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The synthetic cobalt vanadium selenite, $Co_2V_2Se_2O_{11}$

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Key indicators: single-crystal X-ray study; T = 292 K; mean σ(Se–O) = 0.003 Å; R factor = 0.032; wR factor = 0.048; data-to-parameter ratio = 18.0.

The crystal structure of dicobalt(II) divanadium(V) diselenium(IV) undecaoxide, $Co_2V_2Se_2O_{11}$, exhibits a three-dimensional framework, the building units being distorted CoO_6 octahedra and VO_5 square pyramids arranged so as to form alternate chains along [010]. The framework has channels along [100] and [010] in which the two Ψ-SeO_3E (site symmetries m; E being the $4s^2$ lone electron pair of Se^{IV}) tetrahedra reside and connect to the other building blocks. The structure contains corner- and edge-sharing CoO_6 octahedra, corner- and edge-sharing VO_5 square pyramids and edge-sharing Ψ-SeO_3E tetrahedra. $Co_2V_2Se_2O_{11}$ is the first oxide containing all the cations Co^{II}, V^{V} and Se^{IV}.

Related literature

For general background, including bond-valence-sum calculations, see: Brown & Altermatt (1985). For related structures, see: Allen *et al.* (2004); Becker *et al.* (2007*a*,*b*); Jiang *et al.* (2008); Millet *et al.* (1999); Pitzschenke & Jansen (2007); Sauerbrei *et al.* (1974).

Experimental

Crystal data

$Co_2V_2Se_2O_{11}$
M_r = 553.66
Monoclinic, $P2_1/m$
a = 4.7913 (2) Å
b = 8.8680 (4) Å
c = 10.6156 (5) Å
β = 101.115 (5)°
V = 442.59 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 14.01 mm^{-1}
T = 292 K
0.05 × 0.03 × 0.02 mm

Data collection

Oxford Diffraction Xcalibur Sapphire3 diffractometer
Absorption correction: analytical [*CrysAlis RED* (Oxford Diffraction, 2007), based on expressions derived by Clark & Reid (1995)]
T_{min} = 0.659, T_{max} = 0.756
4219 measured reflections
1534 independent reflections
1023 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.048
S = 0.76
1534 reflections
85 parameters
$\Delta\rho_{max}$ = 1.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.98 e Å^{-3}

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2421).

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supplementary materials

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Comment

The synthesis and crystal structure determination of the new compound $Co_2V_2Se_2O_{11}$ is a result of an ongoing investigation of the structural chemistry of selenium and tellurium oxides and oxohalides. Transition metal oxides and oxohalides containing *p*-block cations, such as Se^{IV} and Te^{IV}, with stereochemically active lone pairs frequently show a low-dimensional arrangement of the metal ions. The Se^{IV} lone pairs act as 'chemical scissors' and help to reduce the dimensionality of the atomic arrangements in the crystal structure (Becker *et al.*, 2007*a,b*). The aim of the present study was to test the synthesis concept in a system containing two transition metals taking different coordination polyhedra: CoO-V_2O_5—SeO_2. The present compound is, to the best of our knowledge, the first oxide to contain all the cations Co^{II}, V^V and Se^{IV}. A few selenites containing vanadium plus another transition metal have previously been described; $Cd_6V_2Se_5O_{21}$ (Jiang *et al.*, 2008), α-$CuVSe_2O_7$ and β-$CuVSe_2O_7$ (Millet *et al.*, 1999), $AgVSeO_5$ and $ZnVSe_2O_7$ (Pitzschenke & Jansen, 2007). The stereochemically active lone electron pairs open up the crystal structures by creating non-bonding volumes and occupy space similar to that taken by an oxygen anion in the crystal structure. α-$CuVSe_2O_7$ is a layered compound with only weak van der Waals interactions in between the layers while the others are three-dimensional framework structures where the lone pairs on Se^{IV} are located in voids in the crystal structure.

$Co_2V_2Se_2O_{11}$ crystallizes in the centrosymmetric monoclinic space group $P2_1/m$. The Co^{II} ions are in a slightly distorted octahedral environment. The CoO_6 octahedra are connected *via* $O2^{iii}\cdots O2^{v}$ and $O1\cdots O3^{iii}$ edge sharing [symmetry code: (iii) $x + 1,y,z$; (v) $-x + 1,y + 1/2,-z + 1$] to form zigzag chains having the formula $[CoO_4]_n$ along [100]. The Co···O bonds are in the range 2.074 (3) Å to 2.123 (3) Å which is comparable to what is found in *e.g.* $Co_2V_2O_7$ (Sauerbrei *et al.*, 1974). There are two Co—Co distances within a chain; 3.160 (1) Å and 3.179 (2) Å. The V^V atoms are surrounded by five O atoms forming a very distorted square pyramid comprising two V1=O vanadyl double bonds of 1.627 (3) Å and 1.635 (3) Å and two long V1–O bonds 2.038 (3) Å and 2.087 (3) Å (Fig. 1). As a consequence, the V atom is located above the square plane. Bond valence sum analysis (Brown & Altermatt, 1985) confirms the coordination, with the calculated valence (V^V, the bond valence parameter $R_o = 1.803$) equal to 5.15. The VO_5 square pyramids are connected *via* $O5\cdots O5^{ii}$ edge sharing and O7 corner sharing [symmetry code: (ii) $-x + 1,-y + 1,z - 2$] to form chains having the formula $[V_2O_7]_n$ along [010]. The V···V distances in a chain are 3.328 (1) Å and 3.443 (2) Å. The chains of CoO_6 and VO_5 bridge by corner sharing at O4 and O6. The Se^{IV} ions have both one sided SeO_3 coordination owing to the presence of the $4s^2$ stereochemically active lone pair, E, and they do not polymerize. The crystal structure can be described as being a three-dimensional framework structure made up of $[CoO_4]_n$– and $[V_2O_7]_n$ chains (Fig. 2 and 3). The SeO_3 groups connect to the metal-oxide framework by corner sharing (Fig. 3). The stereochemically active Se^{IV} lone pairs are located in voids in the structure. Those voids are present as tunnels along (100) and (010) respectively.

Bond valence sum analysis (Brown & Altermatt, 1985) confirms the coordination for all the ions and give 2.04 for Co1, 5.15 for V1, 4.01 for Se1, 3.84 for Se2, 2.07 for O1, 2.02 for O2, 2.11 for O3, 1.92 for O4 and 2.36 for O5.

Experimental

Single crystals of $Co_2V_2Se_2O_{11}$ are non-hygroscopic and were synthesized *via* chemical vapour transport reactions in sealed evacuated silica tubes. The starting materials were 0.150 g (2 mmol) CoO (ABCR GmbH 97.999%), 0.182 g (1 mmol) V_2O_5 (ABCR GmbH 99.9%), and 0.222 g (2 mmol) SeO_2, (Alfa Aesar 99.4%) mixed in a stoichiometric 2:1:2 molar ratio and placed in a 5 cm long silica tube which was first dried for 1 h at 100°C and subsequently evacuated and sealed. The silica tube was treated in a muffle furnace at 500°C for 100 h followed by slow cooling at a rate of 10°C/h to room temperature. The synthesis products were a mixture of red single crystals of $Co_2V_2Se_2O_{11}$ and a brown-red powder of undetermined composition.

Refinement

The structure was solved using SHELXS97 (Sheldrick, 2008), and refined by full-matrix least-squares using SHELXL97 (Sheldrick, 2008).

Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED* (Oxford Diffraction, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *enCIFer* (Allen *et al.* 2004).

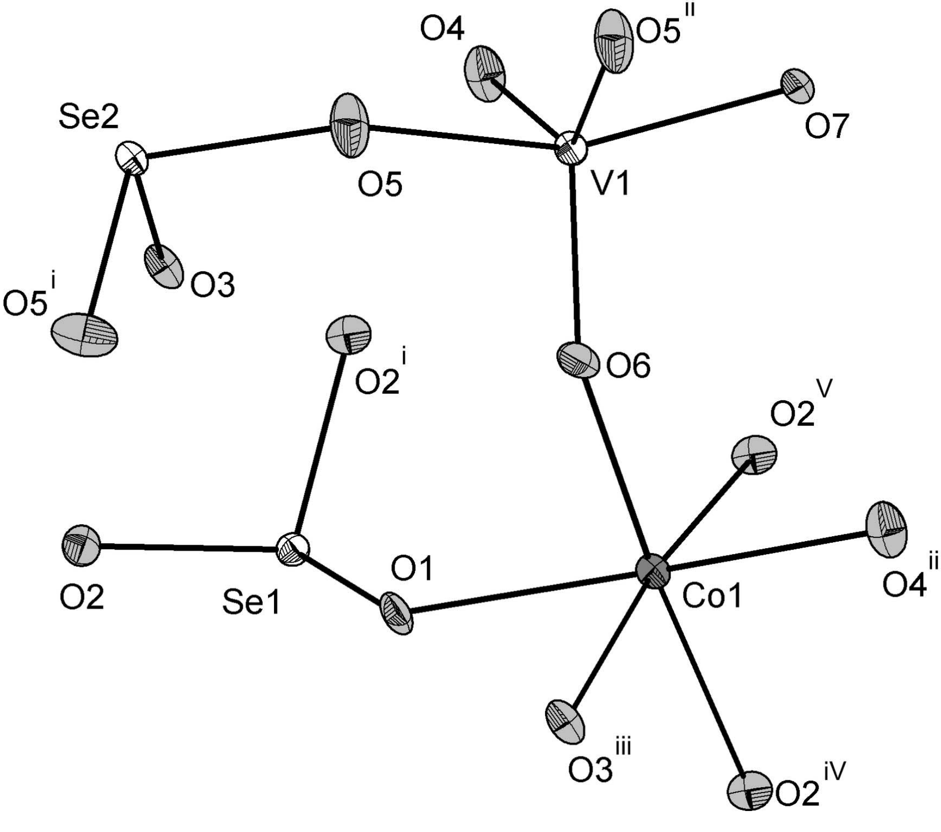

Figure 1

A displacement ellipsoid diagram showing the coordination around the cations. Atomic displacement parameters are given at the 50% probability level [Symmetry codes: (i) $x,-y + 1/2,z$; (ii) $-x + 1,-y - 1,z - 2$; (iii) $x + 1,y,z$; (iv) $x + 1,-y + 1/2,z$; (v) $-x + 1,y + 1/2,-z + 1$].

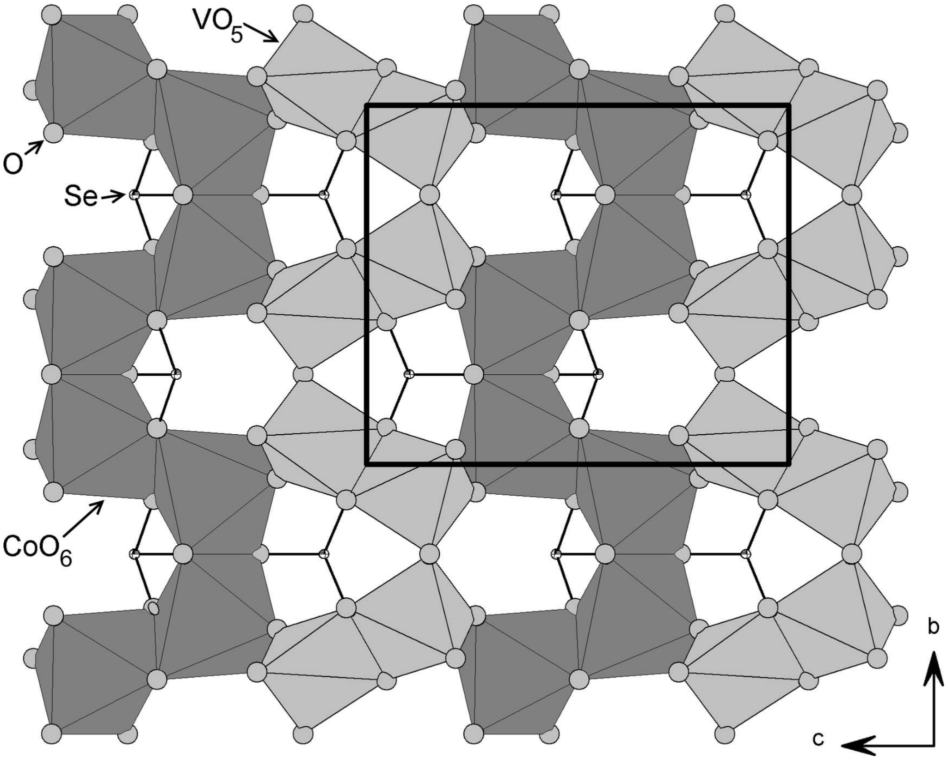

Figure 2

A view of the structure of $Co_2V_2Se_2O_{11}$ along (100).

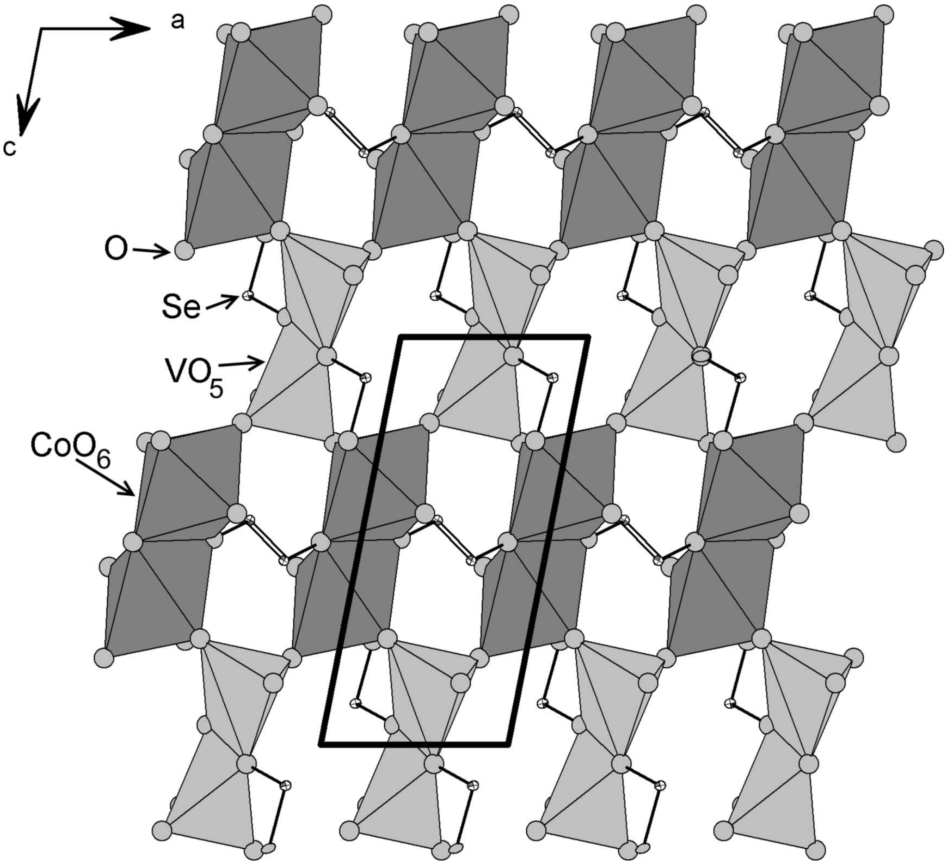

Figure 3

A view of the structure of $Co_2V_2Se_2O_{11}$ along (010).

dicobalt(II) divanadium(V) diselenium(IV) undecaoxide

Crystal data

$Co_2V_2Se_2O_{11}$
$M_r = 553.66$
Monoclinic, $P2_1/m$
Hall symbol: -P 2yb
$a = 4.7913$ (2) Å
$b = 8.8680$ (4) Å
$c = 10.6156$ (5) Å
$\beta = 101.115$ (5)°
$V = 442.59$ (3) Å^3
$Z = 2$
$F(000) = 512$
$D_x = 4.155$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1387 reflections
$\theta = 3.9$–32.2°
$\mu = 14.01$ mm^{-1}
$T = 292$ K
Block, red
0.05 × 0.03 × 0.02 mm

Data collection

Oxford Diffraction Xcalibur Sapphire3 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.5 pixels mm^{-1}
ω scans
Absorption correction: analytical [*CrysAlis RED* (Oxford Diffraction, 2007), based on expressions derived by Clark & Reid (1995)]
$T_{min} = 0.659$, $T_{max} = 0.756$
4219 measured reflections
1534 independent reflections
1023 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.051
$\theta_{\rm max}$ = 32.3°, $\theta_{\rm min}$ = 3.9°
$h = -7 \rightarrow 7$
$k = -11 \rightarrow 12$
$l = -15 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.048$
$S = 0.76$
1534 reflections
85 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0114P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max}$ = 1.28 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.98 e Å^{-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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Se1	0.38839 (12)	0.2500	0.45047 (6)	0.00668 (13)
Se2	0.14374 (12)	0.2500	0.89926 (5)	0.00653 (13)
Co1	0.95757 (12)	0.42816 (6)	0.63219 (5)	0.00751 (13)
V1	0.53298 (15)	0.56239 (8)	0.85002 (6)	0.00660 (15)
O1	0.6860 (8)	0.2500	0.5658 (4)	0.0105 (9)
O6	0.7568 (6)	0.4597 (3)	0.7887 (3)	0.0118 (6)
O5	0.3738 (6)	0.4001 (3)	0.9523 (3)	0.0107 (6)
O2	0.2107 (6)	0.0989 (3)	0.4958 (3)	0.0093 (6)
O3	0.1701 (8)	0.2500	0.7454 (4)	0.0088 (9)
O4	0.2448 (6)	0.5786 (3)	0.7407 (3)	0.0132 (7)
O7	0.6843 (8)	0.7500	0.8501 (4)	0.0077 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Se1	0.0068 (3)	0.0069 (3)	0.0064 (3)	0.000	0.0014 (2)	0.000
Se2	0.0080 (3)	0.0051 (3)	0.0063 (3)	0.000	0.0008 (2)	0.000
Co1	0.0080 (3)	0.0063 (3)	0.0082 (3)	0.0001 (2)	0.0016 (2)	0.0001 (2)
V1	0.0078 (3)	0.0063 (3)	0.0058 (3)	−0.0003 (3)	0.0017 (3)	0.0000 (3)
O1	0.008 (2)	0.005 (2)	0.017 (2)	0.000	−0.0012 (18)	0.000
O6	0.0140 (16)	0.0077 (15)	0.0148 (16)	0.0010 (12)	0.0059 (13)	−0.0014 (12)
O5	0.0153 (16)	0.0113 (15)	0.0045 (14)	−0.0088 (12)	−0.0003 (12)	−0.0024 (11)
O2	0.0106 (15)	0.0103 (16)	0.0071 (15)	−0.0021 (12)	0.0021 (12)	−0.0024 (11)
O3	0.012 (2)	0.006 (2)	0.007 (2)	0.000	−0.0022 (17)	0.000

O4	0.0139 (16)	0.0101 (16)	0.0132 (16)	−0.0020 (12)	−0.0031 (13)	0.0025 (12)
O7	0.009 (2)	0.005 (2)	0.010 (2)	0.000	0.0024 (17)	0.000

Geometric parameters (Å, º)

Se1—O1	1.691 (4)	Co1—O6	2.093 (3)
Se1—O2	1.706 (3)	Co1—O4$^{\mathrm{iv}}$	2.095 (3)
Se1—O2$^{\mathrm{i}}$	1.706 (3)	Co1—O3$^{\mathrm{iv}}$	2.122 (3)
Se2—O3	1.663 (4)	V1—O4	1.630 (3)
Se2—O5	1.750 (3)	V1—O6	1.635 (3)
Se2—O5$^{\mathrm{i}}$	1.750 (3)	V1—O7	1.8147 (17)
Co1—O2$^{\mathrm{ii}}$	2.074 (3)	V1—O5	2.038 (3)
Co1—O1	2.081 (3)	V1—O5$^{\mathrm{v}}$	2.086 (3)
Co1—O2$^{\mathrm{iii}}$	2.090 (3)		
O1—Se1—O2	101.12 (13)	O2$^{\mathrm{ii}}$—Co1—O3$^{\mathrm{iv}}$	91.59 (13)
O1—Se1—O2$^{\mathrm{i}}$	101.12 (13)	O1—Co1—O3$^{\mathrm{iv}}$	80.04 (12)
O2—Se1—O2$^{\mathrm{i}}$	103.52 (19)	O2$^{\mathrm{iii}}$—Co1—O3$^{\mathrm{iv}}$	172.01 (14)
O3—Se2—O5	98.85 (13)	O6—Co1—O3$^{\mathrm{iv}}$	83.90 (13)
O3—Se2—O5$^{\mathrm{i}}$	98.85 (13)	O4$^{\mathrm{iv}}$—Co1—O3$^{\mathrm{iv}}$	88.29 (11)
O5—Se2—O5$^{\mathrm{i}}$	98.97 (19)	O4—V1—O6	107.24 (15)
O2$^{\mathrm{ii}}$—Co1—O1	95.00 (14)	O4—V1—O7	101.71 (16)
O2$^{\mathrm{ii}}$—Co1—O2$^{\mathrm{iii}}$	80.44 (12)	O6—V1—O7	102.62 (15)
O1—Co1—O2$^{\mathrm{iii}}$	101.07 (12)	O4—V1—O5	95.11 (13)
O2$^{\mathrm{ii}}$—Co1—O6	171.78 (11)	O6—V1—O5	99.22 (13)
O1—Co1—O6	90.99 (14)	O7—V1—O5	146.92 (14)
O2$^{\mathrm{iii}}$—Co1—O6	103.94 (11)	O4—V1—O5$^{\mathrm{v}}$	133.61 (14)
O2$^{\mathrm{ii}}$—Co1—O4$^{\mathrm{iv}}$	92.69 (12)	O6—V1—O5$^{\mathrm{v}}$	117.38 (13)
O1—Co1—O4$^{\mathrm{iv}}$	166.17 (13)	O7—V1—O5$^{\mathrm{v}}$	81.09 (14)
O2$^{\mathrm{iii}}$—Co1—O4$^{\mathrm{iv}}$	91.51 (11)	O5—V1—O5$^{\mathrm{v}}$	66.81 (12)
O6—Co1—O4$^{\mathrm{iv}}$	80.34 (11)		

Symmetry codes: (i) *x*, −*y*+1/2, *z*; (ii) *x*+1, −*y*+1/2, *z*; (iii) −*x*+1, *y*+1/2, −*z*+1; (iv) *x*+1, *y*, *z*; (v) −*x*+1, −*y*+1, −*z*+2.