Supporting Information

Interplay of Dual-Site Metal Disorder on the Thermodynamic Stability and Electronic Structures of Cu(I)-Containing Molybdovanadate and Tungstovanadate Compounds

Machima Mongkhonratanachai,[1] Subhendu Jana,[1] and Paul A. Maggard[1,*]

[1] *Department of Chemistry and Biochemistry, Baylor University, Waco, Texas, 76798, USA*

[*] Corresponding author e-mail: Paul_Maggard@baylor.edu

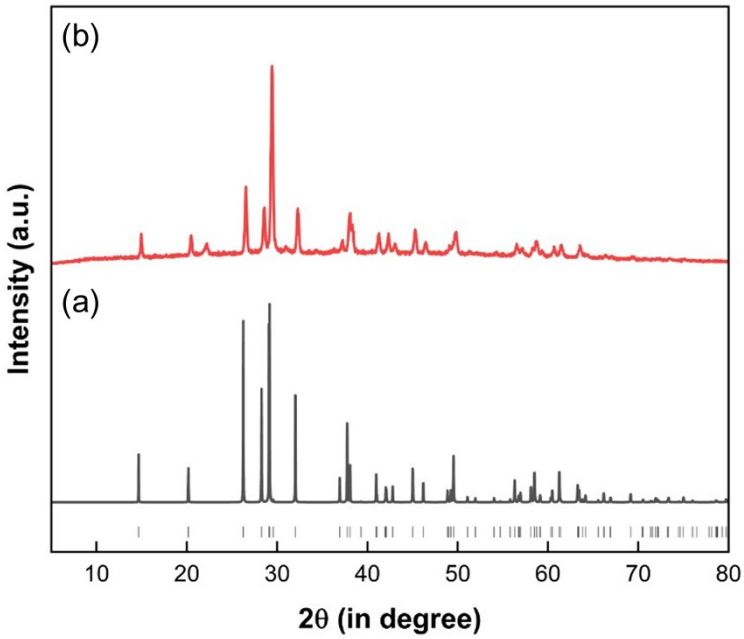

Figure S1. The simulated (a; black line) and experimental (b; red line) powder X-ray diffraction plots for the crystal structure of $CuVMoO_6$ (**1**).

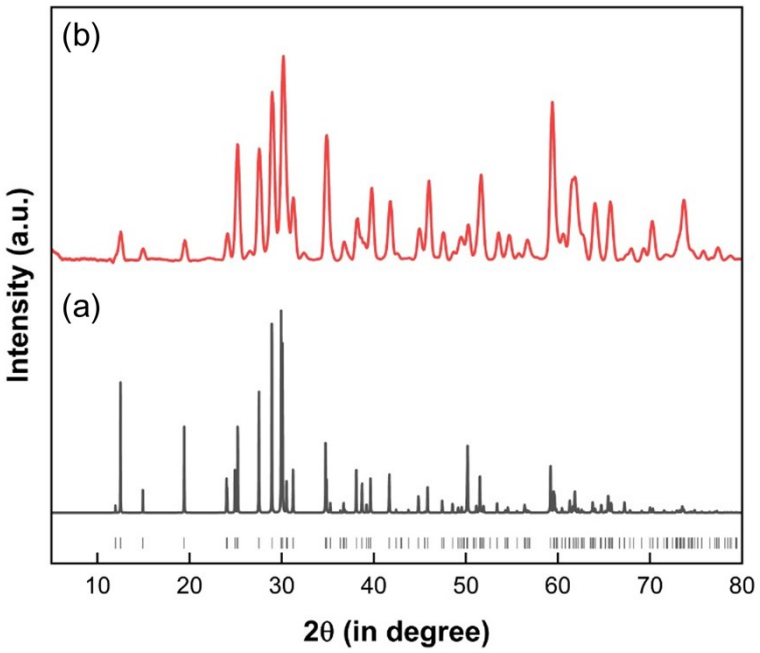

Figure S2. The simulated (a; black line) and experimental (b; red line) powder X-ray diffraction plots for the crystal structure of $Cu_{1.51(1)}V_{3.57(1)}Mo_{0.43(1)}O_{11}$ (**2**).

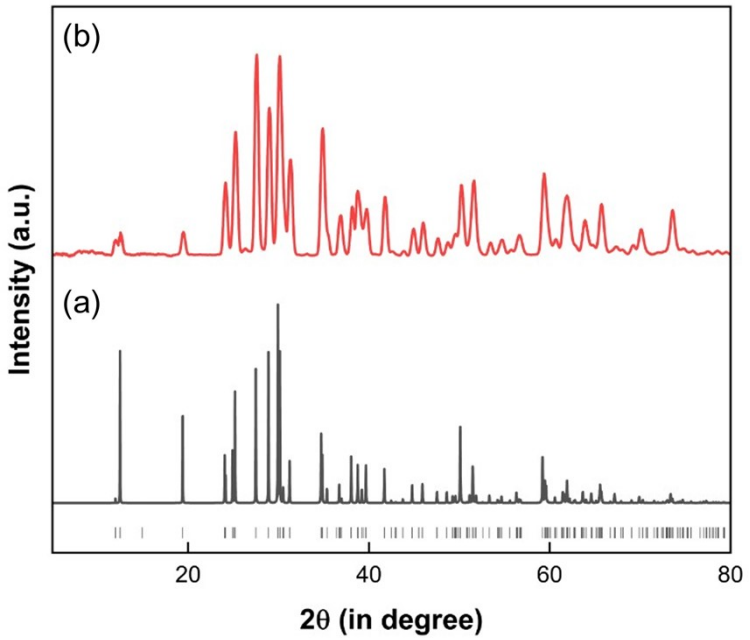

Figure S3. The simulated (a; black line) and experimental (b; red line) powder X-ray diffraction plots for the crystal structure of $Cu_{1.59(1)}V_{3.52(1)}W_{0.48(1)}O_{11}$ (**3**).

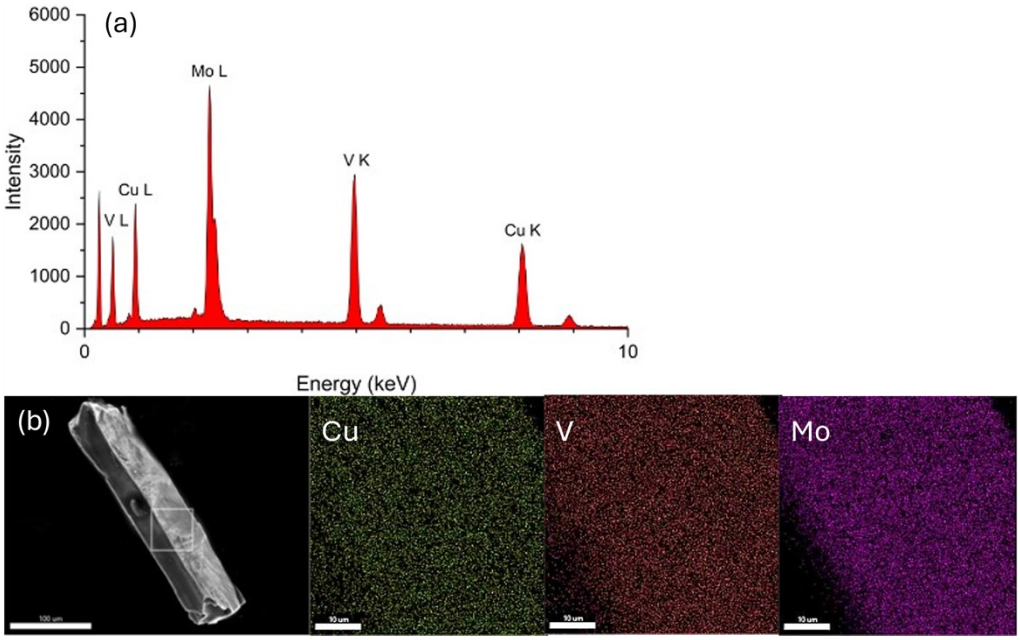

Figure S4. (a) Energy dispersive X-ray spectrum and (b) elemental mapping for a single crystal of $CuVMoO_6$ (**1**), showing a homogeneous distribution of Cu, V, and Mo in the molar percentages of 32.1%, 30.6%, 37.3%, respectively.

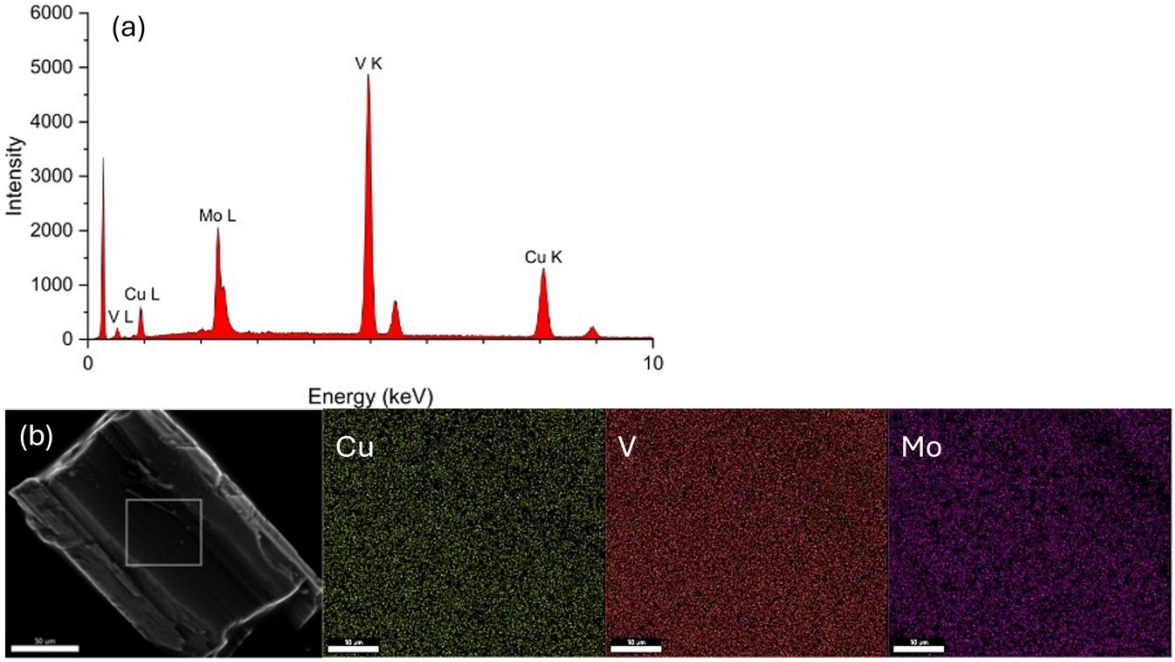

Figure S5. (a) Energy dispersive X-ray spectrum and (b) elemental mapping for a single crystal of $Cu_{1.51(1)}V_{3.57(1)}Mo_{0.43(1)}O_{11}$ (**2**), exhibiting a homogeneous distribution of Cu, V, and Mo in the molar percentages of 27.0%, 61.1%, and 11.9%, respectively.

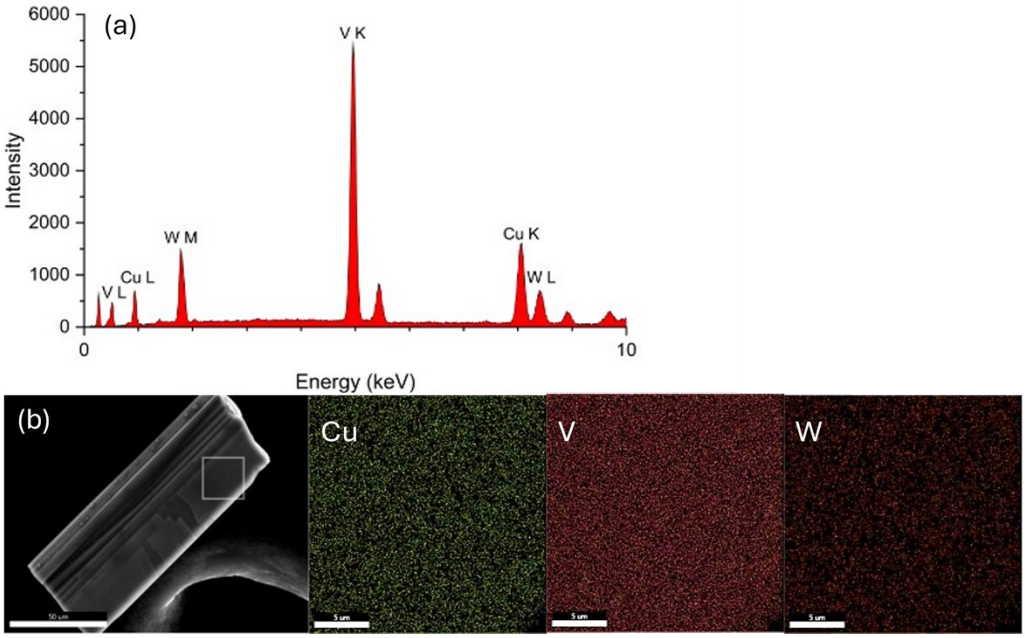

Figure S6. (a) Energy dispersive X-ray spectrum and (b) elemental mapping for a single crystal of $Cu_{1.59(1)}V_{3.52(1)}W_{0.48(1)}O_{11}$ (**3**), showing a homogeneous distribution of Cu, V, and W in the molar percentages of 28.3%, 59.4%, and 12.2%, respectively.

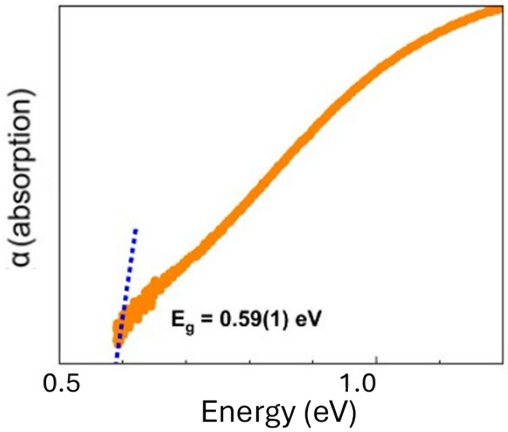

Figure S7. Kubelka-Munk plot of the UV-Vis data for compound **1**.

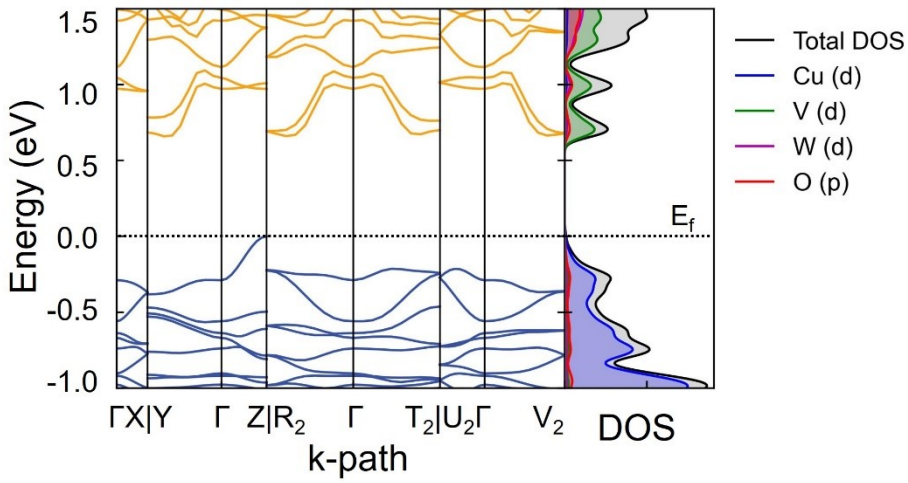

Figure S8. Calculated density-of-states (DOS; left) and band structure (right) for hypothetical "$CuVWO_6$" with the Fermi level (E_f) at 0 eV and the individual atomic contributions projected out by orbital type.

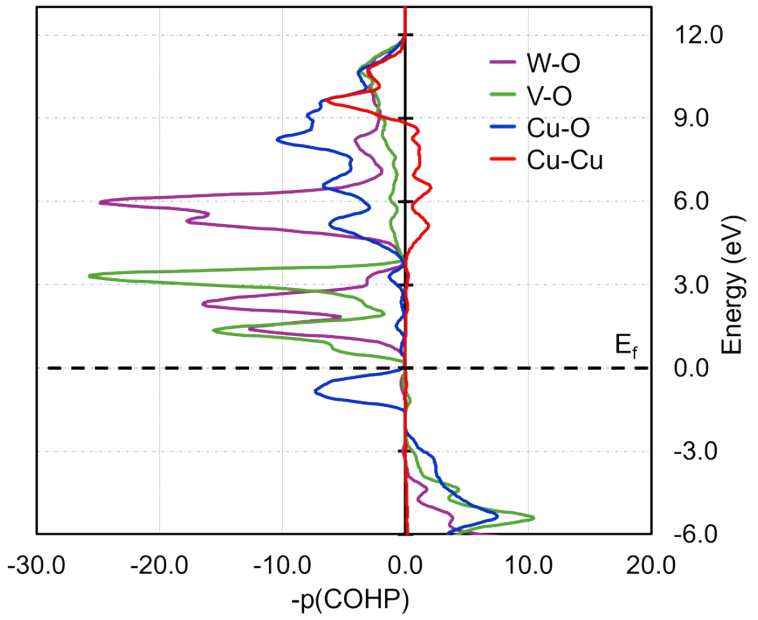

Figure S9. Calculated Crystal Orbital Hamilton Populations (COHP) for the Mo-O, V-O, Cu-O, and Cu-Cu interactions for the calculated hypothetical $CuVWO_6$ with the Fermi level (E_f) labeled at 0 eV.

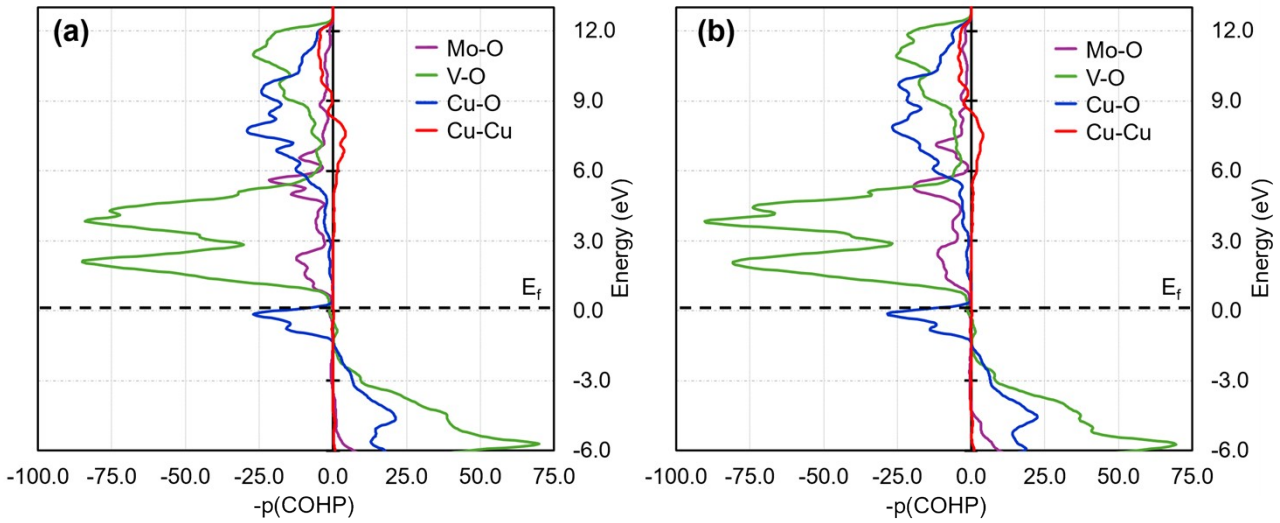

Figure S10. Calculated Crystal Orbital Hamilton Populations (COHP) for the Mo-O, V-O, Cu-O, and Cu-Cu interactions for **2** ($Cu_{1.51(1)}V_{3.57(1)}Mo_{0.43(1)}O_{11}$) for the α (a) and β (b) polymorphs. The Fermi levels (E_f) are labeled at 0 eV.

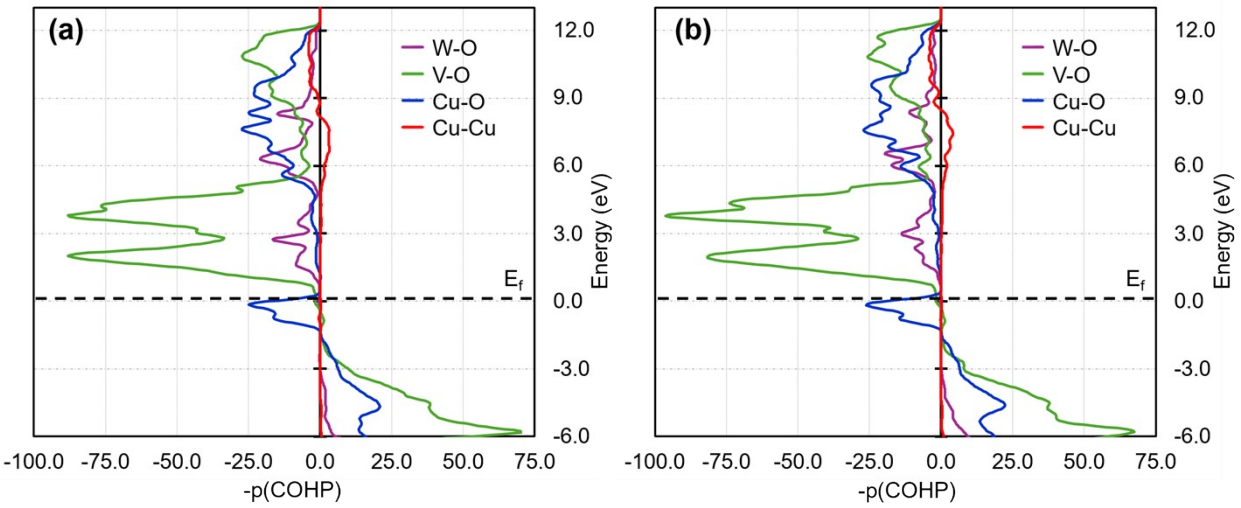

Figure S11. Calculated Crystal Orbital Hamilton Populations (COHP) for the W-O, V-O, Cu-O, and Cu-Cu interactions for **3** ($Cu_{1.59(1)}V_{3.52(1)}W_{0.48(1)}O_{11}$) for the α (a) and β (b) polymorphs. The Fermi levels (E_f) are labeled at 0 eV.

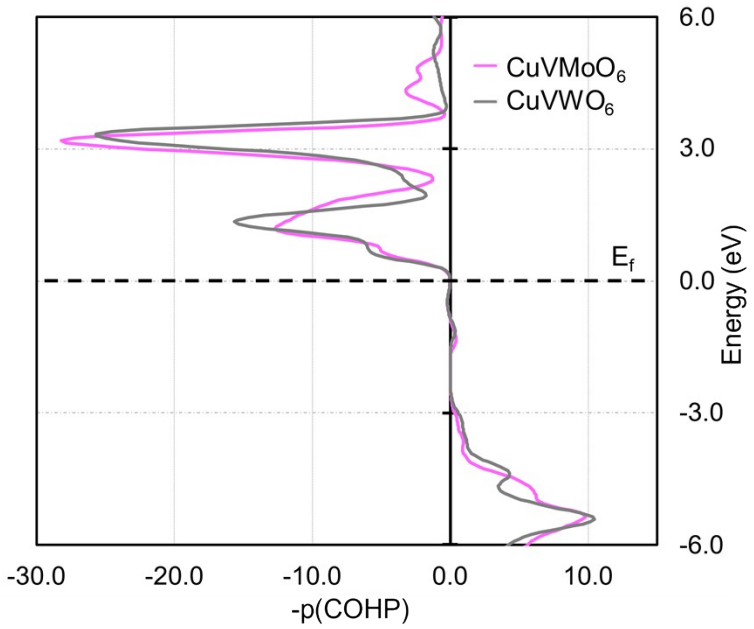

Figure S12. Calculated Crystal Orbital Hamilton Populations (COHP) for the V-O interactions for $CuVMoO_6$ (**1**) and $CuVWO_6$ with the Fermi level (E_f) labeled at 0 eV.

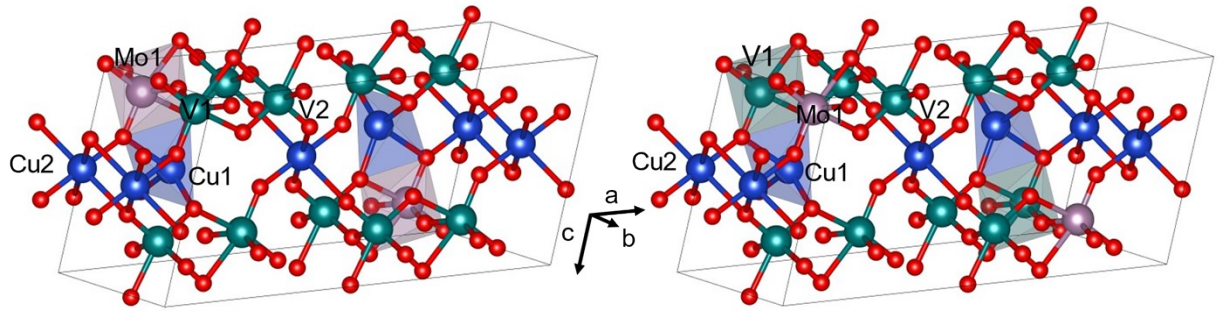

Figure S13. Structural models of the α (left) and β (right) polymorphs for $Cu_{1.51(1)}V_{3.57(1)}Mo_{0.43(1)}O_{11}$ (**2**), with the occupied Cu1-site edge-bridging to an MoO_6 or VO_6 octahedron, respectively.

Table S1: Atomic coordinates, Wyckoff positions, site symmetries, site occupancies and equivalent isotropic displacement parameters in the structure of $CuVMoO_6$ (**1**).

Atom	Wyckoff Position	Site Symmetry	*x*	*y*	*z*	U_{eq}	Occupancy
V1	4i	m	0.18335(6)	0	0.14758(8)	0.00779 (19)	0.5
Mo1	4i	m	0.18335(6)	0	0.14758(8)	0.00779 (19)	0.5
Cu1	2c	2/m	0	0	0.5	0.0422 (4)	1
O1	4i	m	0.0222(4)	0	0.2134(5)	0.0115 (7)	1
O2	4i	m	0.3291(4)	0	0.3918(5)	0.0134 (7)	1
O3	4i	m	0.6899(4)	0	0.0633(5)	0.0107 (7)	1

Table S2: Atomic thermal displacement parameters ($Å^2$) for $CuVMoO_6$ (**1**).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.0097(3)	0.0064(3)	0.0087(3)	0	0.0049(2)	0
Mo1	0.0097(3)	0.0064(3)	0.0087(3)	0	0.0049(2)	0
Cu1	0.0207(6)	0.0914(11)	0.0147(5)	0	0.0069(4)	0
O1	0.0105(16)	0.0084(16)	0.0159(16)	0	0.0051(13)	0
O2	0.0101(16)	0.0163(17)	0.0144(15)	0	0.0050(13)	0
O3	0.0129(17)	0.0064(15)	0.0145(15)	0	0.0070(14)	0

Table S3: List of bond distances and angles (Å,º) for $CuVMoO_6$ (**1**).

Mo1—O1i	2.433 (3)	Cu1—O1v	1.945 (3)
Mo1—O1	1.725 (3)	Cu1—O1	1.945 (3)
Mo1—O2	1.676 (3)	Cu1—O2vi	2.376 (2)
Mo1—O3ii	2.122 (3)	Cu1—O2iv	2.376 (2)
Mo1—O3iii	1.9254 (9)	Cu1—O2vii	2.376 (2)

Mo1—O3iv	1.9254 (9)	Cu1—O2iii	2.377 (2)
O1—Mo1—O1i	76.88 (14)	O1v—Cu1—O2vii	90.97 (10)
O1—Mo1—O3iii	101.14 (10)	O1v—Cu1—O2vi	90.97 (10)
O1—Mo1—O3ii	156.47 (14)	O1—Cu1—O2vii	89.03 (10)
O1—Mo1—O3iv	101.14 (10)	O1—Cu1—O2iii	90.97 (10)
O2—Mo1—O1	105.07 (15)	O2iii—Cu1—O2iv	101.35 (12)
O2—Mo1—O1i	178.05 (12)	O2iv—Cu1—O2vii	180.00 (17)
O2—Mo1—O3iv	99.66 (10)	O2iii—Cu1—O2vii	78.65 (12)
O2—Mo1—O3iii	99.66 (10)	O2vi—Cu1—O2iii	180.00 (17)
O2—Mo1—O3ii	98.46 (14)	O2vi—Cu1—O2iv	78.65 (12)
O3iii—Mo1—O1i	79.86 (10)	O2vi—Cu1—O2vii	101.33 (12)
O3iv—Mo1—O1i	79.86 (10)	Mo1—O1—Mo1i	103.13 (14)
O3ii—Mo1—O1i	79.59 (11)	Mo1—O1—Cu1	130.55 (19)
O3iv—Mo1—O3ii	74.50 (9)	Cu1—O1—Mo1i	126.33 (15)
O3iii—Mo1—O3ii	74.50 (9)	Mo1—O2—Cu1viii	120.88 (9)
O3iii—Mo1—O3iv	145.42 (17)	Mo1—O2—Cu1ix	120.88 (9)
O1v—Cu1—O1	180	Cu1viii—O2—Cu1ix	101.35 (12)
O1—Cu1—O2iv	90.97 (10)	Mo1viii—O3—Mo1ii	105.50 (9)
O1v—Cu1—O2iii	89.03 (10)	Mo1ix—O3—Mo1ii	105.50 (9)
O1v—Cu1—O2iv	89.03 (10)	Mo1viii—O3—Mo1ix	145.42 (17)
O1—Cu1—O2vi	89.03 (10)		
O1i—Mo1—O1—Mo1i	0.000 (1)	O3iv—Mo1—O1—Cu1	−103.30 (10)
O1i—Mo1—O1—Cu1	180	O3ii—Mo1—O1—Cu1	180.000 (1)
O1—Mo1—O2—Cu1viii	−115.66 (13)	O3iii—Mo1—O1—Cu1	103.30 (10)
O1—Mo1—O2—Cu1ix	115.66 (13)	O3iii—Mo1—O2—Cu1ix	11.25 (17)
O2—Mo1—O1—Mo1i	180.000 (1)	O3ii—Mo1—O2—Cu1ix	−64.34 (13)

O2—Mo1—O1—Cu1	0	O3iii—Mo1—O2—Cu1viii	139.93 (15)
O3iv—Mo1—O1—Mo1i	76.70 (10)	O3iv—Mo1—O2—Cu1ix	−139.93 (15)
O3iii—Mo1—O1—Mo1i	−76.70 (10)	O3iv—Mo1—O2—Cu1viii	−11.25 (17)
O3ii—Mo1—O1—Mo1i	0.000 (1)	O3ii—Mo1—O2—Cu1viii	64.34 (13)

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

Table S4: Atomic coordinates, Wyckoff positions, site symmetries, occupancies and equivalent isotropic displacement parameters for the structure of $Cu_{1.51(1)}V_{3.57(1)}Mo_{0.43(1)}O_{11}$ (**2**).

Atom	Wyckoff Position	Site Symmetry	*x*	*y*	*z*	U_{eq}	Occupancy
V1	4i	m	0.11280 (6)	0	0.15673 (12)	0.0150 (3)	0.783(9)
Mo1	4i	m	0.11280 (6)	0	0.15673 (12)	0.0150 (3)	0.217(9)
V2	4i	m	0.32964 (6)	0	0.15616 (12)	0.0069 (3)	1
Cu1	4i	m	0.2360 (3)	0	0.5516 (5)	0.0285 (13)	0.253(5)
Cu2	2c	2/m	0	0	0.5	0.0788 (10)	1
O1	4i	m	0.0909 (3)	0	0.3677 (7)	0.0208 (10)	1
O2	4i	m	0.2542 (3)	0	0.2973 (7)	0.0208 (10)	1
O3	4i	m	0.4284 (3)	0	0.3061 (7)	0.0222 (10)	1
O4	4i	m	0.6320 (3)	0	0.1035 (6)	0.0151 (8)	1
O5	4i	m	0.8157 (3)	0	0.0731 (7)	0.0169 (9)	1
O6	2a	2/m	0	0	0	0.0192 (13)	1

Table S5: Atomic thermal displacement parameters for (Å^2) for $Cu_{1.51(1)}V_{3.57(1)}Mo_{0.43(1)}O_{11}$ (**2**).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.0226 (5)	0.0079 (4)	0.0205 (5)	0	0.0165 (3)	0
Mo1	0.0226 (5)	0.0079 (4)	0.0205 (5)	0	0.0165 (3)	0
V2	0.0055 (4)	0.0054 (4)	0.0110 (5)	0	0.0040 (3)	0
Cu1	0.039 (2)	0.032 (2)	0.0149 (17)	0	0.0069 (13)	0
Cu2	0.0273 (8)	0.176 (3)	0.0419 (10)	0	0.0243 (7)	0
O1	0.018 (2)	0.024 (2)	0.024 (2)	0	0.0108 (17)	0
O2	0.013 (2)	0.030 (3)	0.021 (2)	0	0.0066 (17)	0
O3	0.015 (2)	0.027 (3)	0.024 (2)	0	0.0058 (17)	0
O4	0.0166 (19)	0.010 (2)	0.021 (2)	0	0.0103 (16)	0
O5	0.018 (2)	0.013 (2)	0.023 (2)	0	0.0102 (17)	0
O6	0.012 (3)	0.017 (3)	0.025 (3)	0	−0.001 (2)	0

Table S6: Selected bond distances and angles (Å, º) for $Cu_{1.51(1)}V_{3.57(1)}Mo_{0.43(1)}O_{11}$ (**2**).

V1—Cu1	3.021 (4)	Cu2—O1	1.890 (5)
V1—O5i	2.232 (5)	Cu2—O1iv	1.890 (5)
V1—O4ii	1.8963 (12)	Cu2—O3ii	2.392 (3)
V1—O4iii	1.8963 (12)	Cu2—O3v	2.392 (3)
V1—O2	2.148 (5)	Cu2—O3vi	2.392 (3)
V1—O1	1.663 (5)	Cu2—O3iii	2.392 (3)
V1—O6	1.8134 (9)	Cu1—Cu1vi	2.055 (4)
V2—O5ii	1.9100 (14)	Cu1—Cu1v	2.055 (4)
V2—O5iii	1.9100 (14)	Cu1—O2	1.953 (6)
V2—O5i	2.421 (5)	Cu1—O2vi	2.112 (3)
V2—O4i	2.130 (4)	Cu1—O2v	2.112 (3)

V2—O2	1.737 (5)	Cu1—O1	2.284 (6)
V2—O3	1.627 (5)		
O5i—V1—Cu1	114.52 (15)	O3v—Cu2—O3ii	180
O4ii—V1—Cu1	96.03 (14)	O3v—Cu2—O3vi	98.83 (17)
O4iii—V1—Cu1	96.03 (14)	Cu1v—Cu1—V1	77.67 (19)
O4ii—V1—O5i	73.32 (12)	Cu1vi—Cu1—V1	77.67 (19)
O4iii—V1—O5i	73.32 (12)	Cu1vi—Cu1—Cu1v	124.3 (4)
O4ii—V1—O4iii	146.6 (2)	Cu1vi—Cu1—O2v	163.6 (4)
O4iii—V1—O2	84.73 (14)	Cu1v—Cu1—O2vi	163.6 (4)
O4ii—V1—O2	84.73 (14)	Cu1v—Cu1—O2v	55.88 (14)
O2—V1—Cu1	40.10 (15)	Cu1vi—Cu1—O2vi	55.88 (14)
O2—V1—O5i	74.42 (17)	Cu1v—Cu1—O1	92.7 (2)
O1—V1—Cu1	48.36 (19)	Cu1vi—Cu1—O1	92.7 (2)
O1—V1—O5i	162.9 (2)	O2v—Cu1—V1	116.41 (15)
O1—V1—O4iii	105.65 (13)	O2vi—Cu1—V1	116.41 (15)
O1—V1—O4ii	105.65 (13)	O2—Cu1—V1	45.11 (15)
O1—V1—O2	88.5 (2)	O2—Cu1—Cu1vi	63.56 (18)
O1—V1—O6	101.66 (17)	O2—Cu1—Cu1v	63.56 (18)
O6—V1—Cu1	150.02 (9)	O2—Cu1—O2vi	119.43 (15)
O6—V1—O5i	95.46 (12)	O2v—Cu1—O2vi	118.6 (3)
O6—V1—O4ii	92.44 (14)	O2—Cu1—O2v	119.43 (15)
O6—V1—O4iii	92.44 (14)	O2v—Cu1—O1	103.70 (18)
O6—V1—O2	169.88 (13)	O2vi—Cu1—O1	103.70 (18)
O5ii—V2—O5i	76.76 (14)	O2—Cu1—O1	78.1 (2)
O5iii—V2—O5i	76.76 (14)	O1—Cu1—V1	32.97 (13)
O5ii—V2—O5iii	144.0 (3)	V1i—O5—V2i	91.07 (17)

O5ii—V2—O4i	75.50 (13)	V2vii—O5—V1i	101.75 (14)
O5iii—V2—O4i	75.50 (13)	V2viii—O5—V1i	101.75 (14)
O4i—V2—O5i	78.21 (17)	V2vii—O5—V2i	103.24 (14)
O2—V2—O5i	77.25 (19)	V2viii—O5—V2i	103.24 (14)
O2—V2—O5ii	98.75 (14)	V2vii—O5—V2viii	144.0 (3)
O2—V2—O5iii	98.75 (14)	V1vii—O4—V1viii	146.6 (2)
O2—V2—O4i	155.5 (2)	V1viii—O4—V2i	106.04 (13)
O3—V2—O5ii	102.95 (14)	V1vii—O4—V2i	106.04 (13)
O3—V2—O5i	178.6 (2)	V2—O2—V1	117.3 (2)
O3—V2—O5iii	102.95 (14)	V2—O2—Cu1	148.0 (3)
O3—V2—O4i	100.4 (2)	V2—O2—Cu1vi	110.07 (17)
O3—V2—O2	104.1 (2)	V2—O2—Cu1v	110.07 (17)
O1—Cu2—O1iv	180	Cu1vi—O2—V1	100.30 (18)
O1iv—Cu2—O3iii	91.05 (15)	Cu1v—O2—V1	100.30 (18)
O1—Cu2—O3v	91.05 (15)	Cu1—O2—V1	94.8 (2)
O1iv—Cu2—O3vi	88.95 (15)	Cu1—O2—Cu1v	60.57 (15)
O1—Cu2—O3iii	88.95 (15)	Cu1—O2—Cu1vi	60.57 (15)
O1iv—Cu2—O3v	88.95 (15)	Cu1v—O2—Cu1vi	118.6 (3)
O1—Cu2—O3vi	91.05 (15)	V1—O1—Cu2	145.8 (3)
O1—Cu2—O3ii	88.95 (15)	V1—O1—Cu1	98.7 (2)
O1iv—Cu2—O3ii	91.05 (15)	Cu2—O1—Cu1	115.6 (2)
O3ii—Cu2—O3iii	98.83 (17)	V1—O6—V1ix	180.00 (4)
O3ii—Cu2—O3vi	81.17 (17)	V2—O3—Cu2vii	127.36 (11)
O3iii—Cu2—O3vi	180	V2—O3—Cu2viii	127.36 (11)
O3v—Cu2—O3iii	81.17 (17)	Cu2vii—O3—Cu2viii	98.83 (17)
Cu1—V1—O1—Cu2	180.000 (1)	O4i—V2—O2—Cu1vi	113.7 (2)

O5i—V1—O1—Cu2	180.000 (1)	O4i—V2—O2—Cu1	180.000 (1)
O5i—V1—O1—Cu1	0.000 (1)	O4i—V2—O2—Cu1v	−113.7 (2)
O5ii—V2—O2—V1	−74.19 (14)	O4i—V2—O3—Cu2viii	−107.2 (3)
O5iii—V2—O2—V1	74.19 (14)	O4i—V2—O3—Cu2vii	107.2 (3)
O5i—V2—O2—V1	0.000 (1)	O2—V1—O1—Cu2	180.000 (1)
O5iii—V2—O2—Cu1v	−39.5 (3)	O2—V1—O1—Cu1	0.000 (1)
O5ii—V2—O2—Cu1	105.81 (14)	O2—V2—O3—Cu2viii	72.8 (3)
O5iii—V2—O2—Cu1vi	−172.1 (2)	O2—V2—O3—Cu2vii	−72.8 (3)
O5i—V2—O2—Cu1	180.000 (1)	O6—V1—O1—Cu2	0.000 (1)
O5iii—V2—O2—Cu1	−105.81 (14)	O6—V1—O1—Cu1	180.000 (1)
O5i—V2—O2—Cu1v	−113.7 (2)	O3—V2—O2—V1	180.000 (1)
O5ii—V2—O2—Cu1v	172.1 (2)	O3—V2—O2—Cu1	0.000 (1)
O5ii—V2—O2—Cu1vi	39.5 (3)	O3—V2—O2—Cu1v	66.3 (2)
O5i—V2—O2—Cu1vi	113.7 (2)	O3—V2—O2—Cu1vi	−66.3 (2)
O5ii—V2—O3—Cu2viii	−29.8 (3)	O3v—Cu2—O1—V1	−130.58 (9)
O5iii—V2—O3—Cu2vii	29.8 (3)	O3vi—Cu2—O1—V1	130.58 (9)
O5ii—V2—O3—Cu2vii	−175.5 (3)	O3ii—Cu2—O1—V1	49.42 (9)
O5iii—V2—O3—Cu2viii	175.5 (3)	O3iii—Cu2—O1—V1	−49.42 (9)
O4ii—V1—O1—Cu2	−95.91 (16)	O3v—Cu2—O1—Cu1	49.42 (9)
O4iii—V1—O1—Cu2	95.91 (16)	O3ii—Cu2—O1—Cu1	−130.58 (9)
O4ii—V1—O1—Cu1	84.09 (16)	O3iii—Cu2—O1—Cu1	130.58 (9)
O4iii—V1—O1—Cu1	−84.09 (16)	O3vi—Cu2—O1—Cu1	−49.42 (9)
O4i—V2—O2—V1	0.000 (1)		

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

Table S7: Atomic coordinates, Wyckoff positions, site symmetries, occupancies and equivalent isotropic displacement parameters for the structure of $Cu_{1.59(1)}V_{3.52(1)}W_{0.48(1)}O_{11}$ (**3**).

Atom	Wyckoff Position	Site Symmetry	*x*	*y*	*z*	U_{eq}	Occupancy
V1	4i	m	0.11216 (5)	0	0.15353 (10)	0.0111 (3)	0.762 (4)
W1	4i	m	0.11216 (5)	0	0.15353 (10)	0.0111 (3)	0.238 (4)
V2	4i	m	0.32980 (7)	0	0.15513 (16)	0.0042 (3)	1
Cu1	4i	m	0.2365 (3)	0	0.5522 (6)	0.0301 (15)	0.293 (6)
Cu2	2c	2/m	0	0	0.5	0.0702 (11)	1
O1	4i	m	0.0906 (4)	0	0.3667 (9)	0.0214 (13)	1
O2	4i	m	0.2536 (4)	0	0.2971 (9)	0.0199 (13)	1
O3	4i	m	0.4277 (4)	0	0.3050 (9)	0.0231 (13)	1
O4	4i	m	0.6315 (4)	0	0.1029 (9)	0.0164 (12)	1
O5	4i	m	0.8160 (4)	0	0.0734 (9)	0.0179 (12)	1
O6	2a	2/m	0	0	0	0.0177 (17)	1

Table S8: Atomic thermal displacement parameters (Å^2) for $Cu_{1.59(1)}V_{3.52(1)}W_{0.48(1)}O_{11}$ (**3**).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.0159 (4)	0.0065 (4)	0.0153 (4)	0	0.0119 (3)	0
W1	0.0159 (4)	0.0065 (4)	0.0153 (4)	0	0.0119 (3)	0
V2	0.0040 (5)	0.0028 (5)	0.0068 (5)	0	0.0031 (4)	0
Cu1	0.035 (3)	0.040 (3)	0.015 (2)	0	0.0047 (16)	0
Cu2	0.0270 (11)	0.151 (3)	0.0408 (13)	0	0.0229 (10)	0
O1	0.018 (3)	0.026 (3)	0.023 (3)	0	0.010 (2)	0
O2	0.012 (3)	0.030 (3)	0.017 (3)	0	0.004 (2)	0

O3	0.020 (3)	0.028 (3)	0.023 (3)	0	0.008 (2)	0
O4	0.017 (3)	0.014 (3)	0.021 (3)	0	0.011 (2)	0
O5	0.022 (3)	0.012 (3)	0.022 (3)	0	0.010 (2)	0
O6	0.011 (4)	0.016 (4)	0.023 (4)	0	−0.002 (3)	0

Table S9: Selected bond distances and angles (Å, º) for $Cu_{1.59(1)}V_{3.52(1)}W_{0.48(1)}O_{11}$ (**3**).

V1—Cu1	3.055 (4)	Cu1—Cu1iv	2.056 (4)
V1—O1	1.677 (6)	Cu1—Cu1v	2.056 (4)
V1—O2	2.152 (6)	Cu1—O1	2.299 (8)
V1—O4i	1.8947 (16)	Cu1—O2v	2.114 (4)
V1—O4ii	1.8947 (17)	Cu1—O2	1.953 (7)
V1—O5iii	2.214 (6)	Cu1—O2iv	2.114 (4)
V1—O6	1.7964 (8)	Cu2—O1vi	1.887 (6)
V2—O2	1.748 (6)	Cu2—O1	1.887 (6)
V2—O3	1.616 (7)	Cu2—O3v	2.402 (4)
V2—O4iii	2.120 (6)	Cu2—O3ii	2.402 (4)
V2—O5ii	1.9100 (19)	Cu2—O3iv	2.402 (4)
V2—O5i	1.9100 (19)	Cu2—O3i	2.402 (4)
V2—O5iii	2.424 (6)		
O1—V1—Cu1	48.0 (2)	O2—Cu1—Cu1v	63.6 (2)
O1—V1—O2	87.4 (3)	O2—Cu1—Cu1iv	63.6 (2)
O1—V1—O4i	105.07 (18)	O2—Cu1—O1	77.3 (3)
O1—V1—O4ii	105.07 (18)	O2iv—Cu1—O1	103.8 (2)
O1—V1—O5iii	162.3 (3)	O2v—Cu1—O1	103.8 (2)

O1—V1—O6	101.6 (2)	O2—Cu1—O2v	119.42 (18)
O2—V1—Cu1	39.48 (19)	O2v—Cu1—O2iv	118.8 (3)
O2—V1—O5iii	74.8 (2)	O2—Cu1—O2iv	119.42 (18)
O4i—V1—Cu1	95.59 (19)	O1vi—Cu2—O1	180
O4ii—V1—Cu1	95.59 (19)	O1vi—Cu2—O3i	91.2 (2)
O4ii—V1—O2	84.74 (19)	O1vi—Cu2—O3iv	88.8 (2)
O4i—V1—O2	84.74 (19)	O1vi—Cu2—O3v	88.8 (2)
O4i—V1—O4ii	147.5 (3)	O1—Cu2—O3i	88.8 (2)
O4ii—V1—O5iii	73.79 (17)	O1—Cu2—O3iv	91.2 (2)
O4i—V1—O5iii	73.79 (17)	O1vi—Cu2—O3ii	91.2 (2)
O5iii—V1—Cu1	114.33 (19)	O1—Cu2—O3ii	88.8 (2)
O6—V1—Cu1	149.58 (10)	O1—Cu2—O3v	91.2 (2)
O6—V1—O2	170.94 (17)	O3ii—Cu2—O3iv	180
O6—V1—O4i	92.80 (19)	O3i—Cu2—O3ii	98.4 (2)
O6—V1—O4ii	92.80 (19)	O3i—Cu2—O3iv	81.6 (2)
O6—V1—O5iii	96.09 (17)	O3v—Cu2—O3i	180
O2—V2—O4iii	155.5 (3)	O3v—Cu2—O3ii	81.6 (2)
O2—V2—O5iii	77.1 (2)	O3v—Cu2—O3iv	98.4 (2)
O2—V2—O5ii	98.60 (19)	V1—O1—Cu1	99.2 (3)
O2—V2—O5i	98.60 (19)	V1—O1—Cu2	145.7 (4)
O3—V2—O2	103.7 (3)	Cu2—O1—Cu1	115.0 (3)
O3—V2—O4iii	100.7 (3)	V2—O2—V1	116.6 (3)
O3—V2—O5ii	102.88 (19)	V2—O2—Cu1	147.3 (4)
O3—V2—O5iii	179.2 (3)	V2—O2—Cu1iv	109.9 (2)
O3—V2—O5i	102.88 (19)	V2—O2—Cu1v	109.9 (2)
O4iii—V2—O5iii	78.4 (2)	Cu1—O2—V1	96.1 (3)

O5i—V2—O4iii	75.75 (18)	Cu1v—O2—V1	100.7 (2)
O5ii—V2—O4iii	75.75 (18)	Cu1iv—O2—V1	100.7 (2)
O5i—V2—O5iii	76.95 (19)	Cu1—O2—Cu1iv	60.58 (18)
O5i—V2—O5ii	144.5 (4)	Cu1—O2—Cu1v	60.58 (18)
O5ii—V2—O5iii	76.95 (19)	Cu1v—O2—Cu1iv	118.8 (3)
Cu1iv—Cu1—V1	77.2 (2)	V2—O3—Cu2vii	127.68 (16)
Cu1v—Cu1—V1	77.2 (2)	V2—O3—Cu2viii	127.68 (16)
Cu1iv—Cu1—Cu1v	124.4 (4)	Cu2vii—O3—Cu2viii	98.4 (2)
Cu1iv—Cu1—O1	92.1 (3)	V1vii—O4—V1viii	147.5 (3)
Cu1v—Cu1—O1	92.1 (3)	V1viii—O4—V2iii	105.52 (18)
Cu1v—Cu1—O2v	55.85 (18)	V1vii—O4—V2iii	105.52 (18)
Cu1v—Cu1—O2iv	164.0 (4)	V1iii—O5—V2iii	91.5 (2)
Cu1iv—Cu1—O2v	164.0 (4)	V2vii—O5—V1iii	101.50 (19)
Cu1iv—Cu1—O2iv	55.85 (18)	V2viii—O5—V1iii	101.50 (19)
O1—Cu1—V1	32.81 (17)	V2viii—O5—V2iii	103.05 (19)
O2iv—Cu1—V1	116.40 (19)	V2vii—O5—V2viii	144.5 (4)
O2v—Cu1—V1	116.40 (19)	V2vii—O5—V2iii	103.05 (19)
O2—Cu1—V1	44.5 (2)	V1—O6—V1ix	180
Cu1—V1—O1—Cu2	180.000 (1)	O4iii—V2—O2—Cu1v	−113.7 (3)
O2—V1—O1—Cu1	0.000 (1)	O4iii—V2—O3—Cu2vii	106.9 (4)
O2—V1—O1—Cu2	180.000 (1)	O4iii—V2—O3—Cu2viii	−106.9 (4)
O2—V2—O3—Cu2viii	73.1 (4)	O5iii—V1—O1—Cu1	0.000 (1)
O2—V2—O3—Cu2vii	−73.1 (4)	O5iii—V1—O1—Cu2	180.000 (1)
O3—V2—O2—V1	180.000 (1)	O5ii—V2—O2—V1	74.40 (19)
O3—V2—O2—Cu1iv	−66.3 (3)	O5i—V2—O2—V1	−74.40 (19)
O3—V2—O2—Cu1	0.000 (1)	O5iii—V2—O2—V1	0.000 (1)

O3—V2—O2—Cu1v	66.3 (3)	O5ii—V2—O2—Cu1v	−39.3 (3)
O3i—Cu2—O1—V1	49.23 (12)	O5ii—V2—O2—Cu1	−105.60 (19)
O3v—Cu2—O1—V1	−130.77 (12)	O5iii—V2—O2—Cu1	180.000 (1)
O3ii—Cu2—O1—V1	−49.23 (12)	O5i—V2—O2—Cu1	105.60 (19)
O3iv—Cu2—O1—V1	130.77 (12)	O5i—V2—O2—Cu1iv	39.3 (3)
O3ii—Cu2—O1—Cu1	130.77 (12)	O5iii—V2—O2—Cu1iv	113.7 (3)
O3iv—Cu2—O1—Cu1	−49.23 (12)	O5iii—V2—O2—Cu1v	−113.7 (3)
O3v—Cu2—O1—Cu1	49.23 (12)	O5i—V2—O2—Cu1v	171.9 (3)
O3i—Cu2—O1—Cu1	−130.77 (12)	O5ii—V2—O2—Cu1iv	−171.9 (3)
O4i—V1—O1—Cu1	83.9 (2)	O5ii—V2—O3—Cu2vii	29.3 (5)
O4ii—V1—O1—Cu1	−83.9 (2)	O5i—V2—O3—Cu2viii	−29.3 (5)
O4i—V1—O1—Cu2	−96.1 (2)	O5ii—V2—O3—Cu2viii	175.4 (4)
O4ii—V1—O1—Cu2	96.1 (2)	O5i—V2—O3—Cu2vii	−175.4 (4)
O4iii—V2—O2—V1	0.000 (1)	O6—V1—O1—Cu1	180.000 (1)
O4iii—V2—O2—Cu1	180.000 (1)	O6—V1—O1—Cu2	0.000 (1)
O4iii—V2—O2—Cu1iv	113.7 (3)		

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