Supplementary Materials

Investigating the formation of different $(NH_4)_2[M(H_2O)_5(NH_3CH_2CH_2COO)]_2[V_{10}O_{28}]\cdot nH_2O$ (M = Co^{II}, Ni^{II}, Zn^{II}, n = 4; M = Cd^{II}, Mn^{II}, n = 2) crystallohydrates

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Table S1. Crystallographic data for the compounds **1–5**.

Compound	**1**	**2**	**3**	**4**	**5**
CCDC No.	2366040	2366041	2366042	2366043	2366044
COD ID	3000552	3000553	3000554	3000555	3000556
Empirical formula	$C_6H_{50}N_4O_{46}Co_2V_{10}$	$C_6H_{50}N_4O_{46}Ni_2V_{10}$	$C_6H_{46}N_4O_{44}Cd_2V_{10}$	$C_6H_{50}N_4O_{46}Zn_2V_{10}$	$C_6H_{46}N_4O_{44}Mn_2V_{10}$
M_r, $F(000)$	1541.76, 1532	1541.32, 1536	1612.67, 1576	1554.64, 1544	1497.75, 1484
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Unit cell dimensions	Determined from 11212 reflections	Determined from 11888 reflections	Determined from 5732 reflections	Determined from 50787 reflections	Determined from 9943 reflections
a[Å], α[°]	8.96877(17), 90	8.9270(2), 90	9.8240(8), 90	8.91183(7), 90	9.7536(4), 90
b[Å], β[°]	18.0653(4), 102.237(2)	18.0166(3), 102.276(2)	22.9500(15), 110.168(10)	18.01144(10), 101.8149(7)	22.7609(8), 110.239(5)
c[Å], γ[°]	13.8448(3), 90	13.8496(3), 90	10.1212(9), 90	13.83383(9), 90	10.0154(4), 90
V[Å^3]	2192.22(8)	2176.56(8)	2142.0(3)	2173.49(3)	2086.15(15)
Z, Z'	2, 0.5	2, 0.5	2, 0.5	2, 0.5	2, 0.5
μ [mm^{-1}], ρ(calcd.) [g.cm^{-3}]	2.891, 2.336	3.015, 2.352	3.171, 2.500	3.257, 2.375	2.842, 2.384
Absorption correction, T_{min}, T_{max}	Multiscan, 0.644, 1.000	Multiscan, 0.582, 1.000	Multiscan, 0.429, 1.000	Analytical, 0.528, 0.723	Analytical, 0.321, 0.840
Crystal size [mm]	0.36 × 0.28 × 0.15	0.43 × 0.27 × 0.18	0.53 × 0.13 × 0.05	0.33 × 0.27 × 0.15	0.54 × 0.22 × 0.09
Crystal habit, color	Prism, reddish orange	Prism, greenish orange	Needle, light orange	Prism, light orange	Prism, orange
θ range for data collection [°]	3.01–27.11	3.01–27.10	3.06–27.20	3.38–27.11	3.45–27.19
Completeness to θ [°]	99.8 % to 27.11°	99.8 % to 27.10°	99.8 % to 25.242°	99.7 % to 27.11°	99.8 % to 25.242°
Limiting indices	$h = -11 \rightarrow 11$ $k = -23 \rightarrow 22$ $l = -17 \rightarrow 16$	$h = -11 \rightarrow 11$ $k = -23 \rightarrow 23$ $l = -17 \rightarrow 17$	$h = -12 \rightarrow 12$ $k = -29 \rightarrow 29$ $l = -12 \rightarrow 12$	$h = -11 \rightarrow 11$ $k = -22 \rightarrow 23$ $l = -17 \rightarrow 17$	$h = -12 \rightarrow 12$ $k = -29 \rightarrow 29$ $l = -12 \rightarrow 12$

R_{int}, R_{σ}	0.0336, 0.0283	0.0379, 0.0283	0.0529, 0.0291	0.0178, 0.0073	0.0551, 0.0328
Reflections collected/unique/observed [$I > 2\sigma(I)$]	20252/4833/4282	18863/4800/4363	45382/8555/6913	68632/4783/4695	101530/8388/6503
Data/restraints/parameters	4833/68/365	4800/68/365	8555/97/351	4783/68/366	8388/97/351
Secondary extinction correction	–	–	–	0.00324(15) (SHELXL)	–
S/restrained S	1.078/1.085	1.077/1.084	1.047/1.053	1.086/1.092	1.044/1.048
Final R indices [$I > 2\sigma(I)$]	$R(F^2)$ = 0.0289, $wR(F^2)$ = 0.0752	$R(F^2)$ = 0.0278, $wR(F^2)$ = 0.0741	$R(F^2)$ = 0.0348, $wR(F^2)$ = 0.0850	$R(F^2)$ = 0.0152, $wR(F^2)$ = 0.0426	$R(F^2)$ = 0.0276, $wR(F^2)$ = 0.0693
Final R indices [all data]	$R(F^2)$ = 0.0350, $wR(F^2)$ = 0.0794	$R(F^2)$ = 0.0322, $wR(F^2)$ = 0.0767	$R(F^2)$ = 0.0483, $wR(F^2)$ = 0.0899	$R(F^2)$ = 0.0156, $wR(F^2)$ = 0.0426	$R(F^2)$ = 0.0426, $wR(F^2)$ = 0.0725
$\Delta\rho_{max}/\Delta\rho_{min}$ [e Å^{-3}]	0.622/–0.378	0.478/–0.501	0.562/–0.519	0.344/–0.275	0.599/—0.494

Table S2. Selected bond lengths *d* [Å], bond valences *s* and bond valence sums Σ*s* in the compounds **1–5**.

	1		**2**		**3**		**4**		**5**	
	***d* [Å]**	***s***	***d* [Å]**	***s***	***d* [Å]**	***s***	***d* [Å]**	***s***	***d* [Å]**	***s***
V–O$_T$										
O1–V1	1.6208(17)	1.64	1.6169(17)	1.65	1.594(3)	1.76	1.6266(10)	1.61	1.5943(18)	1.76
O2–V2	1.6147(18)	1.66	1.6164(17)	1.66	1.609(3)	1.69	1.6235(10)	1.62	1.6069(17)	1.70
O3–V3	1.5997(19)	1.73	1.5993(17)	1.73	1.602(3)	1.72	1.6050(10)	1.71	1.6024(18)	1.72
O4–V5	1.6066(17)	1.70	1.6025(17)	1.72	1.598(3)	1.74	1.6089(10)	1.69	1.5983(17)	1.74
V–O(μ$_2$)										
O5–V4	1.6986(16)	1.33	1.6964(16)	1.33	1.690(3)	1.35	1.7012(9)	1.32	1.6889(16)	1.36
O5–V5	2.0267(17)	0.55	2.0273(16)	0.55	2.051(3)	0.52	2.0254(10)	0.55	2.0381(17)	0.53
Σ*s*(O5)		**1.87**		**1.88**		**1.87**		**1.86**		**1.89**
O6–V3	2.0632(17)	0.49	2.0645(17)	0.49	2.054(3)	0.51	2.0623(10)	0.50	2.0538(17)	0.51
O6–V4	1.6791(17)	1.40	1.6788(16)	1.40	1.691(3)	1.35	1.6800(9)	1.39	1.6917(17)	1.35
Σ*s*(O6)		**1.89**		**1.89**		**1.86**		**1.89**		**1.86**
O7–V3	1.8244(17)	0.94	1.8218(17)	0.95	1.830(3)	0.93	1.8238(10)	0.95	1.8256(17)	0.94
O7–V5	1.8447(17)	0.89	1.8462(17)	0.89	1.844(3)	0.90	1.8454(10)	0.89	1.8447(17)	0.89
Σ*s*(O7)		**1.84**		**1.84**		**1.82**		**1.84**		**1.83**
O8–V1	1.7941(17)	1.02	1.7968(16)	1.01	1.816(3)	0.97	1.7857(10)	1.05	1.8103(18)	0.98
O8–V3	1.8761(17)	0.82	1.8765(17)	0.82	1.882(3)	0.80	1.8809(10)	0.81	1.8813(18)	0.81
Σ*s*(O8)		**1.84**		**1.84**		**1.77**		**1.86**		**1.79**
O10–V2	1.8158(16)	0.97	1.8159(16)	0.97	1.810(3)	0.98	1.8051(10)	0.99	1.8076(17)	0.99
O10–V5	1.8785(17)	0.82	1.8779(17)	0.82	1.881(3)	0.81	1.8937(10)	0.78	1.8903(17)	0.79
Σ*s*(O10)		**1.78**		**1.78**		**1.79**		**1.78**		**1.78**
O13–V2	1.8121(17)	0.98	1.8118(16)	0.98	1.826(3)	0.94	1.8185(10)	0.96	1.8266(17)	0.94
O13–V3	1.8815(18)	0.81	1.8835(17)	0.80	1.868(3)	0.84	1.8792(10)	0.81	1.8586(17)	0.86
Σ*s*(O13)		**1.78**		**1.78**		**1.78**		**1.77**		**1.80**

O14–V1	1.8327(16)	0.92	1.8291(16)	0.93	1.838(3)	0.91	1.8404(9)	0.90	1.8411(17)	0.90
O14–V5	1.8605(17)	1.86	1.8624(17)	0.85	1.861(3)	0.85	1.8526(10)	0.87	1.8423(17)	0.90
Σ*s*(O14)		**1.78**		**1.78**		**1.76**		**1.78**		**1.80**
V–O(μ_3)										
O9–V1	1.9835(15)	0.61	1.9836(15)	0.61	1.986(3)	0.61	1.9795(9)	0.62	1.9794(17)	0.62
O9–V2	2.0219(16)	0.55	2.0217(15)	0.55	2.009(3)	0.57	2.0145(9)	0.56	2.0051(17)	0.58
O9–V4	1.9302(16)	0.71	1.9290(15)	0.71	1.930(3)	0.71	1.9349(9)	0.70	1.9267(17)	0.72
Σ*s*(O9)		**1.88**		**1.88**		**1.89**		**1.89**		**1.92**
O12–V1	2.0200(16)	0.56	2.0209(16)	0.55	2.019(3)	0.56	2.0244(9)	0.55	2.0180(17)	0.56
O12–V2	2.0010(16)	0.59	1.9984(16)	0.59	2.013(3)	0.57	2.0051(9)	0.58	2.0138(17)	0.57
O12–V4	1.9111(16)	0.75	1.9108(16)	0.75	1.901(2)	0.77	1.9107(9)	0.75	1.9049(16)	0.76
Σ*s*(O12)		**1.89**		**1.89**		**1.89**		**1.88**		**1.88**
V–O(μ_6)										
O11–V1	2.2357(16)	0.31	2.2355(15)	0.31	2.257(2)	0.29	2.2384(9)	0.31	2.2565(17)	0.29
O11–V2	2.2271(16)	0.32	2.2272(16)	0.32	2.228(2)	0.32	2.2247(9)	0.32	2.2226(17)	0.32
O11–V3	2.3045(16)	0.26	2.3062(15)	0.26	2.314(2)	0.25	2.3078(9)	0.26	2.3090(16)	0.25
O11–V4	2.0939(15)	0.46	2.0895(15)	0.46	2.105(2)	0.44	2.0909(9)	0.46	2.1012(17)	0.45
O11–V4′	2.1444(15)	0.40	2.1422(15)	0.40	2.129(2)	0.41	2.1376(9)	0.40	2.1245(16)	0.42
O11–V5	2.3194(15)	0.25	2.3195(15)	0.25	2.306(2)	0.26	2.3203(9)	0.25	2.2987(17)	0.26
Σ*s*(O11)		**1.99**		**1.99**		**1.97**		**1.99**		**1.99**
***M*–O**										
M–O51	2.088(2)	0.34	2.0505(18)	0.36	2.275(3)	0.37	2.0915(10)	0.35	2.1821(19)	0.35
M–O52	2.087(2)	0.34	2.052(2)	0.36	2.232(3)	0.41	2.0879(11)	0.35	2.1369(19)	0.39
M–O53	2.070(2)	0.35	2.038(2)	0.37	2.279(3)	0.36	2.0665(11)	0.38	2.1699(18)	0.36
M–O54	2.082(2)	0.34	2.0523(19)	0.36	2.275(3)	0.37	2.0844(10)	0.36	2.1977(19)	0.34
M–O55	2.1195(19)	0.31	2.0729(19)	0.34	2.327(3)	0.32	2.1152(10)	0.33	2.2197(18)	0.32
M–O91	2.0928(19)	0.33	2.0614(18)	0.35	2.200(3)	0.45	2.0961(10)	0.35	2.0988(17)	0.43
Σ*s*(*M*)		**2.01**		**1.80**		**1.83**		**1.77**		**1.76**

Table S3. Hydrogen bonds in the structures of **1–5**. Values given in italics are normalized to neutron distances [27, 34, 35].

D–H…A	*d*(D–H) [Å]	*d*(H…A) [Å]	d(D…A) [Å]	∠ D–H…A [°]
$(NH_4)_2[Co(H_2O)_5(NH_3CH_2CH_2COO)]_2V_{10}O_{28}\cdot 4H_2O$ (1)				
N1–H1A…O3^{i}	0.88	2.63	3.269(3)	129.9
	1.030	*2.540*		*127.32*
N1–H1A…O92	0.88	2.49	3.018(3)	119.1
	1.030	*2.419*		*116.11*
N1–H1A…O4^{ii}	0.88	2.57	3.181(3)	126.8
	1.030	2.488		124.08
N1–H1B…O55^{i}	0.88	2.31	3.121(3)	153.2
	1.030	*2.177*		*151.50*
N1–H1C…O14^{iii}	0.88	2.01	2.830(3)	153.9
	1.030	*1.879*		*151.96*
N2–H1…O1^{iv}	0.845(16)	2.31(2)	3.103(3)	157(3)
	1.030	*2.137*		*155.23*
N2–H1…O8^{iv}	0.845(16)	2.54(4)	2.957(3)	112(3)
	1.030	*2.478*		*107.55*
N2–H2…O13^{v}	0.845(16)	2.000(17)	2.837(3)	171(4)
	1.030	*1.818*		*169.74*
N2–H3…O4	0.848(16)	2.089(19)	2.919(3)	166(4)
	1.030	*1.913*		*164.60*
N2–H4…O2W	0.846(16)	2.03(2)	2.840(4)	161(4)
	1.030	*1.856*		*158.66*
O51–H51A…O7^{iii}	0.792(12)	1.931(14)	2.710(3)	168(3)
	0.938	*1.788*		*166.78*
O51–H51B…O1^{v}	0.792(12)	1.928(13)	2.705(2)	167(3)
	0.938	*1.786*		*165.70*
O52–H52A…O2W	0.798(12)	1.958(15)	2.742(4)	167(3)
	0.938	*1.822*		*166.17*
O52–H52B…O2^{v}	0.795(12)	2.080(16)	2.832(3)	158(3)
	0.938	*1.948*		*156.28*
O53–H53A…O1W	0.789(12)	1.984(14)	2.763(3)	169(3)
	0.938	*1.838*		*168.45*
O53–H53B…O10	0.788(12)	1.950(12)	2.736(3)	176(3)
	0.938	*1.800*		*175.53*
O54–H54A…O12^{vi}	0.799(12)	1.984(14)	2.771(2)	168(3)
	0.938	*1.849*		*167.14*
O54–H54B…O5	0.791(12)	1.964(13)	2.750(2)	172(3)
	0.938	*1.818*		*171.55*
O55–H55A…O9	0.796(12)	1.931(13)	2.719(2)	170(3)
	0.938	*1.791*		*169.50*
O55–H55B…O92	0.795(12)	1.888(16)	2.652(3)	161(3)
	0.938	*1.753*		*159.49*
O1W–H11W…O2^{vii}	0.742(19)	2.12(2)	2.850(3)	168(4)
	0.938	*1.929*		*166.62*
O1W–H12W…O92^{vii}	0.740(19)	2.06(2)	2.795(3)	175(5)
	0.938	*1.860*		*174.57*
O2W–H21W…O91^{viii}	0.738(19)	2.12(2)	2.840(3)	165(4)
	0.938	*1.927*		*163.93*
O2W–H22W…O1W	0.738(19)	2.15(2)	2.862(3)	162(5)

	0.938	*1.961*		*160.29*

Symmetry codes: (i) *x*+1/2, −*y*+3/2, *z*+1/2; (ii) −*x*+3/2, *y*+1/2, −*z*+1/2; (iii) *x*−1/2, −*y*+3/2, *z*+1/2; (iv) −*x*+3/2, *y*−1/2, −*z*+1/2; (v) *x*−1, *y*, *z*; (vi) −*x*+1, −*y*+1, −*z*; (vii) −*x*+2, −*y*+1, −*z*+1; (viii) −*x*+1, −*y*+1, −*z*+1.

$(NH_4)_2[Ni(H_2O)_5(NH_3CH_2CH_2COO)]_2V_{10}O_{28}\cdot 4H_2O$ (2)

N1–H1A…O3^{i}	0.84	2.62	3.272(3)	135.2
	1.030	*2.490*		*132.20*
N1–H1A…O92	0.84	2.54	3.024(3)	117.9
	1.030	*2.454*		*114.03*
N1–H1A…O4^{ii}	0.84	2.62	3.167(3)	123.2
	1.030	*2.527*		*119.71*
N1–H1B…O55^{i}	0.84	2.31	3.111(3)	157.9
	1.030	*2.141*		*156.05*
N1–H1C…O14^{iii}	0.84	2.02	2.828(3)	159.6
	1.030	*1.848*		*157.63*
N2–H1…O1^{iv}	0.817(16)	2.35(2)	3.129(3)	159(4)
	1.030	*2.153*		*157.49*
N2–H1…O8^{iv}	0.817(16)	2.47(4)	2.939(3)	117(3)
	1.030	*2.383*		*112.74*
N2–H2…O13^{v}	0.819(16)	2.005(17)	2.823(3)	176(4)
	1.030	*1.795*		*175.38*
N2–H3…O4	0.819(16)	2.109(18)	2.915(3)	168(4)
	1.030	*1.904*		*166.41*
N2–H4…O2W	0.819(16)	2.07(2)	2.845(4)	159(4)
	1.030	*1.870*		*156.58*
O51–H51A…O7^{iii}	0.799(12)	1.920(14)	2.706(2)	168(3)
	0.938	*1.783*		*167.22*
O51–H51B…O1^{v}	0.800(12)	1.929(14)	2.713(2)	167(3)
	0.938	*1.794*		*165.66*
O52–H52A…O2W	0.800(12)	1.954(14)	2.746(4)	171(3)
	0.938	*1.818*		*169.81*
O52–H52B…O2^{v}	0.800(12)	2.108(18)	2.840(3)	152(3)
	0.938	*1.988*		*150.21*
O53–H53A…O1W	0.795(12)	1.989(15)	2.766(3)	166(3)
	0.938	*1.851*		*164.58*
O53–H53B…O10	0.793(12)	1.946(13)	2.735(3)	173(3)
	0.938	*1.803*		*172.38*
O54–H54A…O12^{vi}	0.802(12)	1.976(13)	2.771(2)	171(3)
	0.938	*1.841*		*170.56*
O54–H54B…O5	0.796(12)	1.949(13)	2.742(2)	175(3)
	0.938	*1.807*		*174.69*
O55–H55A…O9	0.801(12)	1.920(13)	2.720(2)	175(3)
	0.938	*1.784*		*174.91*
O55–H55B…O92	0.800(12)	1.855(14)	2.635(3)	164(3)
	0.938	*1.723*		*163.22*
O1W–H11W…O2^{vii}	0.75(2)	2.12(2)	2.841(3)	164(5)
	0.938	*1.934*		*162.22*
O1W–H12W…O92^{vii}	0.75(2)	2.06(2)	2.804(3)	178(5)
	0.938	*1.867*		*178.28*
O2W–H21W…O91^{viii}	0.74(2)	2.12(2)	2.846(3)	166(5)
	0.938	*1.932*		*164.26*
O2W–H22W…O1W	0.74(2)	2.13(2)	2.856(3)	166(5)

	0.938	*1.942*		*164.14*

Symmetry codes: (i) *x*+1/2, −*y*+3/2, *z*+1/2; (ii) −*x*+3/2, *y*+1/2, −*z*+1/2; (iii) *x*−1/2, −*y*+3/2, *z*+1/2; (iv) −*x*+3/2, *y*−1/2, −*z*+1/2; (v) *x*−1, *y*, *z*; (vi) −*x*+1, −*y*+1, −*z*; (vii) −*x*+2, −*y*+1, −*z*+1; (viii) −*x*+1, −*y*+1, −*z*+1.

$(NH_4)_2[Cd(H_2O)_5(NH_3CH_2CH_2COO)]_2V_{10}O_{28}\cdot 2H_2O$ (3)

N1–H1A…O92^{i}	0.88	1.88	2.752(5)	170.5
	1.030	*1.733*		*169.66*
N1–H1B…O91	0.88	2.02	2.725(5)	135.8
	1.030	*1.919*		*132.71*
N1–H1B…O53	0.88	2.71	3.476(6)	147.0
	1.030	*2.580*		*145.18*
N1–H1C…O5^{ii}	0.88	2.25	2.989(4)	141.2
	1.030	*2.138*		*138.62*
N2–H1…O14^{iii}	0.81(2)	1.98(2)	2.765(4)	162(4)
	1.030	*1.774*		*160.15*
N2–H2…O54	0.81(2)	2.42(3)	3.180(6)	158(4)
	1.030	*2.212*		*155.85*
N2–H2…O55	0.81(2)	2.62(3)	3.153(6)	125(3)
	1.030	*2.498*		*120.86*
N2–H3…O12	0.81(2)	2.01(2)	2.802(4)	168(4)
	1.030	*1.789*		*166.76*
N2–H4…O3^{iv}	0.81(2)	2.15(3)	2.845(5)	143(3)
	1.030	*1.980*		*139.72*
O51–H51A…O13	0.755(18)	1.97(3)	2.702(4)	162(7)
	0.938	*1.801*		*160.28*
O51–H51B…O6^{iv}	0.755(18)	2.03(2)	2.777(4)	173(8)
	0.938	*1.845*		*171.94*
O52–H52A…O9^{iv}	0.760(18)	1.94(2)	2.699(4)	172(6)
	0.938	*1.768*		*170.86*
O52–H52B…1W^{v}	0.759(18)	2.03(2)	2.779(5)	170(6)
	0.938	*1.852*		*169.03*
O53–H53A…O1W^{vi}	0.758(18)	2.06(3)	2.789(5)	163(6)
	0.938	*1.886*		*160.91*
O53–H53B…O10^{v}	0.757(18)	2.038(19)	2.795(4)	179(6)
	0.938	*1.857*		*179.19*
O54–H54A…O8^{vii}	0.758(18)	1.96(2)	2.696(4)	164(6)
	0.938	*1.788*		*161.96*
O54–H54B…O7^{vi}	0.759(18)	2.06(3)	2.782(4)	158(6)
	0.938	*1.899*		*155.91*
O55–H55A…O4^{vi}	0.754(18)	2.02(3)	2.732(5)	158(6)
	0.938	*1.851*		*155.44*
O55–H55B…O2	0.754(18)	2.02(2)	2.769(5)	169(6)
	0.938	*1.844*		*168.22*
O1W–H1W…O92	0.760(18)	1.924(19)	2.684(5)	179(6)
	0.938	*1.746*		*178.84*
O1W–H2W…O7	0.757(18)	2.46(4)	3.080(4)	141(6)
	0.938	*2.319*		*137.83*
O1W–H2W…O10	0.757(18)	2.55(3)	3.235(4)	151(6)
	0.938	*2.397*		*148.65*

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

$(NH_4)_2[Zn(H_2O)_5(NH_3CH_2CH_2COO)]_2V_{10}O_{28}\cdot 4H_2O$ (4)

N1–H1A…O3[i]	0.87	2.55	3.2541(16)	139.4
	1.030	*2.425*		*136.90*
N1–H1A…O92	0.87	2.54	3.0264(15)	116.8
	1.030	*2.466*		*113.37*
N1–H1A…O4[ii]	0.87	2.66	3.1933(16)	120.8
	1.030	*2.582*		*117.70*
N1–H1B…O55[i]	0.87	2.25	3.0852(15)	160.4
	1.030	*2.102*		*158.95*
N1–H1C…O14[iii]	0.87	1.99	2.8217(15)	160.6
	1.030	*1.836*		*158.88*
N2–H1…O1[iv]	0.860(10)	2.232(12)	3.0674(16)	163.7(18)
	1.030	*2.070*		*162.42*
N2–H1…O8[iv]	0.860(10)	2.474(18)	2.9808(15)	118.4(15)
	1.030	*2.398*		*114.83*
N2–H2…O13[v]	0.864(10)	1.925(11)	2.7881(16)	176.1(19)
	1.030	*1.760*		*175.78*
N2–H3…O4	0.862(10)	2.058(11)	2.9104(16)	169.9(19)
	1.030	*1.893*		*169.06*
N2–H4…O2W	0.862(10)	1.990(12)	2.8157(17)	160.1(18)
	1.030	*1.833*		*158.31*
O51–H51A…O7[iii]	0.784(9)	1.922(10)	2.6982(14)	170.3(19)
	0.938	*1.771*		*169.45*
O51–H51B…O1[v]	0.786(9)	1.930(9)	2.7020(14)	167.1(18)
	0.938	*1.782*		*166.08*
O52–H52A…O2W	0.792(9)	1.952(10)	2.7404(16)	173.6(17)
	0.938	*1.807*		*173.10*
O52–H52B…O2[v]	0.791(9)	2.055(11)	2.8099(14)	159.7(16)
	0.938	*1.917*		*158.21*
O53–H53A…O1W	0.784(9)	1.985(9)	2.7578(16)	168.8(19)
	0.938	*1.834*		*167.89*
O53–H53B…O10	0.780(9)	1.944(9)	2.7222(14)	176(2)
	0.938	*1.786*		*175.24*
O54–H54A…O12[vi]	0.787(9)	1.971(9)	2.7511(14	170.8(19)
	0.938	*1.823*		*170.02*
O54–H54B…O5	0.781(9)	1.965(9)	2.7392(14)	171.5(17)
	0.938	*1.809*		*170.74*
O55–H55A…O9	0.788(9)	1.923(9)	2.7076(13)	174(2)
	0.938	*1.774*		*173.33*
O55–H55B…O92	0.785(9)	1.895(10)	2.6642(14)	166(2)
	0.938	*1.747*		*164.84*
O1W–H11W…O2[vii]	0.786(12)	2.062(12)	2.8380(14)	169(2)
	0.938	*1.914*		*167.99*
O1W–H12W…O92[vii]	0.784(12)	1.994(13)	2.7633(15)	167(2)
	0.938	*1.845*		*165.57*
O2W–H21W…O91[viii]	0.778(12)	2.033(12)	2.8084(15)	175(2)
	0.938	*1.874*		*174.21*
O2W–H22W…O1W	0.781(12)	2.053(12)	2.8088(16)	163(2)
	0.938	*1.904*		*161.46*

Symmetry codes: (i) *x*+1/2, −*y*+3/2, *z*+1/2; (ii) −*x*+3/2, *y*+1/2, −*z*+1/2; (iii) *x*−1/2, −*y*+3/2, *z*+1/2; (iv) −*x*+3/2, *y*−1/2, −*z*+1/2; (v) *x*−1, *y*, *z*; (vi) −*x*+1, −*y*+1, −*z*; (vii) −*x*+2, −*y*+1, −*z*+1; (viii) −*x*+1, −*y*+1, −*z*+1.

$(NH_4)_2[Mn(H_2O)_5(NH_3CH_2CH_2COO)]_2V_{10}O_{28}\cdot 2H_2O$ (5)

N1–H1A…O92^{i}	0.86	1.88	2.721(3)	167.3
	1.030	*1.710*		*166.02*
N1–H1B…O91	0.86	2.07	2.751(3)	135.9
	1.030	*1.949*		*132.47*
N1–H1B…O53	0.86	2.59	3.351(3)	147.6
	1.030	*2.451*		*145.43*
N1–H1C…O5^{ii}	0.86	2.24	2.949(3)	139.5
	1.030	*2.115*		*136.46*
N2–H1…O14^{iii}	0.807(14)	1.982(15)	2.760(3)	162(2)
	1.030	*1.772*		*159.49*
N2–H2…O54	0.801(14)	2.354(16)	3.084(3)	152(2)
	1.030	*2.155*		*149.02*
N2–H2…O55	0.801(14)	2.521(19)	3.113(3)	131.9(19)
	1.030	*2.374*		*127.76*
N2–H3…O12	0.803(14)	1.949(14)	2.751(3)	177(2)
	1.030	*1.722*		*176.72*
N2–H4…O3^{iv}	0.802(14)	2.080(16)	2.829(3)	155(2)
	1.030	*1.875*		*152.56*
O51–H51A…O13	0.721(12)	1.983(12)	2.703(3)	176(3)
	0.938	*1.767*		*175.02*
O51–H51B…O6^{iv}	0.722(12)	2.083(13)	2.792(3)	168(3)
	0.938	*1.873*		*166.09*
O52–H52A…O9^{iv}	0.733(12)	1.970(13)	2.701(2)	174(3)
	0.938	*1.767*		*173.16*
O52–H52B…O1W^{v}	0.730(12)	2.023(12)	2.753(3)	178(3)
	0.938	*1.815*		*177.57*
O53–H53A…O1W^{vi}	0.718(12)	2.043(13)	2.758(3)	174(4)
	0.938	*1.824*		*173.36*
O53–H53B…O10^{v}	0.720(12)	2.047(14)	2.757(2)	169(3)
	0.938	*1.833*		*168.14*
O54–H54A…O8^{vii}	0.724(12)	1.992(14)	2.702(2)	167(3)
	0.938	*1.785*		*164.92*
O54–H54B…O7^{vi}	0.721(12)	2.081(14)	2.790(2)	168(3)
	0.938	*1.870*		*166.32*
O55–H55A…O4^{vi}	0.723(12)	2.025(14)	2.732(3)	166(3)
	0.938	*1.817*		*164.30*
O55–H55B…O2	0.727(12)	2.052(13)	2.771(3)	170(3)
	0.938	*1.844*		*169.03*
O1W–H1W…O92	0.723(12)	1.948(13)	1.948(13)	175(3)
	0.938	*1.734*		*173.92*
O1W–H2W…O7	0.724(12)	2.390(19)	3.044(3)	151(3)
	0.938	*2.205*		*148.30*
O1W–H2W…O10	0.724(12)	2.61(2)	3.230(2)	145(3)
	0.938	*2.438*		*142.12*

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

FT IR/FT Raman Spectroscopy

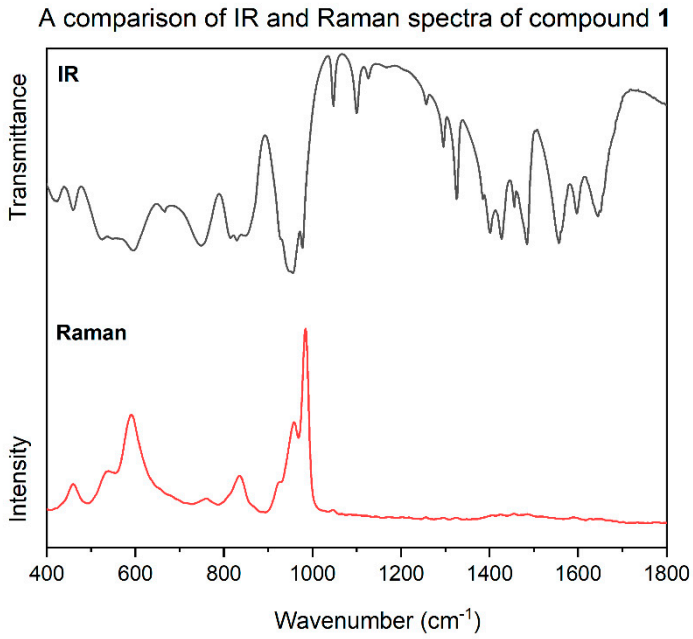

Figure S1a. A comparison of IR and Raman spectra of **1**.

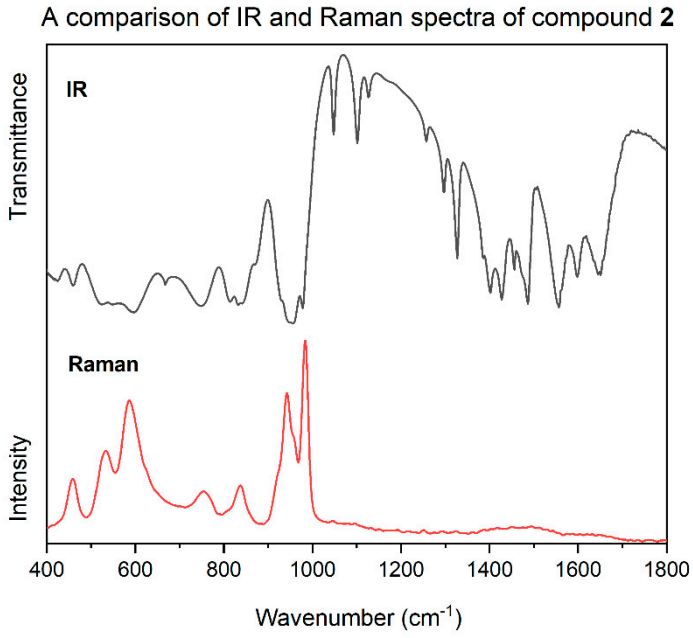

Figure S1b. A comparison of IR and Raman spectra of **2**.

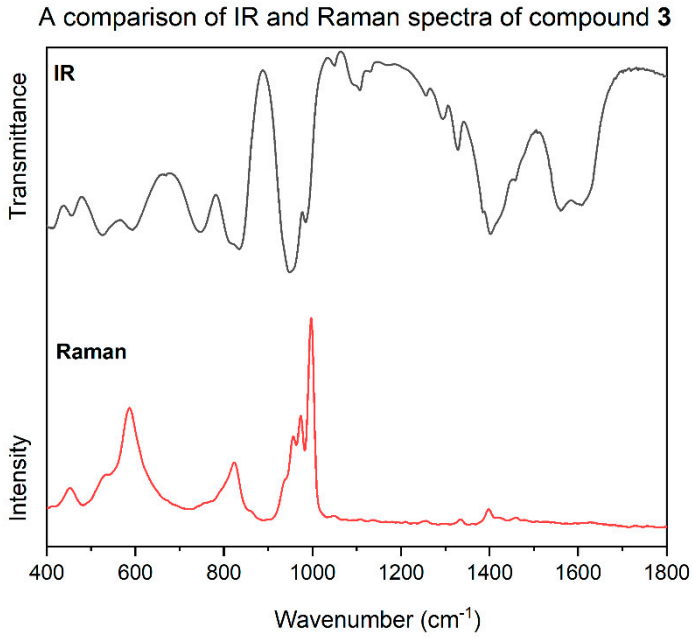

Figure S1c. A comparison of IR and Raman spectra of **3**.

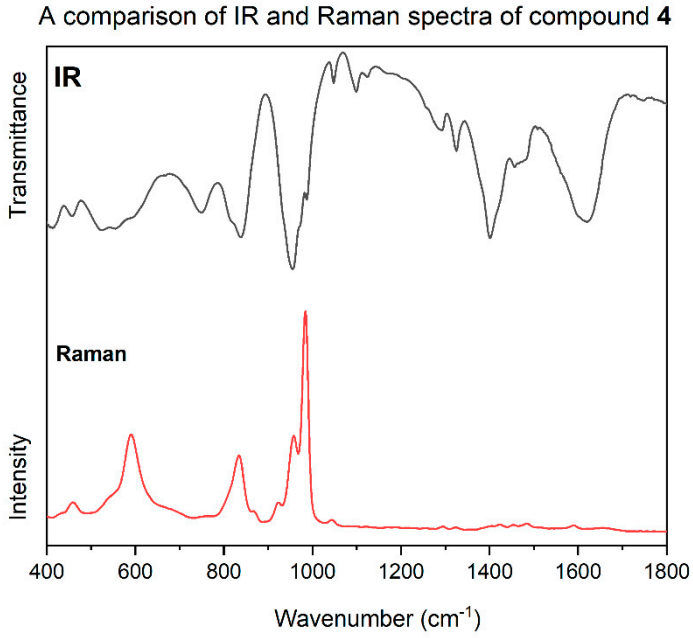

Figure S1d. A comparison of IR and Raman spectra of **4**.

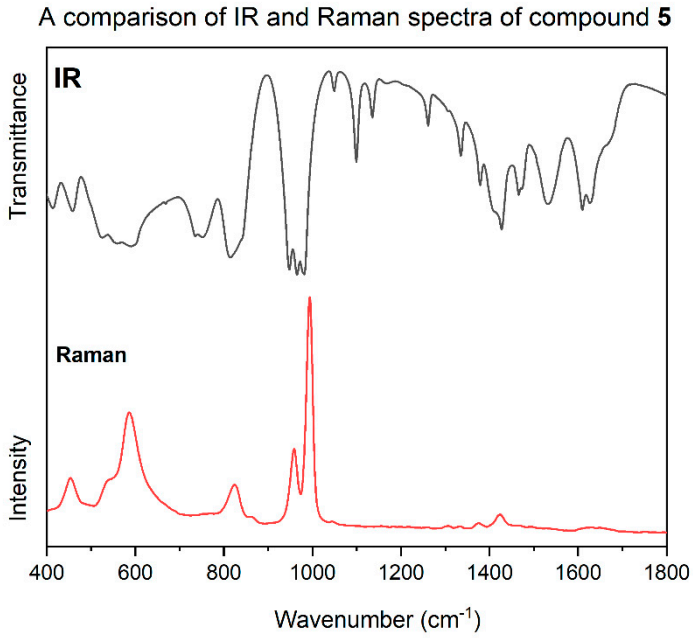

Figure S1e. A comparison of IR and Raman spectra of **5**.

Table S4. Assignments of the IR and Raman absorption bands for compounds **1** – **5** [7, 21, 53].

1		**2**		**3**		**4**		**5**		**Vibrational Assignment** [b]
FT-Raman [a] **[cm⁻¹]**	**FT-IR [cm⁻¹]**	**FT-Raman [cm⁻¹]**	**FT-IR [cm⁻¹]**	**FT-Raman [cm⁻¹]**	**FT-IR [cm⁻¹]**	**FT-Raman [cm⁻¹]**	**FT-IR [cm⁻¹]**	**FT-Raman [cm⁻¹]**	**FT-IR [cm⁻¹]**	
183 s		178 s		177 m		182 s		182 s		$\nu(O–V_6)$
249 m		247 m		248 s		247 m		251 m		$\delta(O–V_3)$
319 s		317 s		319 s		318 m		319 s		$\delta(V–O–V)$
	424 m		424 m		418 m		413 s		414 m	$\delta(V–O_b)$
460 m	460 m	459 m	460 m	452 m	458 m	459 w	459 m	454 m	462 m	$\delta(CCN)$
	526 s		526 s	535 w	527 m		524 s		526 s	$\nu_s(O–V_2)$
539 m	551 s	533 m	551 s			550 sh	559 s	548 sh	557 m	$\nu_s(O–V_2) + \tau(NH_3^+) + \rho(CO_2)$
591 s	594 s	586 s	594 s	587 m	596 m	590 m	592 s	586 s	595 s	$\nu_s(O–V_2) + \tau(NH_3^+) + \rho(CO_2)$
760 w	749 s	754 w	748 s		748 s		749 s		750 br	$\nu_{as}(O–V_2) + \delta(COO^–)$
	814 s		814 s		814 s		818 sh		815 m	$\nu_{as}(O–V_2)$
836 w	830 s	837 w	831 m	823 m	835 s	834 m	838 s	824 m	843 sh	$\nu_{as}(O–V_2) + \nu(C–C)$
	853 s		846 m	851 vw		866 w		861 vw		$\nu_{as}(O–V_2)$
926 m	928 sh	942 br	930 s		934 sh	923 m	933 sh			$\nu(V=O)$
	947 s		947 s	957 m	949 vs	958 m	955 vs	958 m	948 s	$\nu(V=O)$
958 m	956 s	956 sh	957 s	973 m			972 sh		964 s	$\nu(V=O)$
984 s	978 s	984 s	978 s	997 vs	985 m	984 vs	989 m	994 vs	983 s	$\nu(V=O)$
1048 vw	1050 w	1045 vw	1050 w		1051 vw	1044 vw	1050 vw	1044 vw	1050 vw	$\nu_a(CCN)$
	1103 w		1103 w		1100 w		1100 w		1100 m	$\nu_a(CCN)$
	1128 vw		1129 vw		1132 w		1126 vw		1138 w	$\rho_r(NH_3^+)$
1256 vw	1258 vw	1250 vw	1258 vw		1258 w		1260 vw		1262 w	$\rho_r(NH_3^+)$
	1298 w		1298 w		1298 w	1294 vw	1293 w		1306 vw	$\rho_t(CH_2)$
1325 vw	1326 m		1326 m	1334 vw	1328 m	1323 vw	1327 m		1336 m	$\nu_s(COO^–)$
	1385 m		1387 m		1384 m		1382 sh		1380 m	$\delta(C_\beta H_2) + \delta(C_\alpha H_2)$
	1403 s		1402 s	1398 w	1404 s	1405 vw	1403 s	1423 w	1409 m	$\delta(NH_4^+)$
	1427 s		1427 m	1459 vw	1428 sh		1426 m		1428 m	$\delta(C_\beta H_2)$
	1455 m	1494 vw	1455 m		1461 m	1454 vw	1458 m		1468 m	$\delta(C_\alpha H_2)$
	1486 s		1486 s			1484 vw	1485 m		1477 m	$\delta(C_\alpha H_2)$
	1556 m		1556 m		1558 br m		1560 sh		1535 m	$\nu_{as}(COO^–)$
	1597 m		1598 m			1590 vw	1596 sh		1611 m	$\delta_s(NH_3^+)$
	1644 m		1648 m		1610 br m		1618 br m		1629 m	$\delta_d(NH_3^+) + \delta(H_2O)$
2917 w		2915 w		2927 w		2916 w				$\nu(CH_2)$
2967 m		2966 m		2953 w		2967 w				$\nu(CH_2)$
2982 sh		2981 sh		2992 w		2981 w		2987 w		$\nu(CH_2)$
3026 w		3026 w		3033 w		3026 w		3024 vw		$\nu(CH_2)$
					3190 vw, br	3163, 3197 w	3172 vw, br		3178 vw, br	$\nu_s(NH_3^+) + \nu_s(NH_4^+)$
3326 w, br		3332 vw, br				3329 w, br		3328 vw, sh		$\nu_s(NH_3^+) + \nu_s(NH_4^+)$

3481 vw, br	3470 w	3492 vw, br	3484 w	3453 vw, br	3434 w	3473 vw, br	3447 br	3373 w, br	3380 br	ν(O–H) + O–H···O stretch

[a] (s) Strong; (vs) very strong; (m) medium; (w) weak; (vw) very weak; (br) broad; (sh) shoulder;

[b] (ν) stretching: (ν_s) sym. stretching, (ν_{as}) asym. stretching; (δ) bending; (ρ) rocking; (τ) torsion.