Supporting Information

Design and Synthesis of the Purely Inorganic 3D Frameworks Composed of Reduced Vanadium Clusters and Manganese Linkers

Yang-Yang Zhou,[a] Shuang Yao,*[,a] Jing-Hui Yan,[a,b] Li Chen,[b] Ting-Ting Wang,[b] Chun-Jie Wang,[b] and Zhi-Ming Zhang,*[,b]

[a]*College of Chemistry and Environmental Engineering, Changchun University of Science and Technology, Changchun, Jilin 130022, PR. China.*
[b]*Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, PR China.*

CONTENTS:

I. Supplementary Structure Figures

II. Supplementary Characterizations

III. Supplementary Experimental Section

I. Supplementary Structure Figures

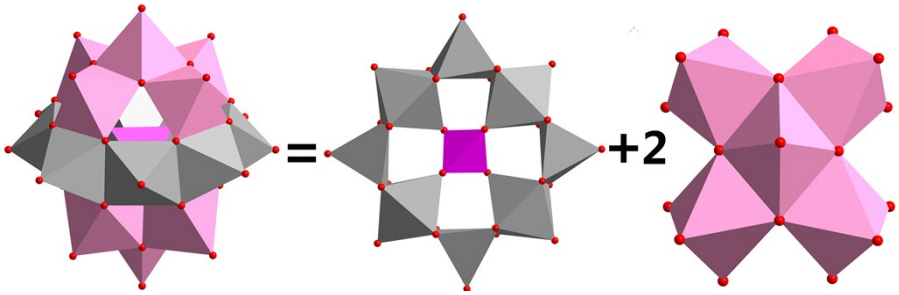

Fig. S1. The $\{PV_{18}\}$ cluster in compound **1**, consisting of the $[PV_8]$ "cycle" and two $[V_5]$ caps.

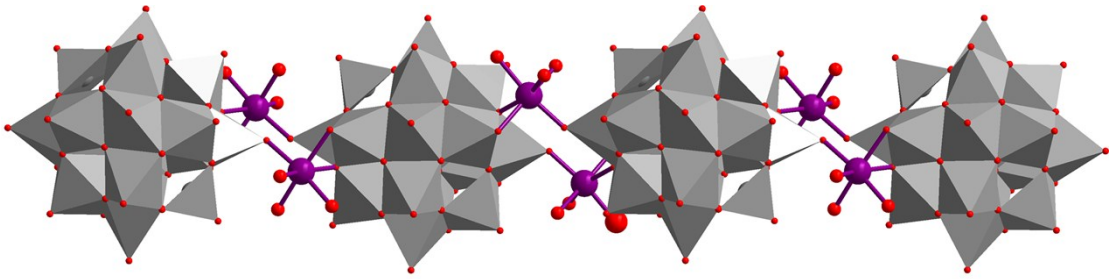

Fig. S2. The 1D polymer chain in compound **1**.

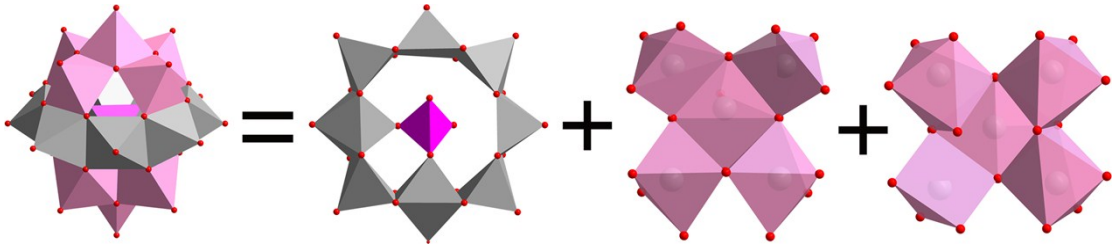

Fig. S3. Structure of the $\{PV_{18}\}$ cluster in compound **2**.

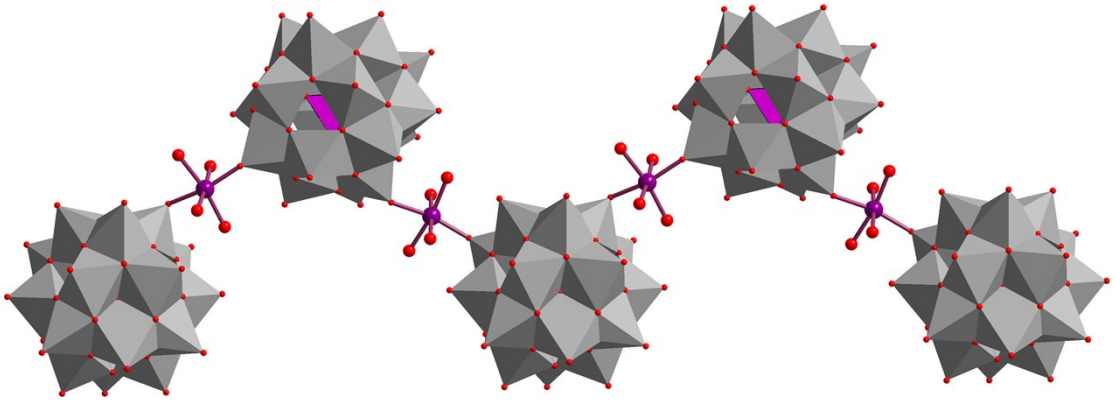

Fig. S4. The 1D wavy chain in compound **2**.

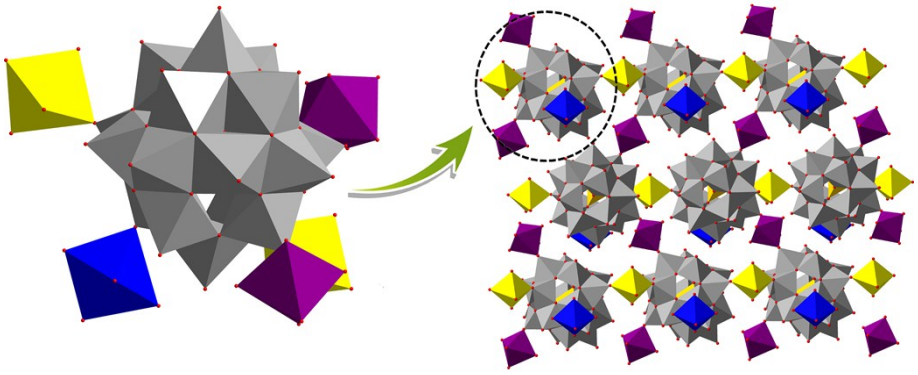

Fig. S5. The different Mn octahedra in 2D layer of **2**. Color code: gray ,V; yellow, Mn(1); blue, Mn(1); amethyst, Mn(2).

II. Supplementary Characterizations

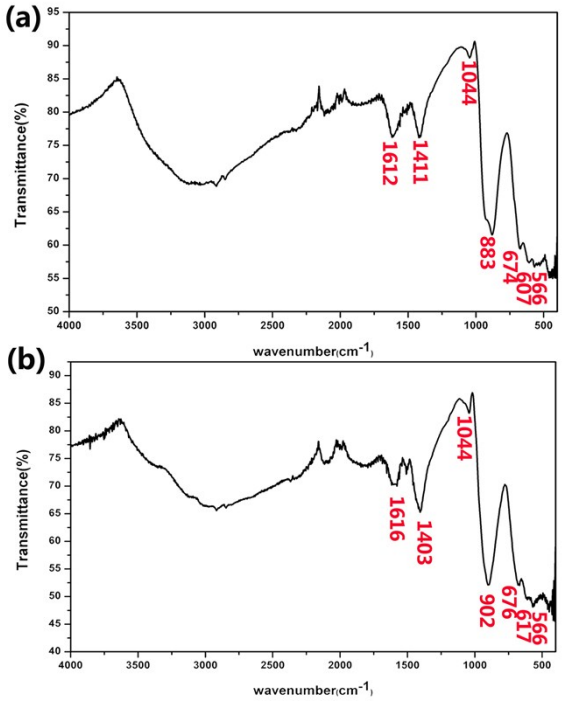

Fig. S6. IR spectra of the compound **1** (a) and compound **2** (b).

The IR spectra of compounds **1** and **2** are shown in Fig. S6. There are five characteristic asymmetric vibrations resulting from heteropolyanions. The weak bond at 1044 cm^{-1} is ascribed to the vibration absorption of υ(P-O). The absorption band at 566, 607, 674, 883 cm^{-1} for **1**, and 559, 617, 676, 902 cm^{-1} for **2** can be assigned to the υ(V-O) and υ(V-O-M) (M = P or V) stretching vibration.

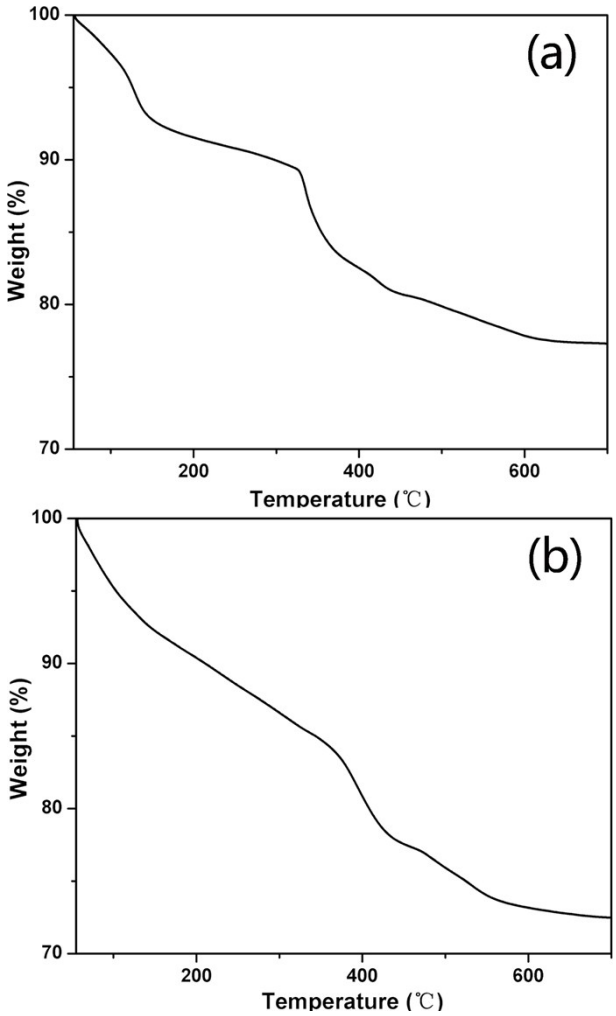

Fig. S7. TG curves of the compounds **1** (a) and **2** (b).

The thermogravimetric analysis (TGA) of **1** was carried out in the flowing N_2 atmosphere with a heating rate of 10 ℃ min^{-1} from 50 to 700 ℃. The TG curve of **1** displays two continuous weight loss stages in the range of 50 to 475 ℃ (Fig. S7a). The first weight loss was 10.50% (calcd. 12.37%) from 50 to 310 ℃, corresponding to the release of four lattice water molecules and eleven coordination water molecules. On further heating, the weight loss was assigned to the collapse of POM framework.

For compound **2**, weitht losse 11.55% at 50 to 250 ℃ was attributed to the release of two lattice water molecules, seven coordinated water molecules and five NH^{4+} cations (calcd. 11.85%). On further heating, the weight loss above 250℃ was assigned to the decomposition of the 1,2-diaminopropane and the collapse of the POM framework.

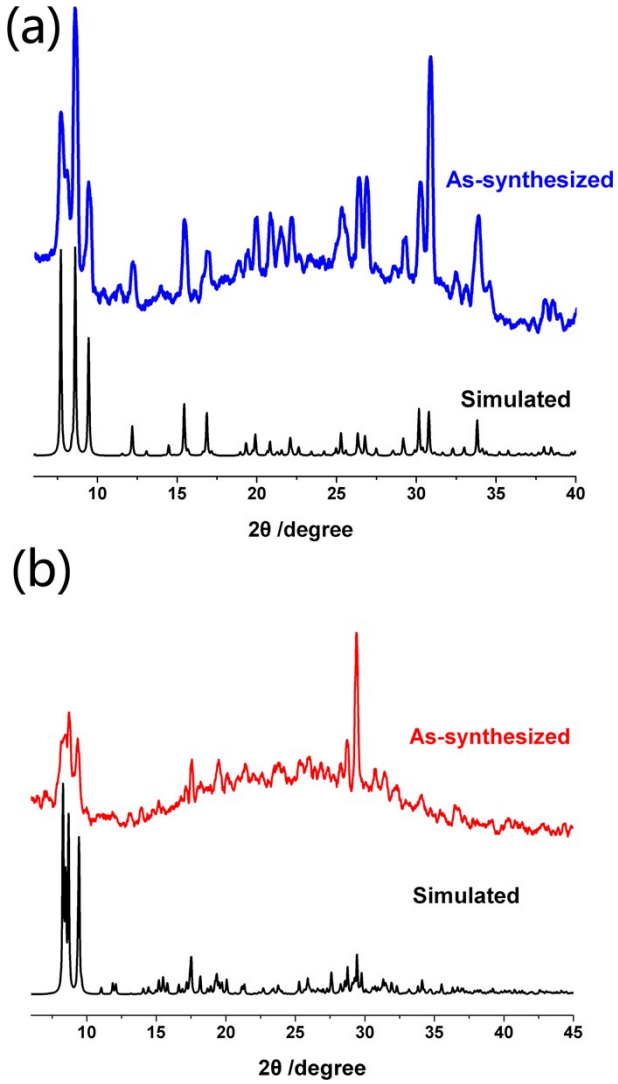

Fig. S8. Comparison of the simulated and experimental PXRD patterns of **1** (a) and **2** (b).

The PXRD pattern of as-synthesized samples is identical to the simulated one from the single-crystal X-ray diffraction data, indicating that the single crystal structure is consistent with the bulk sample.

III. Supplementary Experimental Section

Materials and Methods: All the chemical reagents were commercially purchased and used without further purification. IR spectrum was recorded in the range of 400–4000 cm^{-1} on an Alpha Centauri FT/IR Spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was determined by a Perkin-Elmer TGA7 instrument and carried out flowing N_2 atmosphere with the heating rate of 10 ℃ min^{-1}.

Powder X-ray diffraction (XRD) data were collected by using a Rigaku D/max-2550 diffractometer. The electrochemical measurements were determined by the CHI 600E electrochemical workstation. Platinum gauze was used as counter electrode and Ag/AgCl electrode as reference electrode. A chemically bulk-modified carbon paste electrodes was used as working electrode.

The blank carbon paste electrode was prepared by grinding the mixing of 100 mg graphite power and 10 mg compound **1** in agate mortar to achieve a uniform mixture, and then two drops of paraffin oil was added with stirring. Then the mixture was transferred to Teflon tube with a 2 mm diameter with firm pressure, and the smooth surface of electrode (1-CPE).

Table S1. Bond valence sum calculations of compounds **1** and **2**.[S1,S2]

Compound **1**

Bonds	Bond Length (Å)	BVS	Bonds	Bond Length (Å)	BVS
V(1)-O(12)	1.654(7)	1.417151185	V(4)-O(17)	1.608(7)	1.604758011
V(1)-O(13)	1.933(7)	0.66670647	V(4)-O(23)	1.942(6)	0.650684932
V(1)-O(19)	1.944(6)	0.647177205	V(4)-O(11)	1.948(6)	0.640218378
V(1)-O(10)	1.958(7)	0.623146913	V(4)-O(20)	1.963(6)	0.614782651
V(1)-O(9)	2.008(6)	0.544379803	V(4)-O(9)	1.977(7)	0.591955199
V(1)-O(3)	2.443(7)	0.168001263	V(4)-O(3)	2.444(6)	0.167547818
$V_{V(1)}$ = **4.07**			$V_{V(4)}$ = **4.27**		
V(2)-O(18)	1.616(7)	1.570432959	V(3)-O(22)	1.603(7)	1.626591118
V(2)-O(19)	1.924(6)	0.683122499	V(3)-O(10)	1.906(7)	0.717177125
V(2)-O(14)	1.928(7)	0.675777167	V(3)-O(14)#1	1.927(7)	0.677606062
V(2)-O(15)	1.950(7)	0.636767074	V(3)-O(13)#1	1.933(7)	0.66670647
V(2)-O(16)	2.056(7)	0.478146629	V(3)-O(20)	1.944(7)	0.647177205
$V_{V(2)}$ = **4.04**			$V_{V(3)}$ = **4.33**		
V(5)-O(21)	1.651(7)	1.428688309	V(6)-O(1)	1.667(11)	1.368223952
V(5)-O(19)	1.896(6)	0.736824601	V(6)-O(13)#1	1.899(7)	0.730874502
V(5)-O(11)	1.892(7)	0.744833486	V(6)-O(13)	1.899(7)	0.730874502
V(5)-O(15)	1.979(6)	0.588764074	V(6)-O(10)#1	1.975(6)	0.59516362
V(5)-O(9)	2.007(6)	0.54585309	V(6)-O(10)	1.975(6)	0.59516362
$V_{V(5)}$ = **4.04**			$V_{V(6)}$ = **4.02**		
V(7)-O(24)	1.641(7)	1.467828039	V(9)-O(5)	1.631(7)	1.508040025
V(7)-O(14)	1.875(6)	0.779853928	V(9)-O(11)#1	1.933(6)	0.66670647
V(7)-O(23)#1	1.883(6)	0.763173203	V(9)-O(2)	1.942(7)	0.650684932

V(7)-O(20)#1	1.974(7)	0.596774346	V(9)-O(15)#1	1.951(7)	0.635048405
V(7)-O(16)	2.075(7)	0.454212927	V(9)-O(6)#1	2.027(7)	0.517130789
$V_{V(7)}$ = **4.06**			$V_{V(9)}$ = **3.98**		
V(8)-O(8)	1.642(7)	1.463866292	V(10)-O(7)	1.644(13)	1.455974849
V(8)-O(2)	1.913(7)	0.703736452	V(10)-O(2)	1.892(7)	0.744833486
V(8)-O(23)#1	1.927(6)	0.677606062	V(10)-O(2)#1	1.892(7)	0.744833486
V(8)-O(6)	2.009(7)	0.542910493	V(10)-O(6)	2.047(7)	0.48991983
V(8)-O(16)	2.058(7)	0.475569026	V(10)-O(6)#1	2.047(7)	0.48991983
V(8)-O(4)	2.338(7)	0.22313016	$V_{V(10)}$ = **3.92**		
$V_{V(8)}$ = **4.09**					
Mn(1)-O(21)#2	2.096(7)	0.437347578	Mn(2)-O(24)#4	2.082(7)	0.454212927
Mn(1)-O(26)	2.162(9)	0.365896268	Mn(2)-O(24)	2.082(7)	0.454212927
Mn(1)-O(9)	2.187(6)	0.341990277	Mn(2)-O(28A)	2.11(2)	0.421108455
Mn(1)-O(8)#3	2.195(7)	0.334675259	Mn(2)-O(28)	2.30(4)	0.251986849
Mn(1)-O(25)	2.196(9)	0.333771952	Mn(2)-O(27)	2.168(14)	0.360010665
Mn(1)-O(12)	2.265(7)	0.276987255	Mn(2)-O(27)#4	2.168(14)	0.360010665
$V_{Mn(1)}$ = **2.09**			$V_{Mn(2)}$ = **2.3**		
Mn(3)-O(30)	2.10(2)	0.432644961			
Mn(3)-O(29)	2.117(19)	0.413216428			
Mn(3)-O(5)#3	2.240(8)	0.29634937			
Mn(3)-O(1)	2.239(9)	0.297151398			
Mn(3)-O(7)#5	2.261(10)	0.279997957			
Mn(3)-O(31)	2.29(3)	0.258890173			
$V_{Mn(3)}$ = **1.98**					
		Compound **2**			
V(1)-O(21)	1.635(6)	1.491824698	V(2)-O(34)	1.595(7)	1.662143622
V(1)-O(49)	1.895(6)	0.738818713	V(2)-O(33)	1.919(6)	0.69241654
V(1)-O(44)	1.936(6)	0.661322598	V(2)-O(44)	1.925(6)	0.681278715
V(1)-O(17)	1.946(6)	0.643688387	V(2)-O(48)	1.937(6)	0.659537652
V(1)-O(18)	1.947(6)	0.641951038	V(2)-O(19)	1.939(7)	0.655982202
$V_{V(1)}$ = **4.18**			$V_{V(2)}$ = **4.35**		
V(3)-O(4)	1.622(7)	1.545171852	V(5)-O(40)	1.642(6)	1.463866292
V(3)-O(24)	1.921(6)	0.688683846	V(5)-O(46)	1.914(6)	0.701837029
V(3)-O(33)	1.946(6)	0.643688387	V(5)-O(20)	1.943(6)	0.648928698
V(3)-O(22)	2.047(6)	0.48991983	V(5)-O(23)	1.954(6)	0.629920182
V(3)-O(36)	2.060(6)	0.473005317	V(5)-O(53)	2.066(6)	0.465396818
V(3)-O(28)	2.383(6)	0.197578042	V(5)-O(41)	2.339(6)	0.22252792
$V_{V(3)}$ = **4.04**			$V_{V(5)}$ = **4.13**		
V(4)-O(26)	1.651(7)	1.428688309	V(6)-O(47)	1.621(6)	1.549353641
V(4)-O(1)	1.947(6)	0.641951038	V(6)-O(20)	1.927(6)	0.677606062
V(4)-O(14)	1.951(6)	0.635048405	V(6)-O(25)	1.968(6)	0.60653066

V(4)-O(11)	1.962(6)	0.616446473	V(6)-O(38)	1.970(6)	0.603260961
V(4)-O(23)	1.975(6)	0.59516362	V(6)-O(36)	2.067(7)	0.464140687
$V_{V(4)}$ = **3.92**			$V_{V(6)}$ = **3.9**		
V(7)-O(2)	1.629(6)	1.516213663	V(17)-O(37)	1.621(6)	1.549353641
V(7)-O(46)	1.921(6)	0.688683846	V(17)-O(48)	1.917(6)	0.696169466
V(7)-O(38)	1.954(6)	0.629920182	V(17)-O(24)	1.930(7)	0.672134172
V(7)-O(16)	1.987(6)	0.576170675	V(17)-O(45)	2.036(6)	0.504703685
V(7)-O(45)	2.048(6)	0.48859751	V(17)-O(50)	2.067(6)	0.464140687
V(7)-O(32)	2.456(6)	0.162201009	V(17)-O(32)	2.375(6)	0.201896518
$V_{V(7)}$ = **4.06**			$V_{V(17)}$ = **4.09**		
V(8)-O(52)	1.614(6)	1.57894477	V(9)-O(39)	1.622(6)	1.545171852
V(8)-O(15)	1.928(6)	0.675777167	V(9)-O(18)	1.912(6)	0.705641015
V(8)-O(49)	1.955(6)	0.628219994	V(9)-O(14)	1.949(6)	0.638490394
V(8)-O(25)	1.975(6)	0.59516362	V(9)-O(15)	1.992(6)	0.568436957
V(8)-O(22)	2.08(7)	0.448116201	V(9)-O(53)	2.040(6)	0.499276816
$V_{V(8)}$ = **3.93**			$V_{V(9)}$ = **3.96**		
V(10)-O(13)	1.649(7)	1.436431858	V(11)-O(7)	1.596(8)	1.657657408
V(10)-O(46)	1.903(6)	0.723015713	V(11)-O(38)	1.851(6)	0.832115701
V(10)-O(11)	1.914(6)	0.701837029	V(11)-O(24)	1.899(6)	0.730874502
V(10)-O(16)	1.971(6)	0.601632727	V(11)-O(45)	2.088(7)	0.438531197
V(10)-O(23)	1.991(6)	0.569975351	V(11)-O(36)	2.104(7)	0.419971861
$V_{V(10)}$ = **4.03**			$V_{V(11)}$ = **4.08**		
V(12)-O(30)	1.622(7)	1.545171852	V(13)-O(35)	1.642(7)	1.463866292
V(12)-O(11)	1.924(6)	0.683122499	V(13)-O(12)	1.852(6)	0.829869776
V(12)-O(12)	1.953(6)	0.631624972	V(13)-O(19)	1.909(6)	0.711385686
V(12)-O(16)	1.958(6)	0.623146913	V(13)-O(48)	1.918(7)	0.694290468
V(12)-O(50)	2.059(6)	0.474285439	V(13)-O(50)	2.082(6)	0.445700486
$V_{V(12)}$ = **3.96**			$V_{V(13)}$ = **4.14**		
V(14)-O(42)	1.638(6)	1.479777727	V(16)-O(3)	1.638(8)	1.479777727
V(14)-O(20)	1.865(6)	0.801218471	V(16)-O(49)	1.875(6)	0.779853928
V(14)-O(15)	1.896(6)	0.736824601	V(16)-O(33)	1.918(6)	0.694290468
V(14)-O(25)	1.952(7)	0.633334376	V(16)-O(44)	1.955(7)	0.628219994
V(14)-O(53)	2.083(6)	0.444497517	V(16)-O(22)	2.116(7)	0.40656966
$V_{V(14)}$ = **4.1**			$V_{V(16)}$ = **3.99**		
V(15)-O(10)	1.650(6)	1.432554851	V(18)-O(43)	1.637(7)	1.483782536
V(15)-O(1)	1.921(6)	0.688683846	V(18)-O(18)	1.882(6)	0.765238624
V(15)-O(12)	1.935(6)	0.663112373	V(18)-O(1)	1.950(6)	0.636767074
V(15)-O(17)	1.975(6)	0.59516362	V(18)-O(14)	1.952(6)	0.633334376
V(15)-O(19)	1.984(6)	0.58086132	V(18)-O(17)	2.007(6)	0.54585309
V(15)-O(29)	2.424(7)	0.176853702	$V_{V(18)}$ = **4.09**		
$V_{V(15)}$ = **4.14**					

Mn(1)-O(13)#1	2.140(7)	0.388312075	Mn(2)-O(35)	2.099(7)	0.433815854
Mn(1)-O(26)#2	2.186(7)	0.342915825	Mn(2)-O(21)#3	2.151(6)	0.37693758
Mn(1)-O(31)	2.191(7)	0.338312998	Mn(2)-O(9)	2.180(10)	0.348521954
Mn(1)-O(27)	2.193(7)	0.336489212	Mn(2)-O(6)	2.191(8)	0.338312998
Mn(1)-O(10)	2.201(6)	0.329291859	Mn(2)-O(8)	2.203(10)	0.327516705
Mn(1)-O(51)	2.224(8)	0.309445599	Mn(2)-O(5)	2.270(11)	0.273269362
$V_{Mn(1)}$ = **2.04**			$V_{Mn(2)}$ = **2.1**		

References

S1. The valence sum calculations are performed on a program of bond valence calculator, version 2.00 February 1993, written by C. Hormillosa, with assistance from S. Healy, distributed by I. D. Brown.

S2. I. D. Brown, D. Altermatt, *Acta Crystallogr*., 1985, **B41**, 244.