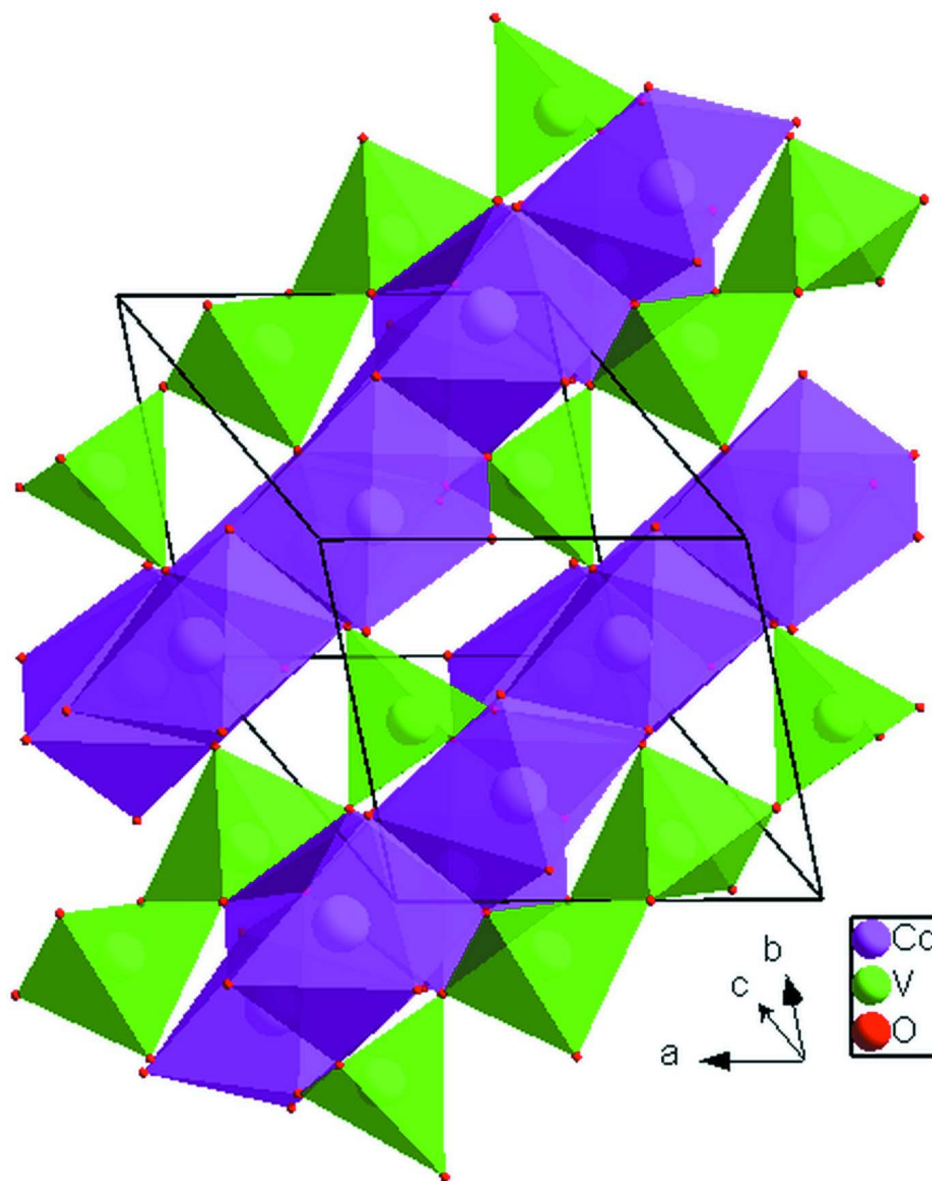
The highest peak and the deepest hole in the final Fourier map are at 1.69 Å and 0.08 Å, from O2 and Cd2, respectively. Reflections (200) and (020) were omitted from the refinement due to large differences between observed and calculated intensities.



**Figure 1**

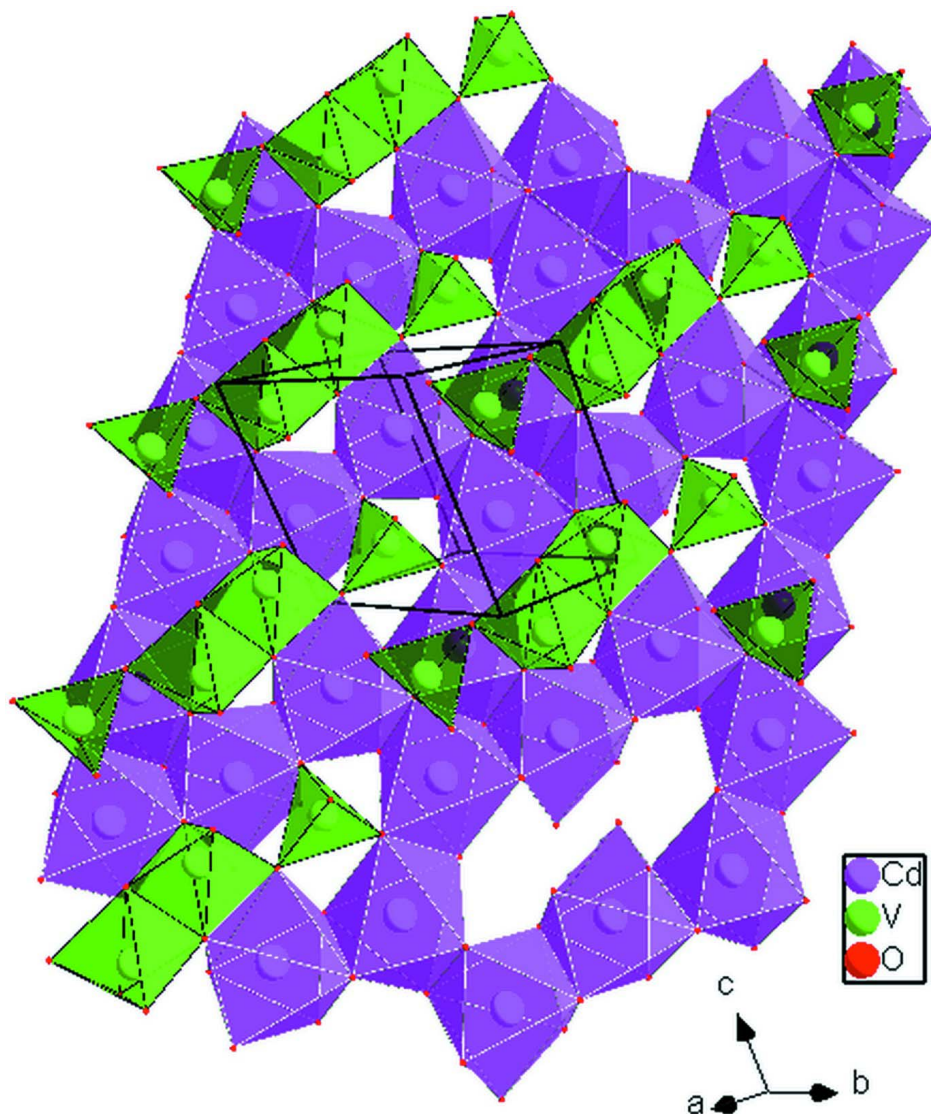
The coordination environment of the Cd and V sites in the crystal structure of the title compound, triclinic  $\text{Cd}_2\text{V}_2\text{O}_7$ .

Displacement ellipsoids are drawn at the 70% probability level. [Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $-x + 1, -y, -z + 1$ ; (iii)  $-x + 1, -y + 1, -z + 1$ ; (iv)  $x - 1, y, z + 1$ ; (v)  $x, y, z + 1$ ; (vi)  $-x + 2, -y, -z + 1$ .]



**Figure 2**

Polyhedral representation of triclinic  $\text{Cd}_2\text{V}_2\text{O}_7$ , showing the sheets of cadmium- and vanadium-oxygen polyhedra.



**Figure 3**

A three dimensional view of the crystal structure of triclinic  $\text{Cd}_2\text{V}_2\text{O}_7$  showing the stacking of the cadmium and vanadium layers that extend parallel to  $(\bar{2}11)$ .

### Dicadmium divanadate(V)

#### Crystal data

$\text{Cd}_2\text{V}_2\text{O}_7$

$M_r = 438.68$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 6.5974(2)\ \text{\AA}$

$b = 6.8994(2)\ \text{\AA}$

$c = 6.9961(2)\ \text{\AA}$

$\alpha = 83.325(1)^\circ$

$\beta = 63.898(1)^\circ$

$\gamma = 80.145(1)^\circ$

$V = 281.45(1)\ \text{\AA}^3$

$Z = 2$

$F(000) = 396$

$D_x = 5.176\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2717 reflections

$\theta = 3.0\text{--}33.1^\circ$

$\mu = 10.65\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, colourless

$0.29 \times 0.17 \times 0.12\ \text{mm}$

*Data collection*

Bruker X8 APEX  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
Absorption correction: multi-scan  
(*SADABS*; Bruker, 2009)  
 $T_{\min} = 0.164$ ,  $T_{\max} = 0.376$

10113 measured reflections  
2134 independent reflections  
2077 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$   
 $\theta_{\max} = 33.1^\circ$ ,  $\theta_{\min} = 3.0^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -10 \rightarrow 10$   
 $l = -10 \rightarrow 10$

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.016$   
 $wR(F^2) = 0.037$   
 $S = 1.21$   
2134 reflections  
100 parameters  
0 restraints

Primary atom site location: structure-invariant  
direct methods  
Secondary atom site location: difference Fourier  
map  
 $w = 1/[\sigma^2(F_o^2) + (0.0148P)^2 + 0.2572P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -1.53 \text{ e } \text{\AA}^{-3}$

*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  $F^2 > 2\sigma(F^2)$  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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	0.24214 (2)	0.336697 (18)	0.83258 (2)	0.00767 (4)
Cd2	0.74980 (2)	0.034380 (18)	0.75748 (2)	0.00845 (4)
V1	0.71038 (5)	0.16450 (4)	0.25864 (4)	0.00469 (5)
V2	0.22836 (5)	0.45517 (4)	0.34409 (5)	0.00542 (5)
O1	0.8612 (2)	0.3328 (2)	0.0816 (2)	0.0100 (2)
O2	0.8622 (2)	0.0439 (2)	0.3907 (2)	0.0099 (2)
O3	0.4592 (2)	0.2893 (2)	0.4363 (2)	0.0092 (2)
O4	0.6546 (2)	-0.00638 (19)	0.1233 (2)	0.0086 (2)
O5	0.2714 (2)	0.29481 (19)	0.1660 (2)	0.0093 (2)
O6	0.3839 (2)	0.6438 (2)	0.2436 (2)	0.0104 (2)
O7	-0.0496 (2)	0.5892 (2)	0.3678 (2)	0.0100 (2)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cd1	0.00672 (6)	0.00774 (6)	0.00900 (6)	-0.00006 (4)	-0.00431 (4)	0.00047 (4)
Cd2	0.00779 (6)	0.00795 (6)	0.00808 (6)	0.00031 (4)	-0.00277 (4)	0.00069 (4)

V1	0.00423 (11)	0.00515 (11)	0.00483 (11)	-0.00033 (8)	-0.00222 (9)	-0.00007 (9)
V2	0.00472 (11)	0.00635 (12)	0.00446 (11)	-0.00089 (9)	-0.00115 (9)	-0.00065 (9)
O1	0.0089 (5)	0.0096 (5)	0.0098 (5)	-0.0031 (4)	-0.0025 (5)	0.0023 (4)
O2	0.0080 (5)	0.0124 (6)	0.0090 (5)	0.0009 (4)	-0.0044 (4)	0.0003 (4)
O3	0.0070 (5)	0.0116 (6)	0.0079 (5)	0.0021 (4)	-0.0032 (4)	-0.0013 (4)
O4	0.0110 (6)	0.0068 (5)	0.0095 (5)	-0.0012 (4)	-0.0054 (5)	-0.0014 (4)
O5	0.0128 (6)	0.0079 (5)	0.0083 (5)	0.0002 (4)	-0.0057 (5)	-0.0015 (4)
O6	0.0081 (5)	0.0079 (5)	0.0147 (6)	-0.0021 (4)	-0.0046 (5)	0.0014 (4)
O7	0.0056 (5)	0.0157 (6)	0.0064 (5)	0.0026 (4)	-0.0020 (4)	0.0004 (4)

*Geometric parameters (Å, °)*

Cd1—O7 <sup>i</sup>	2.2401 (13)	Cd2—O4 <sup>ii</sup>	2.4562 (14)
Cd1—O4 <sup>ii</sup>	2.2898 (13)	V1—O1	1.6882 (13)
Cd1—O6 <sup>iii</sup>	2.3083 (14)	V1—O2	1.7028 (14)
Cd1—O1 <sup>iii</sup>	2.3345 (14)	V1—O3	1.7265 (13)
Cd1—O1 <sup>iv</sup>	2.3476 (13)	V1—O4	1.7708 (13)
Cd1—O5 <sup>v</sup>	2.4043 (13)	V2—O5	1.6612 (14)
Cd1—O3	2.5300 (13)	V2—O6	1.6885 (14)
Cd2—O6 <sup>iii</sup>	2.2449 (14)	V2—O7	1.8530 (13)
Cd2—O5 <sup>ii</sup>	2.2858 (13)	V2—O7 <sup>i</sup>	1.8535 (13)
Cd2—O2 <sup>vi</sup>	2.2894 (14)	V2—O3	2.0348 (13)
Cd2—O2	2.3327 (14)	V2—V2 <sup>i</sup>	2.8482 (6)
Cd2—O4 <sup>v</sup>	2.3459 (13)		
O7 <sup>i</sup> —Cd1—O4 <sup>ii</sup>	114.29 (5)	O2 <sup>vi</sup> —Cd2—O2	74.71 (5)
O7 <sup>i</sup> —Cd1—O6 <sup>iii</sup>	131.24 (5)	O6 <sup>iii</sup> —Cd2—O4 <sup>v</sup>	96.72 (5)
O4 <sup>ii</sup> —Cd1—O6 <sup>iii</sup>	83.66 (5)	O5 <sup>ii</sup> —Cd2—O4 <sup>v</sup>	75.42 (5)
O7 <sup>i</sup> —Cd1—O1 <sup>iii</sup>	85.81 (5)	O2 <sup>vi</sup> —Cd2—O4 <sup>v</sup>	102.17 (5)
O4 <sup>ii</sup> —Cd1—O1 <sup>iii</sup>	157.35 (5)	O2—Cd2—O4 <sup>v</sup>	174.49 (5)
O6 <sup>iii</sup> —Cd1—O1 <sup>iii</sup>	90.73 (5)	O6 <sup>iii</sup> —Cd2—O4 <sup>ii</sup>	81.30 (5)
O7 <sup>i</sup> —Cd1—O1 <sup>iv</sup>	76.73 (5)	O5 <sup>ii</sup> —Cd2—O4 <sup>ii</sup>	75.69 (5)
O4 <sup>ii</sup> —Cd1—O1 <sup>iv</sup>	94.46 (5)	O2 <sup>vi</sup> —Cd2—O4 <sup>ii</sup>	160.52 (5)
O6 <sup>iii</sup> —Cd1—O1 <sup>iv</sup>	149.98 (5)	O2—Cd2—O4 <sup>ii</sup>	98.40 (5)
O1 <sup>iii</sup> —Cd1—O1 <sup>iv</sup>	79.55 (5)	O4 <sup>v</sup> —Cd2—O4 <sup>ii</sup>	83.09 (5)
O7 <sup>i</sup> —Cd1—O5 <sup>v</sup>	153.49 (5)	O1—V1—O2	109.38 (7)
O4 <sup>ii</sup> —Cd1—O5 <sup>v</sup>	74.22 (5)	O1—V1—O3	107.57 (7)
O6 <sup>iii</sup> —Cd1—O5 <sup>v</sup>	73.06 (5)	O2—V1—O3	109.85 (7)
O1 <sup>iii</sup> —Cd1—O5 <sup>v</sup>	83.15 (5)	O1—V1—O4	109.71 (7)
O1 <sup>iv</sup> —Cd1—O5 <sup>v</sup>	77.60 (5)	O2—V1—O4	109.65 (7)
O7 <sup>i</sup> —Cd1—O3	62.10 (5)	O3—V1—O4	110.65 (6)
O4 <sup>ii</sup> —Cd1—O3	86.49 (5)	O5—V2—O6	114.25 (7)
O6 <sup>iii</sup> —Cd1—O3	75.19 (5)	O5—V2—O7	99.11 (7)
O1 <sup>iii</sup> —Cd1—O3	113.31 (5)	O6—V2—O7	98.25 (7)
O1 <sup>iv</sup> —Cd1—O3	134.73 (5)	O5—V2—O7 <sup>i</sup>	121.64 (7)
O5 <sup>v</sup> —Cd1—O3	144.28 (4)	O6—V2—O7 <sup>i</sup>	123.74 (7)
O6 <sup>iii</sup> —Cd2—O5 <sup>ii</sup>	156.37 (5)	O7—V2—O7 <sup>i</sup>	79.57 (6)
O6 <sup>iii</sup> —Cd2—O2 <sup>vi</sup>	116.20 (5)	O5—V2—O3	92.06 (6)

O5 <sup>ii</sup> —Cd2—O2 <sup>vi</sup>	87.38 (5)	O6—V2—O3	93.85 (6)
O6 <sup>iii</sup> —Cd2—O2	88.75 (5)	O7—V2—O3	158.40 (6)
O5 <sup>ii</sup> —Cd2—O2	99.75 (5)	O7 <sup>i</sup> —V2—O3	78.83 (6)

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