A new redox-based and stepwise synthetic strategy lead to an unprecedented mixed-valence Keggin-type tungstovanadophosphate (W^{6+}/V^{4+}) bi-capped by vanadium(V^{3+})-complexes†

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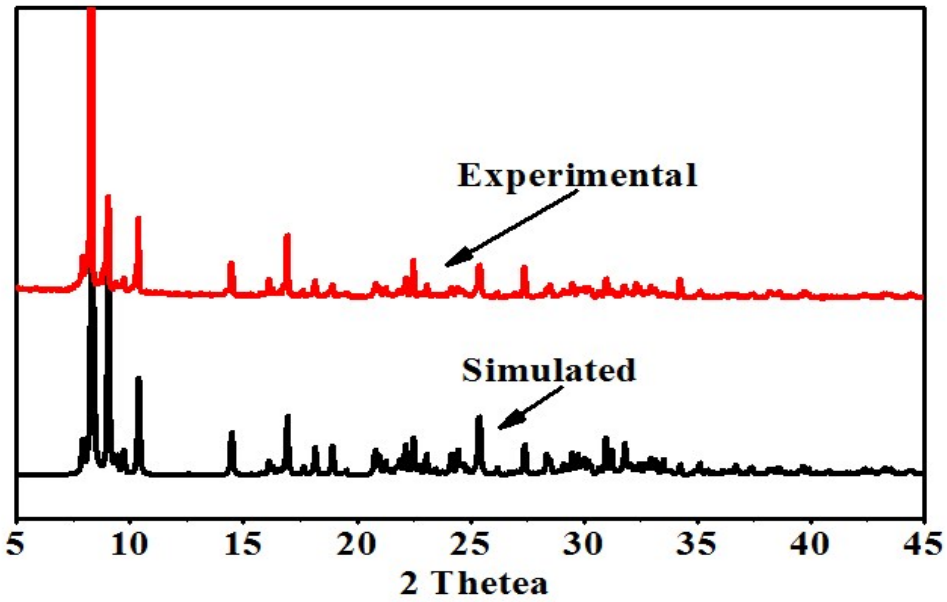

Figure S1. Experimental and simulated powder X-ray diffraction patterns of V^{III}-POWV.

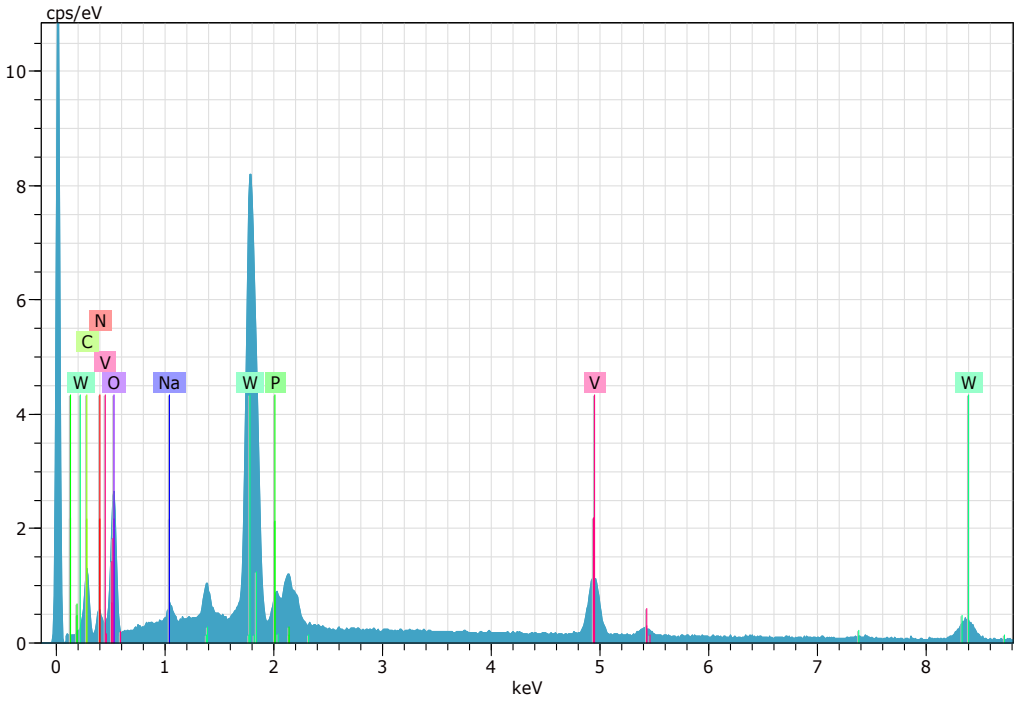

Figure S2. The EDS spectrum of V^{III}-POWV.

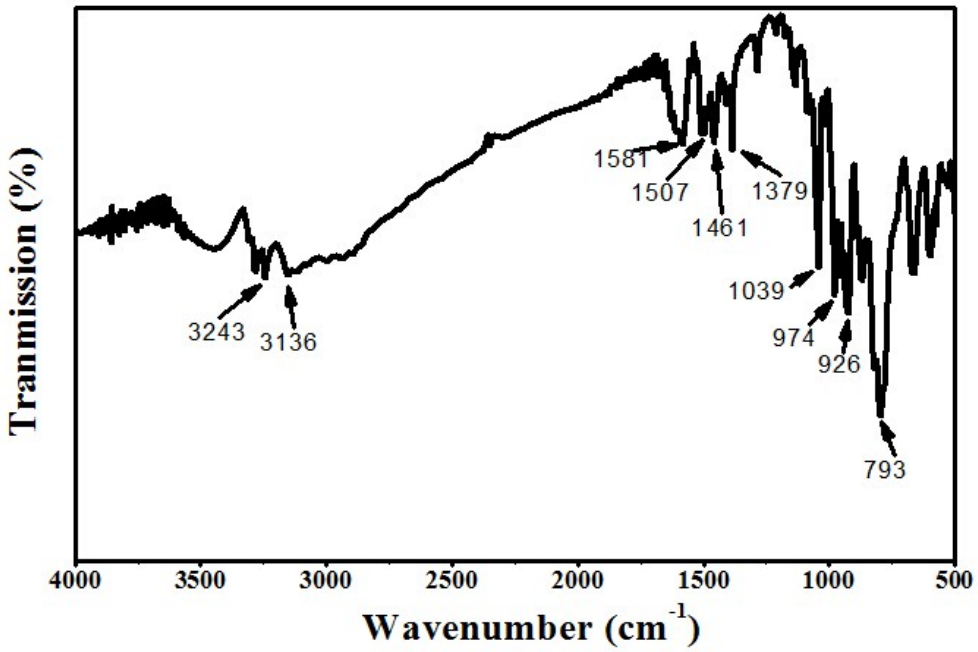

Figure S3. The FT-IR spectrum of V^{III}-POWV.

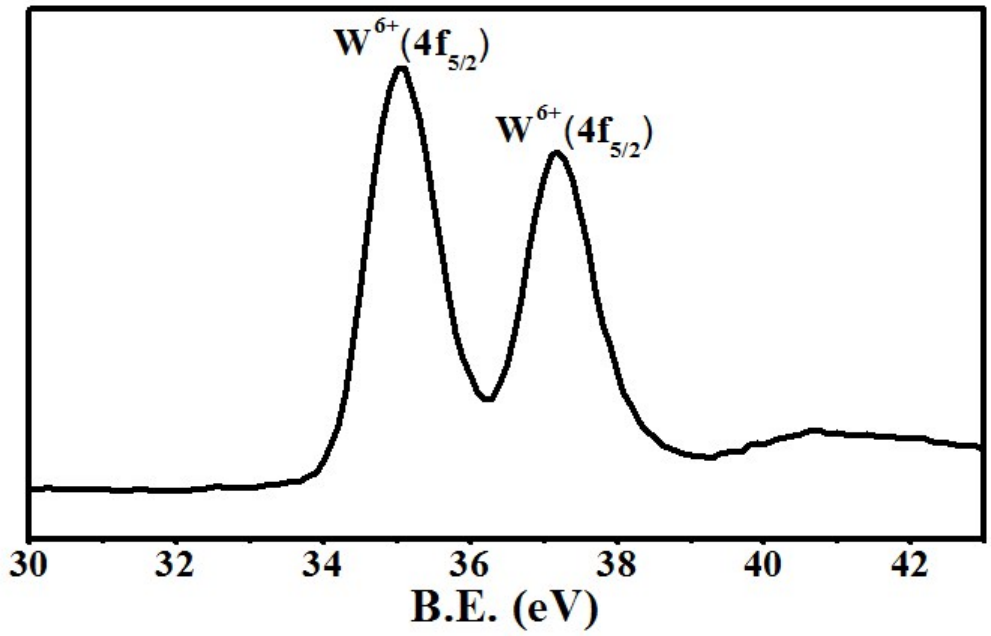

Figure S4. The XPS spectrum for V^{III}-POWV with peaks at 35.31 eV and 37.37 eV in the W4*f* region attributed to $W^{6+}(4f_{7/2})$ and $W^{6+}(4f_{5/2})$, respectively.

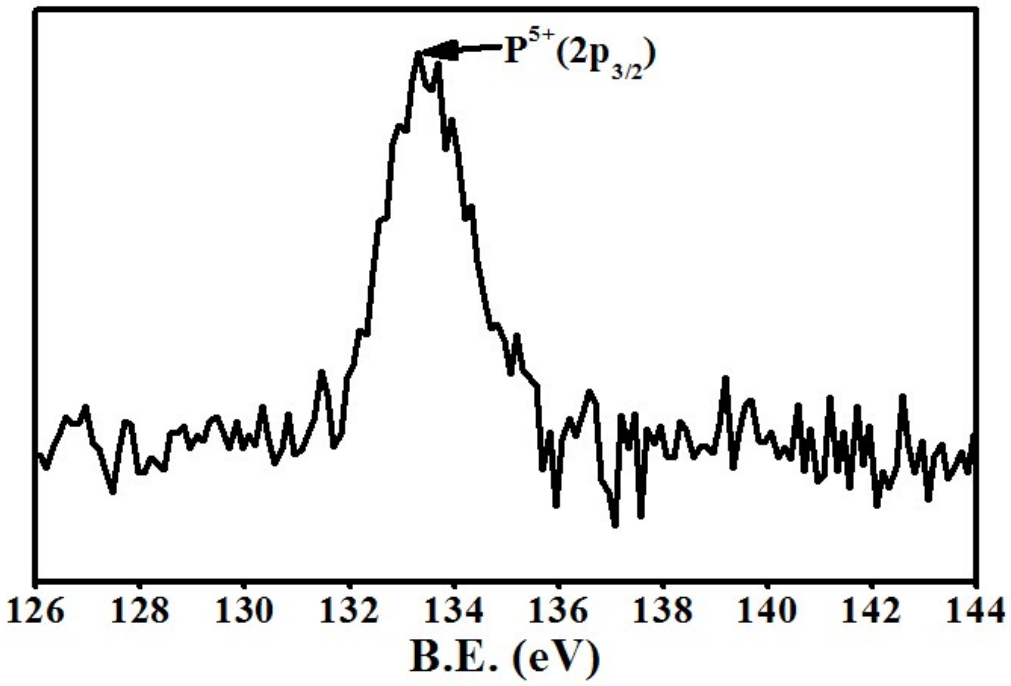

Figure S5. The XPS spectrum for V^{III}-POWV with peak at 133.37 eV in the P2*p* region ascribed to $P^{5+}(2p_{3/2})$.

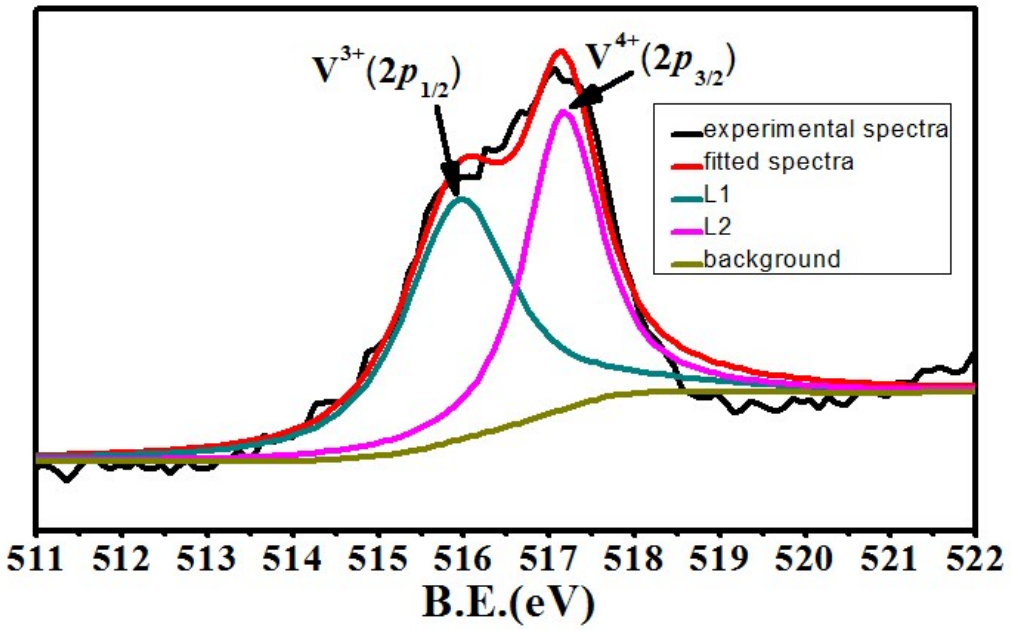

Figure S6. The XPS spectrum for V^{III}-POWV with fitted peaks at 515.86 eV and 517.16 eV in the V2*p* region attributed to $V^{3+}(2p_{1/2})$ and $V^{4+}(2p_{3/2})$, respectively.

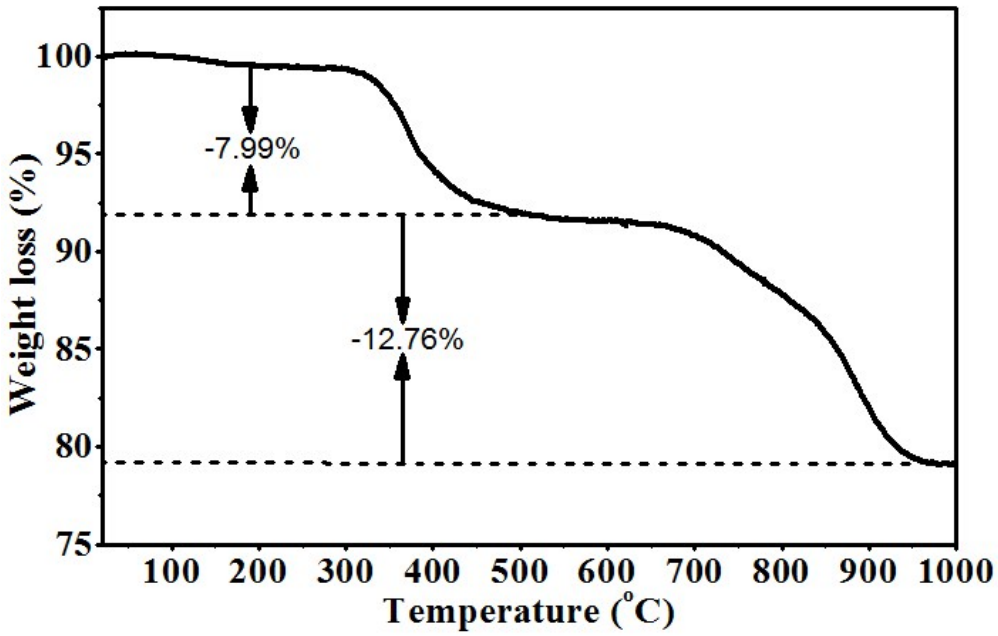

Figure S7. The TG curve of V^{III}-POWV in N_2 atmosphere.

Table S1 Crystal data and structure refinement for V^{III}-POWV

Empirical formula	C32 H116 N24 Na O82 P2 V12 W16
Formula weight	5787.29
Temperature (K), Wavelength (Å)	293(2), 0.71073
Crystal system, space group	Monoclinic, *C2/c*
a (Å)	21.8135(5)
b (Å)	13.0499(3)
c (Å)	37.5978(7)
β (deg)	94.728(2)
Volume ($Å^3$)	10666.3(4)
Z, D_{calc} (g cm^{-3})	4, 3.604
μ (mm^{-1}), *F*(000)	18.32, 10532
Crystal size (mm), color	0.18× 0.16 × 0.13, black
θ range (deg)	3.2 to 25.0
Limiting indices	$-20 \le h \le 25$, $-11 \le k \le 15$, $-44 \le l \le 40$
Reflections collected	25850
Independent reflections	9372 [*R*(int) = 0.050]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9372 / 0 / 718
Goodness-of-fit on F^2	1.127
Final *R* indices [I >2sigma(I)]	R_1 = 0.0467, wR_2 = 0.0691
R indices (all data)	R_1 = 0.0631, wR_2 = 0.0733
Largest diff. peak and hole (e $Å^{-3}$)	2.00 and –2.51

Table S2. The selected bond lengths (Å) and angles (°) for V^{III}-POWV.

W1—O24	2.021 (7)	V1—O14	1.940 (7)
W1—O26	1.805 (8)	V1—O15	1.949 (8)
W1—O27	1.734 (8)	V1—O17	1.600 (8)
W1—O28	2.046 (9)	V1—O18	1.996 (8)
W1—O30	1.830 (7)	V1—O19	2.000 (8)
W1—O31	2.444 (8)	V1—O36	2.468 (8)
W2—O25	2.031 (7)	V1—Na1	3.2033 (19)
W2—O28	2.050 (8)	V2—O1	1.603 (8)
W2—O29	1.750 (8)	V2—O2	1.959 (8)
W2—O31	2.435 (8)	V2—O3	1.952 (8)
W2—O32	1.806 (8)	V2—O30	1.957 (8)
W2—O33	1.804 (7)	V2—O31	2.453 (7)
W3—O19	1.827 (8)	V2—O33	1.977 (8)
W3—O20	1.793 (8)	V3—O16	1.947 (8)
W3—O21	1.729 (8)	V3—O20	1.967 (7)
W3—O22	2.030 (8)	V3—O26	1.965 (8)
W3—O24	2.011 (8)	V3—O34	1.987 (7)
W3—O36	2.428 (7)	V3—O38	1.587 (8)
W3—Na1	3.349 (5)	V3—O39	2.524 (8)
W4—O18	1.867 (8)	V4—O4	1.585 (9)
W4—O22	2.042 (8)	V4—O5	1.959 (7)
W4—O23	1.712 (8)	V4—O11	1.979 (8)
W4—O25	1.990 (8)	V4—O25	2.536 (7)
W4—O36	2.435 (8)	V4—O32	1.968 (8)
W4—O37	1.794 (7)	V4—O37	1.968 (7)
W4—Na1	3.445 (3)	V5—O22	2.157 (8)
W5—O9	2.074 (7)	V5—O24	2.027 (8)
W5—O11	1.820 (8)	V5—O25	2.033 (8)
W5—O12	1.744 (8)	V5—O28	2.092 (7)
W5—O14	1.799 (6)	V5—N1	2.170 (12)
W5—O35	2.382 (8)	V5—N2	2.224 (10)
W5—O40	2.027 (8)	V5—N3	2.200 (12)
W6—O13	1.738 (9)	V6—O8	2.063 (8)
W6—O15	1.836 (7)	V6—O9	2.098 (8)
W6—O16	1.828 (8)	V6—O10	2.104 (8)
W6—O10	2.050 (7)	V6—O40	2.033 (7)
W6—O39	2.402 (8)	V6—N4	2.189 (10)
W6—O40	2.013 (8)	V6—N5	2.226 (10)
W7—O3	1.832 (8)	V6—N6	2.154 (8)
W7—O5	1.826 (9)	P1—O31	1.528 (8)
W7—O7	1.725 (7)	P1—O35	1.548 (8)

W7—O8	2.027 (8)	P1—O36	1.541 (7)
W7—O9	2.012 (8)	P1—O39	1.532 (8)
W7—O35	2.413 (6)	O18—Na1	2.380 (8)
W8—O2	1.848 (8)	O19—Na1	2.328 (9)
W8—O6	1.735 (7)	O22—Na1	2.782 (8)
W8—O8	2.019 (8)	Na1—O18i	2.380 (8)
W8—O10	2.004 (8)	Na1—O19i	2.328 (9)
W8—O34	1.794 (8)	Na1—O22i	2.782 (8)
W8—O39	2.450 (7)		
O24—W1—O28	75.5 (3)	O21—W3—O24	98.5 (4)
O24—W1—O31	82.3 (3)	O21—W3—O36	168.2 (3)
O26—W1—O24	88.2 (3)	O21—W3—Na1	81.3 (3)
O26—W1—O28	155.0 (3)	O22—W3—O36	70.8 (3)
O26—W1—O30	98.2 (3)	O22—W3—Na1	56.0 (2)
O26—W1—O31	88.5 (3)	O24—W3—O22	77.0 (3)
O27—W1—O24	99.0 (3)	O24—W3—O36	83.4 (3)
O27—W1—O26	103.1 (4)	O24—W3—Na1	132.2 (2)
O27—W1—O28	98.1 (4)	O36—W3—Na1	88.75 (19)
O27—W1—O30	100.8 (3)	O18—W4—O22	88.3 (3)
O27—W1—O31	168.3 (4)	O18—W4—O25	155.5 (3)
O28—W1—O31	70.8 (3)	O18—W4—O36	76.2 (3)
O30—W1—O24	157.2 (3)	O18—W4—Na1	41.1 (2)
O30—W1—O28	90.5 (3)	O22—W4—O36	70.5 (3)
O30—W1—O31	76.0 (3)	O22—W4—Na1	53.9 (2)
O25—W2—O28	74.6 (3)	O23—W4—O18	100.6 (4)
O25—W2—O31	80.1 (3)	O23—W4—O22	97.6 (3)
O28—W2—O31	70.9 (3)	O23—W4—O25	100.0 (4)
O29—W2—O25	99.4 (3)	O23—W4—O36	167.6 (3)
O29—W2—O28	98.5 (4)	O23—W4—O37	104.9 (4)
O29—W2—O31	169.2 (4)	O23—W4—Na1	83.5 (3)
O29—W2—O32	103.1 (4)	O25—W4—O22	76.0 (3)
O29—W2—O33	101.4 (4)	O25—W4—O36	80.9 (3)
O32—W2—O25	87.7 (3)	O25—W4—Na1	129.6 (2)
O32—W2—O28	154.0 (3)	O36—W4—Na1	86.44 (19)
O32—W2—O31	87.6 (3)	O37—W4—O18	98.2 (3)
O33—W2—O25	156.6 (4)	O20—W3—O19	97.0 (4)
O33—W2—O28	91.7 (3)	O20—W3—O22	154.8 (3)
O33—W2—O31	77.5 (3)	O20—W3—O24	88.7 (3)
O33—W2—O32	98.0 (3)	O20—W3—O36	87.2 (3)
O19—W3—O22	89.5 (3)	O20—W3—Na1	138.0 (3)
O19—W3—O24	158.2 (3)	O21—W3—O19	100.3 (3)
O19—W3—O36	76.0 (3)	O21—W3—O20	104.5 (4)

O19—W3—Na1	41.7 (2)	O21—W3—O22	98.2 (3)
W1—O24—V5	105.9 (4)	W8—O34—V3	126.9 (4)
W3—O24—W1	141.4 (4)	W5—O35—W7	94.2 (2)
W3—O24—V5	106.4 (3)	P1—O35—W5	126.6 (4)
W2—O25—V5	106.1 (4)	P1—O35—W7	125.2 (4)
W4—O25—W2	142.9 (4)	W3—O36—W4	94.2 (2)
W4—O25—V5	107.7 (3)	W3—O36—V1	87.4 (2)
W1—O26—V3	153.0 (5)	W4—O36—V1	87.5 (2)
W1—O28—W2	120.8 (4)	P1—O36—W3	124.4 (4)
W1—O28—V5	102.6 (4)	P1—O36—W4	124.7 (4)
W2—O28—V5	103.2 (4)	P1—O36—V1	127.4 (4)
W1—O30—V2	124.0 (4)	W4—O37—V4	154.2 (5)
W1—O31—V2	86.2 (3)	W6—O39—W8	93.6 (3)
W2—O31—W1	93.8 (3)	P1—O39—W6	125.8 (4)
W2—O31—V2	85.5 (2)	P1—O39—W8	125.9 (4)
P1—O31—W1	125.2 (4)	W5—O40—V6	105.8 (3)
P1—O31—W2	125.7 (5)	W6—O40—W5	143.1 (4)
P1—O31—V2	127.9 (4)	W6—O40—V6	105.4 (3)
W2—O32—V4	154.6 (4)	W2—O33—V2	122.7 (4)

Symmetry codes: (i) −*x*+1, *y*, −*z*+3/2; (ii) −*x*+1, −*y*+1, −*z*+1.