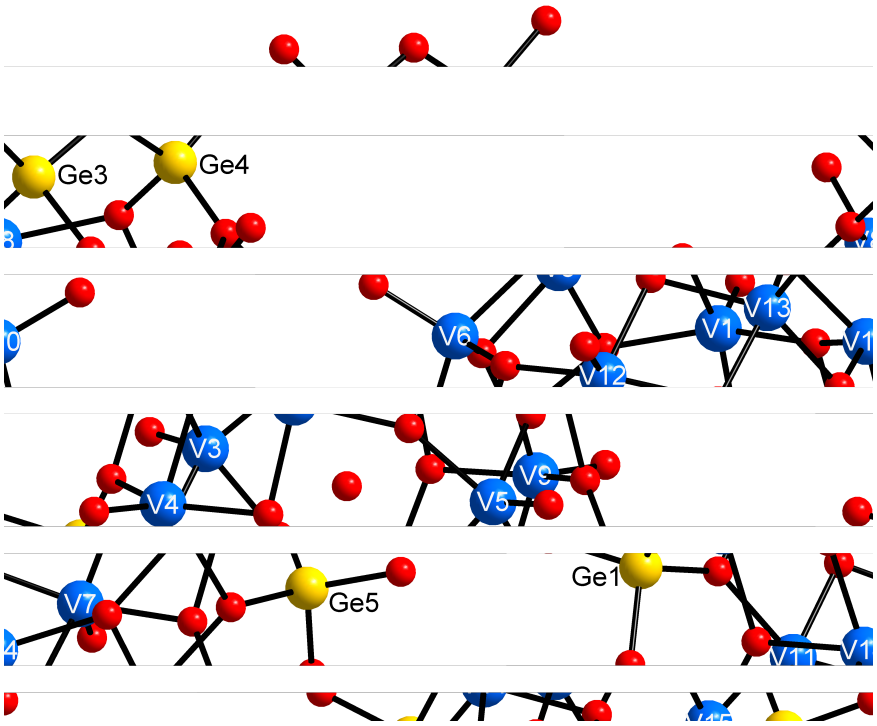
Supplementary Information

Table S1: Selected Bond lengths [Å] for compound **1**. Estimated standard deviations are given in parentheses.

Ge(1)-O(10)	1.720(8)	V(5)-V(15)	3.057(3)
Ge(1)-O(29)	1.733(7)	V(6)-O(23)	1.599(7)
Ge(1)-O(48)	1.744(7)	V(6)-O(26)	1.929(8)
Ge(1)-O(22)	1.753(8)	V(6)-O(36)	1.956(8)
Ge(2)-O(37)	1.707(7)	V(6)-O(27)	1.990(8)
Ge(2)-O(47)	1.748(7)	V(6)-O(48)	2.004(8)
Ge(2)-O(15)	1.753(7)	V(6)-V(8)	3.035(3)
Ge(2)-O(31)	1.757(8)	V(7)-O(9)	1.594(8)
Ge(3)-O(19)	1.700(7)	V(7)-O(40)	1.915(8)
Ge(3)-O(27)	1.750(8)	V(7)-O(34)	1.943(8)
Ge(3)-O(41)	1.759(7)	V(7)-O(1)	1.944(8)
Ge(3)-O(20)	1.768(8)	V(7)-O(15)	2.066(8)
Ge(4)-O(42)	1.709(7)	V(7)-V(11)	2.868(3)
Ge(4)-O(45)	1.744(7)	V(7)-V(9)	3.066(3)
Ge(4)-O(7)	1.746(8)	V(8)-O(16)	1.618(8)
Ge(4)-O(20)	1.763(7)	V(8)-O(35)	1.916(7)
Ge(5)-O(3)	1.722(9)	V(8)-O(26)	1.936(8)
Ge(5)-O(18)	1.745(7)	V(8)-O(27)	1.993(8)
Ge(5)-O(31)	1.751(7)	V(8)-O(7)	2.030(8)
Ge(5)-O(13)	1.767(7)	V(9)-O(2)	1.629(8)
Ge(6)-O(11)	1.687(8)	V(9)-O(40)	1.881(8)
Ge(6)-O(38)	1.747(8)	V(9)-O(12)	1.937(7)
Ge(6)-O(5)	1.750(8)	V(9)-O(13)	1.981(8)
Ge(6)-O(29)	1.785(7)	V(9)-O(15)	2.051(7)
V(1)-O(8)	1.607(8)	V(9)-V(10)	3.035(3)
V(1)-O(35)	1.910(8)	V(10)-O(4)	1.590(9)
V(1)-O(40)	1.935(7)	V(10)-O(12)	1.920(9)
V(1)-O(12)	1.963(8)	V(10)-O(30)	1.958(8)
V(1)-O(7)	2.043(8)	V(10)-O(45)	1.988(7)
V(1)-V(9)	2.903(3)	V(10)-O(13)	2.004(7)
V(1)-V(8)	3.061(3)	V(10)-V(13)	3.028(3)
V(2)-O(21)	1.602(7)	V(11)-O(14)	1.583(8)
V(2)-O(1)	1.917(8)	V(11)-O(34)	1.899(8)
V(2)-O(28)	1.941(8)	V(11)-O(1)	1.938(8)
V(2)-O(5)	1.999(8)	V(11)-O(22)	1.986(8)
V(2)-O(47)	2.003(8)	V(11)-O(5)	1.997(8)
V(2)-V(11)	3.019(3)	V(12)-O(24)	1.590(8)
V(2)-V(15)	3.037(3)	V(12)-O(39)	1.903(7)
V(3)-O(6)	1.566(8)	V(12)-O(46)	1.947(8)
V(3)-O(35)	1.921(8)	V(12)-O(36)	1.948(8)
V(3)-O(34)	1.942(8)	V(12)-O(41)	2.027(8)
V(3)-O(26)	1.945(8)	V(12)-V(13)	3.064(3)
V(3)-O(22)	2.014(8)	V(13)-O(25)	1.586(8)
V(3)-V(8)	2.869(3)	V(13)-O(30)	1.921(7)
V(3)-V(11)	3.057(3)	V(13)-O(46)	1.922(7)
V(4)-O(33)	1.615(8)	V(13)-O(41)	1.985(7)
V(4)-O(39)	1.908(7)	V(13)-O(45)	2.033(8)
V(4)-O(36)	1.938(8)	V(14)-O(17)	1.589(8)
V(4)-O(38)	2.008(7)	V(14)-O(39)	1.942(7)
V(4)-O(48)	2.015(8)	V(14)-O(44)	1.949(8)
V(4)-V(12)	2.877(3)	V(14)-O(28)	1.951(8)
V(4)-V(6)	3.038(3)	V(14)-O(38)	2.015(8)
V(4)-V(14)	3.053(3)	V(14)-V(15)	2.873(3)
V(5)-O(32)	1.603(8)	V(15)-O(43)	1.590(7)

V(5)-O(46)	1.889(7)	V(15)-O(44)	1.929(7)
V(5)-O(44)	1.908(8)	V(15)-O(28)	1.940(8)
V(5)-O(30)	1.940(7)	V(15)-O(47)	2.001(8)
V(5)-O(18)	2.004(7)	V(15)-O(18)	2.017(8)
V(5)-V(13)	2.846(3)		

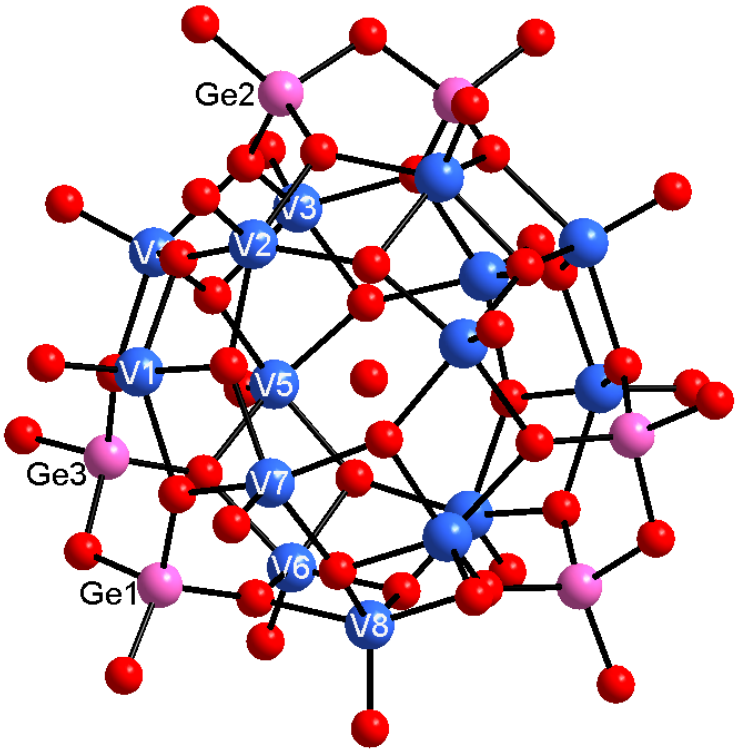


Picture: $\{V_{15}Ge_6\}$ cluster in **1** with atoms labelling for V and Ge

Table S2: Selected bond lengths (Å) for **2**. Estimated standard deviations are given in parentheses.

Ge(1)-O(21)	1.693(4)	V(3)-V(5)	2.8382(13)
Ge(1)-O(1)	1.762(4)	V(3)-V(4)	3.0199(14)
Ge(1)-O(17)	1.769(5)	V(4)-O(12)	1.606(5)
Ge(1)-O(25)#1	1.784(4)	V(4)-O(10)	1.925(4)
Ge(2)-O(23)	1.729(4)	V(4)-O(3)	1.932(4)
Ge(2)-O(6)	1.743(4)	V(4)-O(9)	1.998(4)
Ge(2)-O(9)	1.750(4)	V(4)-O(2)	2.015(4)
Ge(2)-O(22)	1.762(3)	V(4)-V(1)#1	3.0292(14)
Ge(3)-O(24)	1.729(4)	V(5)-O(13)	1.617(4)
Ge(3)-O(14)	1.737(4)	V(5)-O(7)	1.910(4)
Ge(3)-O(2)	1.747(4)	V(5)-O(15)	1.938(4)
Ge(3)-O(25)	1.761(4)	V(5)-O(10)	1.946(4)
V(1)-O(5)	1.622(5)	V(5)-O(14)	2.026(4)
V(1)-O(4)	1.890(4)	V(5)-V(6)	3.0703(13)
V(1)-O(3)#1	1.926(4)	V(6)-O(18)	1.615(4)
V(1)-O(1)	1.994(4)	V(6)-O(15)	1.910(4)
V(1)-O(2)#1	1.995(4)	V(6)-O(16)#1	1.944(4)
V(1)-V(2)	2.8697(14)	V(6)-O(17)#1	1.998(4)
V(1)-V(4)#1	3.0292(14)	V(6)-O(14)	2.002(4)
V(1)-V(7)	3.0384(14)	V(6)-V(7)	2.8942(15)
V(2)-O(8)	1.604(4)	V(6)-V(8)	3.0285(11)
V(2)-O(7)	1.935(4)	V(7)-O(19)	1.609(4)

V(2)-O(4)	1.942(4)	V(7)-O(4)	1.933(4)
V(2)-O(3)#1	1.950(4)	V(7)-O(15)	1.947(4)
V(2)-O(6)#1	2.030(4)	V(7)-O(16)#1	1.959(4)
V(2)-V(3)	3.0949(15)	V(7)-O(1)	2.025(4)
V(3)-O(11)	1.605(4)	V(8)-O(20)	1.615(6)
V(3)-O(7)	1.911(4)	V(8)-O(16)#1	1.928(4)
V(3)-O(10)	1.933(4)	V(8)-O(16)	1.928(4)
V(3)-O(9)	2.005(4)	V(8)-O(17)#1	1.988(4)
V(3)-O(6)#1	2.030(4)	V(8)-O(17)	1.988(4)
		V(8)-V(6)#1	3.0285(11)
Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2 #2 x+1/2,y-1/2,z #3 x-1/2,y+1/2,z			



Picture: $\{V_{15}Ge_6\}$ cluster in **2** with atoms labelling for V and Ge

Table S3: Bond valence sums of the germanium and vanadium atoms in **1** and **2**.

Compound **1**				Compound **2**			
Ge1	4.49	V1	3.99	Ge1	4.34	V1	3.99
Ge2	4.45	V2	3.99	Ge2	4.39	V2	3.98
Ge3	4.42	V3	4.21	Ge3	4.42	V3	3.95
Ge4	4.46	V4	3.92			V4	3.95
Ge5	4.39	V5	4.19			V5	3.99
Ge6	4.45	V6	3.96			V6	3.94
		V7	4.02			V7	3.94
		V8	3.90			V8	3.97
		V9	3.91				
		V10	4.02				
		V11	4.14				
		V12	4.10				
		V13	4.06				
		V14	4.04				
		V15	4.00				
Ge(average)	4.44	V(average)	4.03	Ge(average)	4.38	V(average)	3.96

Table S4: Selected bond lengths (Å) and the angles (°) around the Mn^{2+} cations in **1**. Estimated standard deviations are given in parentheses.

O(11)-Mn(3)	2.026(9)	O(37)#2-Mn(1)-O(42)	81.9(3)	N(22)-Mn(2)-Mn(1)	85.4(3)
O(19)-Mn(4)	1.992(9)	O(37)#2-Mn(1)-N(12)	93.7(4)	O(37)#2-Mn(2)-Mn(1)	42.1(2)
O(32)-Mn(5)	2.258(8)	O(42)-Mn(1)-N(12)	157.5(4)	N(23)-Mn(2)-Mn(1)	114.9(3)
O(37)-Mn(1)#1	2.109(8)	O(37)#2-Mn(1)-N(14)	91.8(4)	N(21)-Mn(2)-Mn(1)	158.2(3)
O(37)-Mn(2)#1	2.297(7)	O(42)-Mn(1)-N(14)	101.8(3)	O(11)-Mn(3)-N(32)	103.3(4)
O(42)-Mn(2)	2.141(8)	N(12)-Mn(1)-N(14)	100.4(4)	O(11)-Mn(3)-N(33)	104.6(4)
O(42)-Mn(1)	2.196(8)	O(37)#2-Mn(1)-N(11)	165.9(4)	N(32)-Mn(3)-N(33)	111.6(4)
Mn(1)-O(37)#2	2.109(8)	O(42)-Mn(1)-N(11)	109.8(4)	O(11)-Mn(3)-N(34)	99.9(5)
Mn(1)-N(12)	2.246(12)	N(12)-Mn(1)-N(11)	78.5(4)	N(32)-Mn(3)-N(34)	107.1(5)
Mn(1)-N(14)	2.251(12)	N(14)-Mn(1)-N(11)	78.3(4)	N(33)-Mn(3)-N(34)	127.2(5)
Mn(1)-N(11)	2.316(13)	O(37)#2-Mn(1)-N(13)	118.9(4)	O(11)-Mn(3)-N(31)	178.7(4)
Mn(1)-N(13)	2.518(13)	O(42)-Mn(1)-N(13)	74.6(4)	N(32)-Mn(3)-N(31)	76.6(5)
Mn(1)-Mn(2)	3.145(3)	N(12)-Mn(1)-N(13)	88.7(4)	N(33)-Mn(3)-N(31)	76.7(4)
Mn(2)-N(24)	2.236(11)	N(14)-Mn(1)-N(13)	147.5(5)	N(34)-Mn(3)-N(31)	78.9(5)
Mn(2)-N(22)	2.281(10)	N(11)-Mn(1)-N(13)	73.0(5)	O(19)-Mn(4)-N(44)	101.6(5)
Mn(2)-O(37)#2	2.297(7)	O(37)#2-Mn(1)-Mn(2)	46.9(2)	O(19)-Mn(4)-N(42)	99.7(5)
Mn(2)-N(23)	2.330(10)	O(42)-Mn(1)-Mn(2)	42.8(2)	N(44)-Mn(4)-N(42)	113.9(5)
Mn(2)-N(21)	2.368(12)	N(12)-Mn(1)-Mn(2)	120.6(3)	O(19)-Mn(4)-N(43)	104.0(4)
Mn(3)-N(32)	2.146(11)	N(14)-Mn(1)-Mn(2)	119.4(3)	N(44)-Mn(4)-N(43)	110.9(6)
Mn(3)-N(33)	2.214(10)	N(11)-Mn(1)-Mn(2)	147.1(3)	N(42)-Mn(4)-N(43)	123.0(6)
Mn(3)-N(34)	2.257(13)	N(13)-Mn(1)-Mn(2)	80.4(3)	O(19)-Mn(4)-N(41)	177.6(5)
Mn(3)-N(31)	2.335(13)	O(42)-Mn(2)-N(24)	96.9(4)	N(44)-Mn(4)-N(41)	79.4(6)
Mn(4)-N(44)	2.164(17)	O(42)-Mn(2)-N(22)	120.0(4)	N(42)-Mn(4)-N(41)	77.9(6)
Mn(4)-N(42)	2.190(14)	N(24)-Mn(2)-N(22)	138.6(4)	N(43)-Mn(4)-N(41)	77.7(5)
Mn(4)-N(43)	2.237(12)	O(42)-Mn(2)-O(37)#2	78.9(3)	N(62)-Mn(5)-N(52)	98.2(6)
Mn(4)-N(41)	2.321(14)	N(24)-Mn(2)-O(37)#2	90.3(3)	N(62)-Mn(5)-N(53)	105.7(7)
Mn(5)-N(62)	2.213(18)	N(22)-Mn(2)-O(37)#2	80.1(3)	N(52)-Mn(5)-N(53)	98.4(6)
Mn(5)-N(52)	2.229(15)	O(42)-Mn(2)-N(23)	87.4(4)	N(62)-Mn(5)-O(32)	86.4(5)
Mn(5)-N(53)	2.250(18)	N(24)-Mn(2)-N(23)	112.5(4)	N(52)-Mn(5)-O(32)	172.6(5)
Mn(5)-N(54)	2.258(19)	N(22)-Mn(2)-N(23)	88.8(4)	N(53)-Mn(5)-O(32)	85.9(4)
Mn(5)-N(51)	2.308(14)	O(37)#2-Mn(2)-N(23)	154.7(4)	N(62)-Mn(5)-N(54)	101.3(7)
		O(42)-Mn(2)-N(21)	156.9(4)	N(52)-Mn(5)-N(54)	93.8(6)
		N(24)-Mn(2)-N(21)	76.9(4)	N(53)-Mn(5)-N(54)	148.3(7)
		N(22)-Mn(2)-N(21)	75.1(4)	O(32)-Mn(5)-N(54)	79.5(5)
		O(37)#2-Mn(2)-N(21)	122.9(4)	N(62)-Mn(5)-N(51)	176.0(6)
		N(23)-Mn(2)-N(21)	74.9(4)	N(52)-Mn(5)-N(51)	78.0(5)
		O(42)-Mn(2)-Mn(1)	44.2(2)	N(53)-Mn(5)-N(51)	76.3(6)
		N(24)-Mn(2)-Mn(1)	113.7(3)	O(32)-Mn(5)-N(51)	97.3(4)
				N(54)-Mn(5)-N(51)	77.8(6)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,y+1/2,-z+1/2 #2 -x+2,y-1/2,-z+1/2

Table S5: Selected bond lengths (Å) and the angles (°) around the Ni^{2+} cations in **2**. Estimated standard deviations are given in parentheses.

Ni(1)-N(1)	2.077(7)	N(4)-Ni(1)-N(3)	95.6(3)
Ni(1)-N(4)	2.082(8)	N(22')-Ni(1)-N(3)	108.6(7)
Ni(1)-N(22')	2.10(2)	N(2)-Ni(1)-N(3)	163.8(3)
Ni(1)-N(2)	2.105(6)	O(5)#2-Ni(1)-N(3)	83.8(3)
Ni(1)-O(5)#2	2.121(5)	N(1)-Ni(1)-N(22)	169.6(4)
Ni(1)-N(3)	2.135(7)	N(4)-Ni(1)-N(22)	106.9(4)
Ni(1)-N(22)	2.192(10)	N(22')-Ni(1)-N(22)	22.1(6)
Ni(2)-N(11)	2.083(6)	N(2)-Ni(1)-N(22)	95.5(3)
Ni(2)-N(12)	2.088(6)	O(5)#2-Ni(1)-N(22)	78.9(3)
Ni(2)-N(23)	2.092(6)	N(3)-Ni(1)-N(22)	96.7(4)
Ni(2)-N(14)	2.100(6)	N(11)-Ni(2)-N(12)	84.0(3)
Ni(2)-N(13)	2.120(6)	N(11)-Ni(2)-N(23)	176.7(2)
Ni(2)-O(13)	2.157(4)	N(12)-Ni(2)-N(23)	98.0(3)

		N(11)-Ni(2)-N(14)	84.0(2)
N(1)-Ni(1)-N(4)	83.5(3)	N(12)-Ni(2)-N(14)	95.6(3)
N(1)-Ni(1)-N(22')	166.5(7)	N(23)-Ni(2)-N(14)	98.4(2)
N(4)-Ni(1)-N(22')	87.1(7)	N(11)-Ni(2)-N(13)	82.4(3)
N(1)-Ni(1)-N(2)	84.1(2)	N(12)-Ni(2)-N(13)	163.0(3)
N(4)-Ni(1)-N(2)	91.0(3)	N(23)-Ni(2)-N(13)	95.1(3)
N(22')-Ni(1)-N(2)	86.4(7)	N(14)-Ni(2)-N(13)	93.1(3)
N(1)-Ni(1)-O(5)#2	90.7(2)	N(11)-Ni(2)-O(13)	92.13(19)
N(4)-Ni(1)-O(5)#2	174.2(3)	N(12)-Ni(2)-O(13)	84.1(2)
N(22')-Ni(1)-O(5)#2	98.6(7)	N(23)-Ni(2)-O(13)	85.5(2)
N(2)-Ni(1)-O(5)#2	88.1(2)	N(14)-Ni(2)-O(13)	176.1(2)
N(1)-Ni(1)-N(3)	82.0(3)	N(13)-Ni(2)-O(13)	86.2(2)
Symmetry transformations used to generate equivalent atoms: #1 -x+2,y+1/2,-z+1/2 #2 -x+2,y-1/2,-z+1/2			

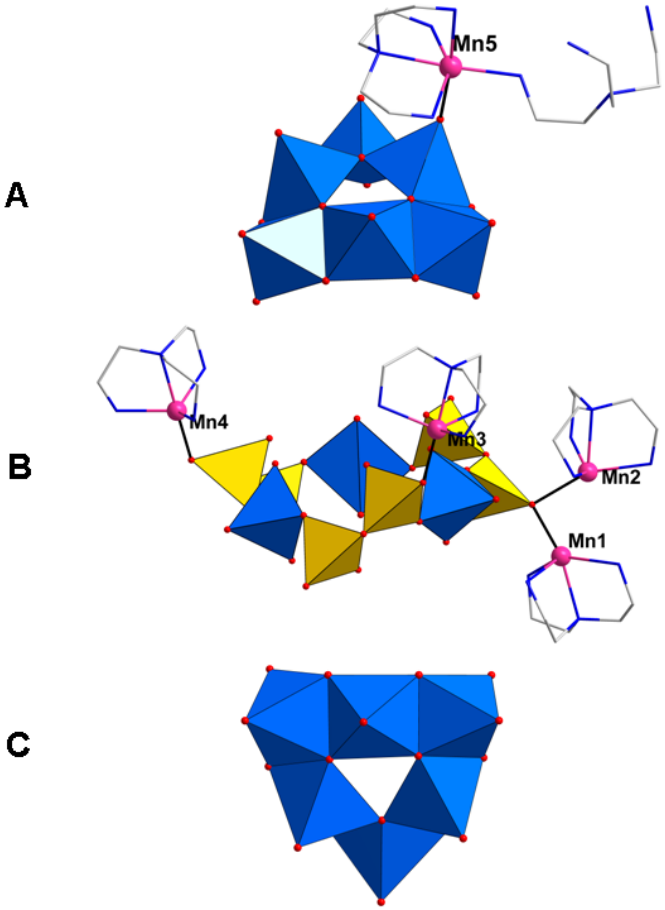


Figure S1: Layer representation of the structure of compound **1.**

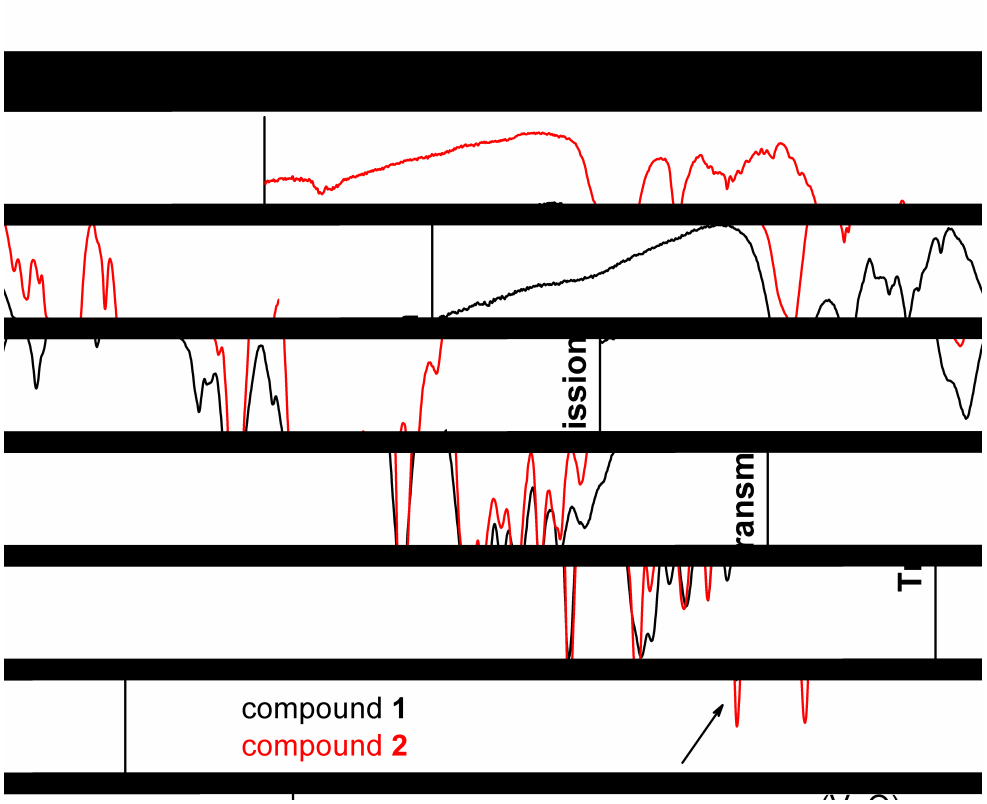


Figure S2: IR spectrum of $[\{Mn(tren)(trenH_2)\}\{Mn(tren)\}_4V_{15}Ge_6O_{48}(H_2O)_{0.5}]\cdot(tren)\cdot 2H_2O$ (**1**, black) and $[\{Ni(tren)\}_4(trenH_2)_2V_{15}Ge_6O_{48}(H_2O)]\cdot 2H_2O$ (**2**, red).

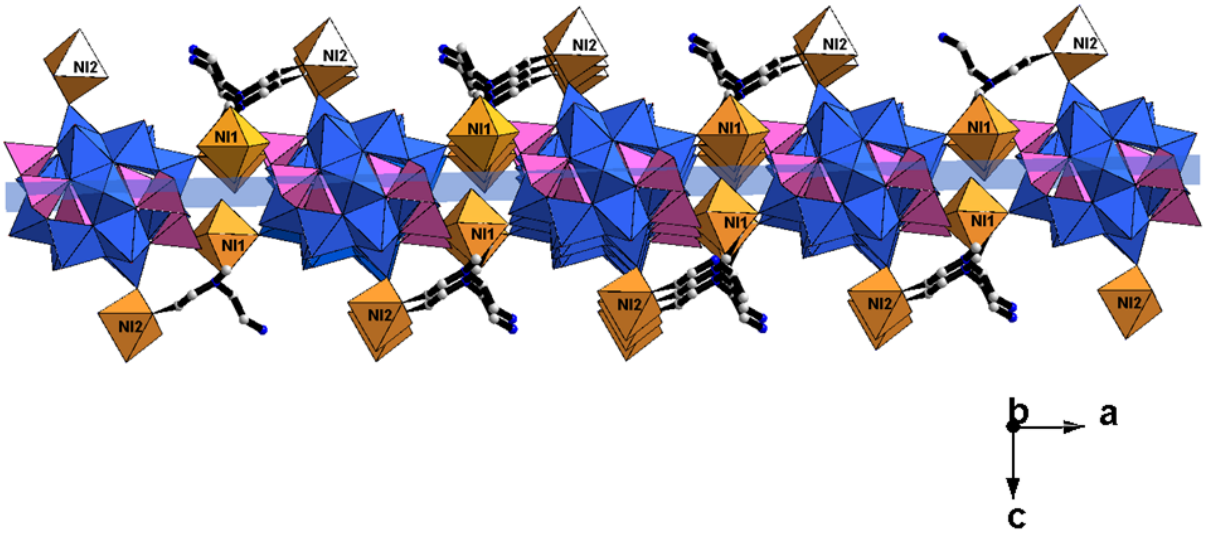


Figure S3: The structure of **2** in the ac plane with numbered Ni^{2+} cations. All H atoms und lattice water molecules are omitted for clarity.

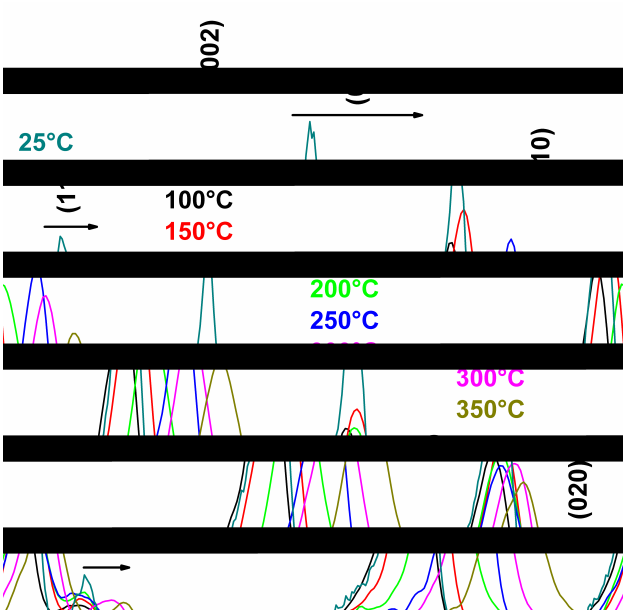


Figure S4: X-ray powder patterns recorded during thermal decomposition of **1** from 100 to 350°C.

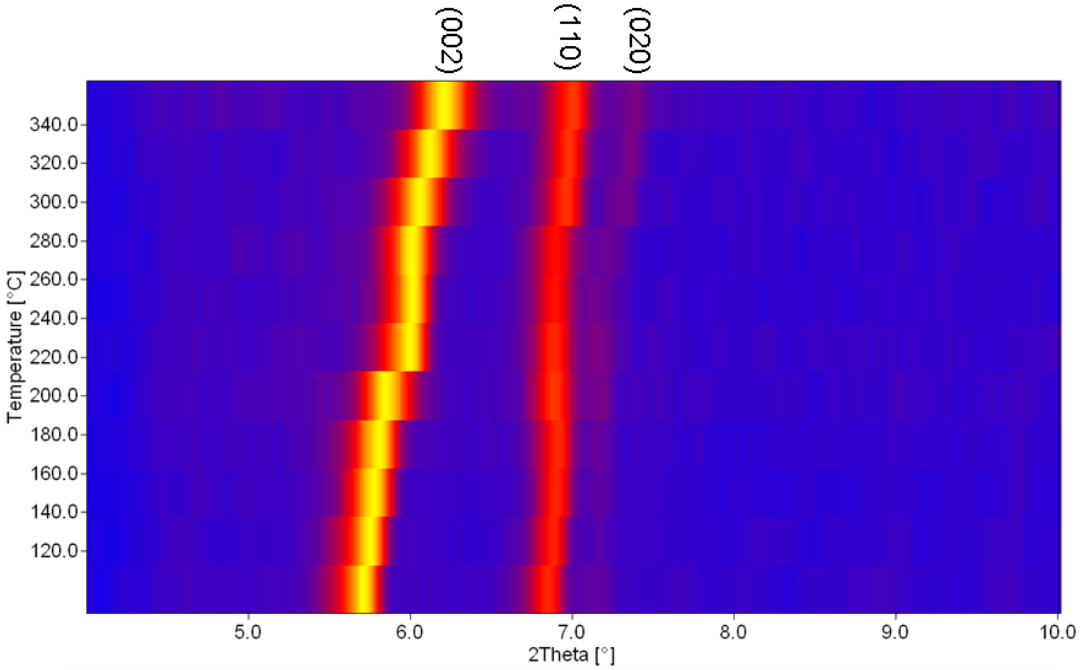


Figure S5: *In-situ* X-ray powder patterns recorded during thermal decomposition of **1** from 100 to 350 °C.

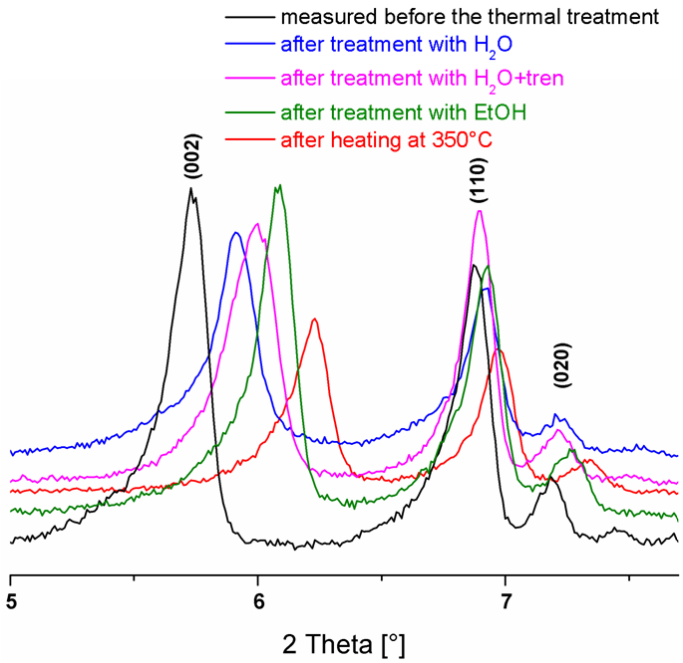


Figure S6: X-ray powder patterns after treatment of the heated compound with different solvents.