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Supporting Information for

The Elusive Vanadate $(V_3O_9)^{3-}$: Isolation, Crystal Structure, and Nonaqueous Solution Behavior

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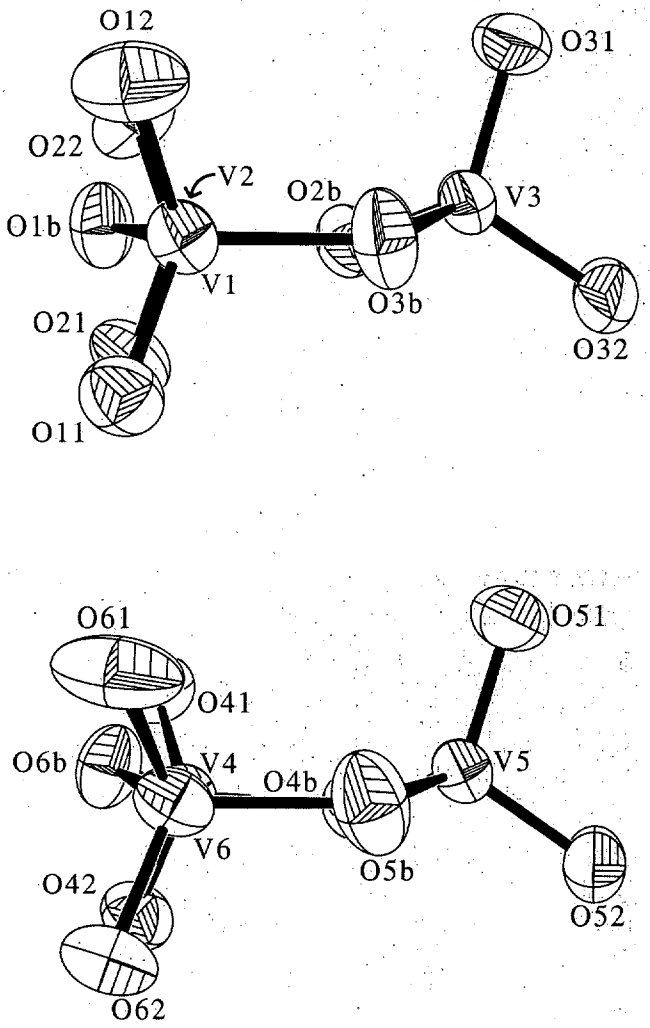

Figure S1. ORTEP representation of the two $(V_3O_9)^{3-}$ anions present in the asymetric unit showing the distorted boat conformation of the anion. The relative orientation between anions is for illustration only and does not reflect the true positions relative to each other in the unit cell.

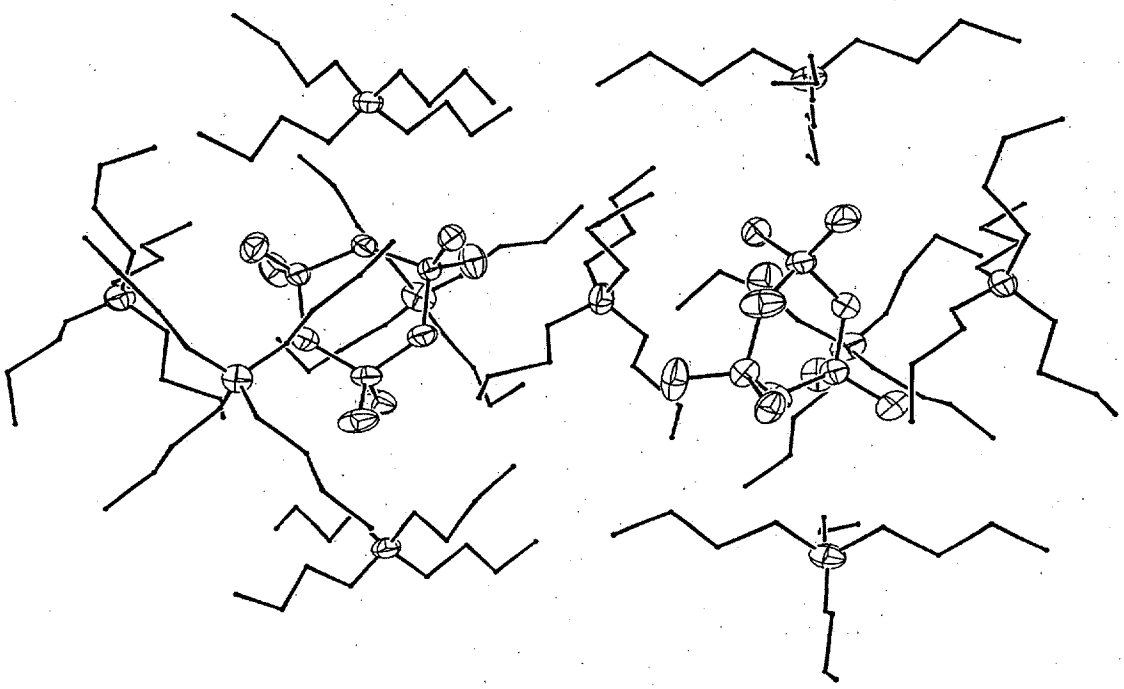

Figure S2. Packing diagram of $[(C_4H_9)_4N]_3(V_3O_9)\cdot 0.5H_2O$ showing $[(C_4H_9)_4N]^+$ cations and $(V_3O_9)^{3-}$ anions with a search distance of 5.2 Å from any point of the anion.

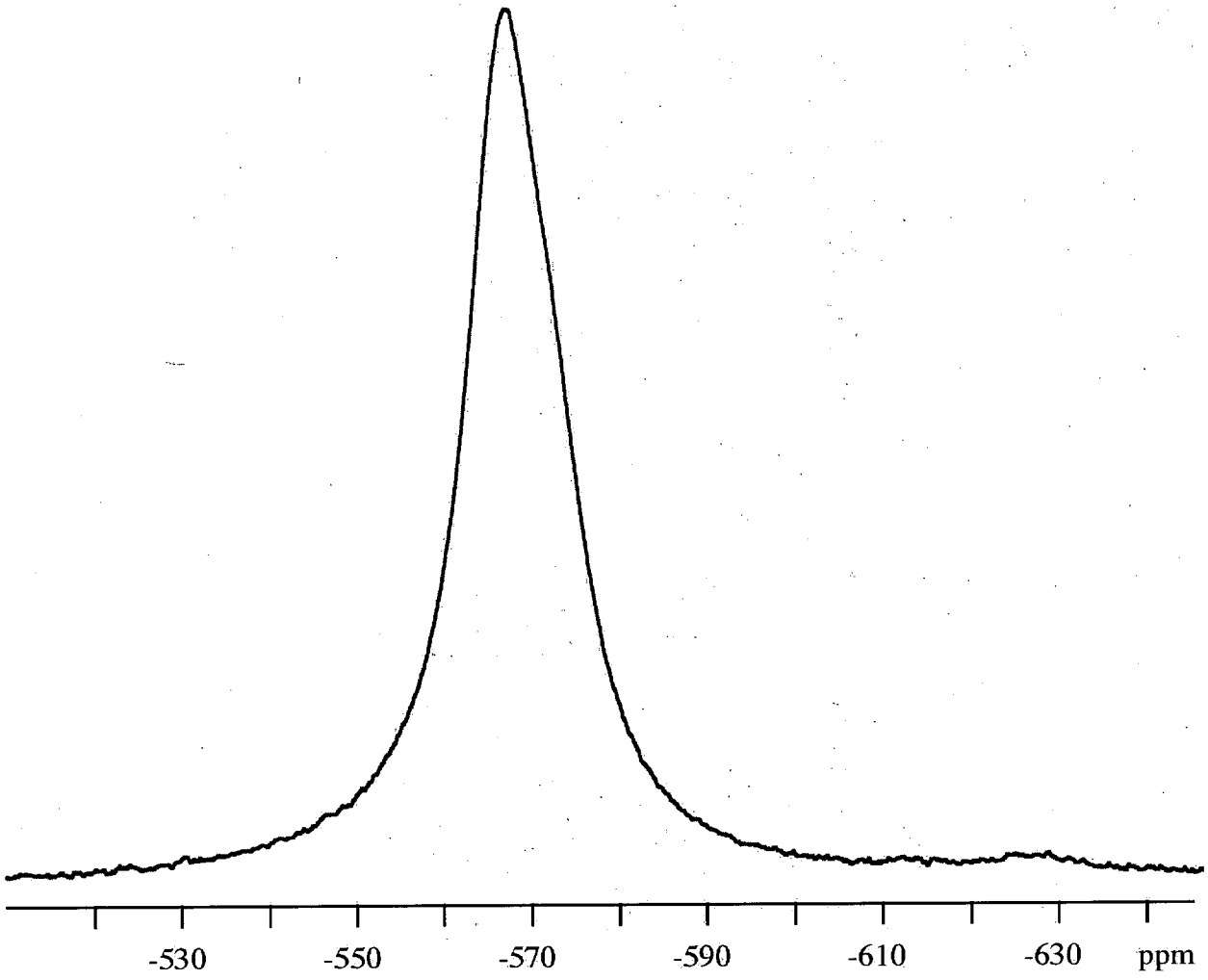

Figure S3. ^{51}V NMR spectrum of 50 mM $[(C_4H_9)_4N]_3(V_3O_9)$ with 150 mM $[(C_4H_9)_4N]Br$ in CD_3CN.

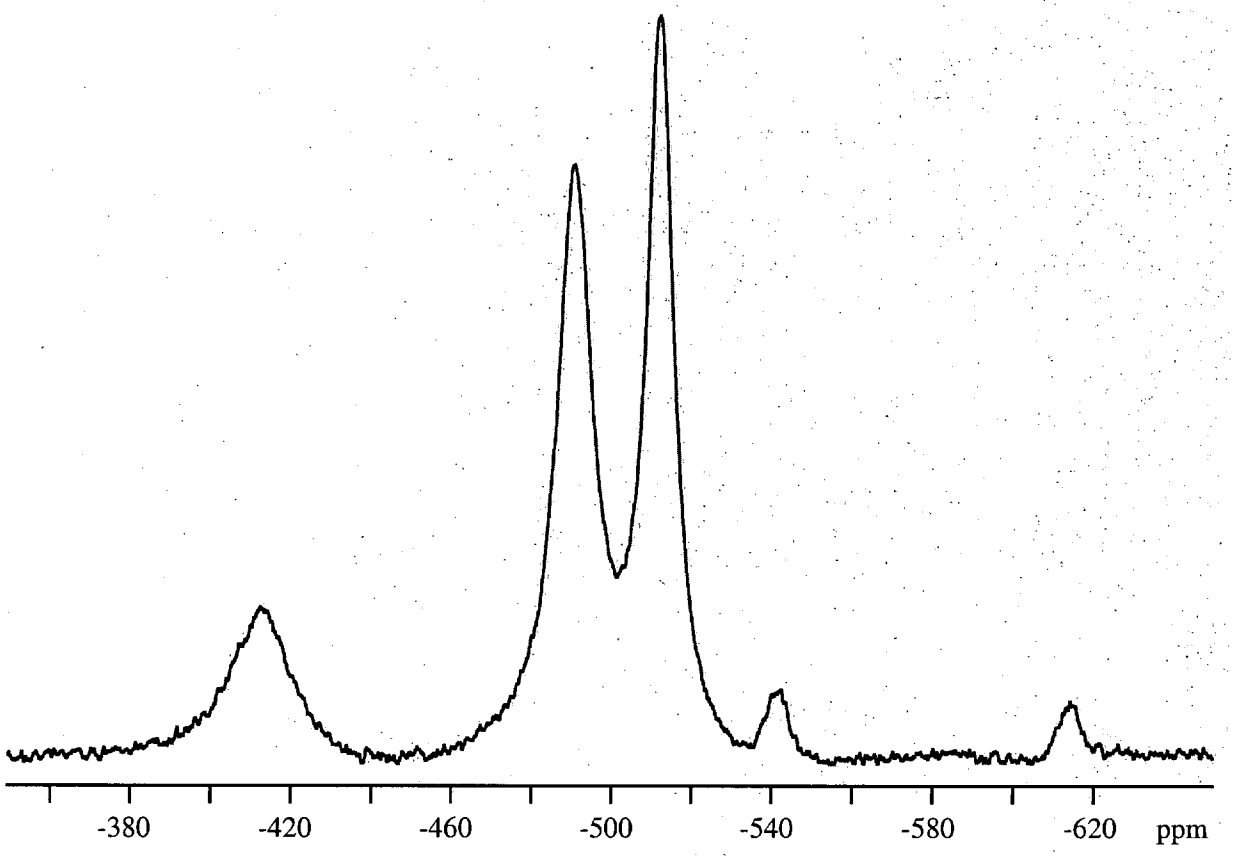

Figure S4. ^{51}V NMR Spectrum of 30 mM $[(C_4H_9)_4N]_3(H_3V_{10}O_{28})$ with 185 mM *N,N*–diisopropylethylamine in CD_3CN.

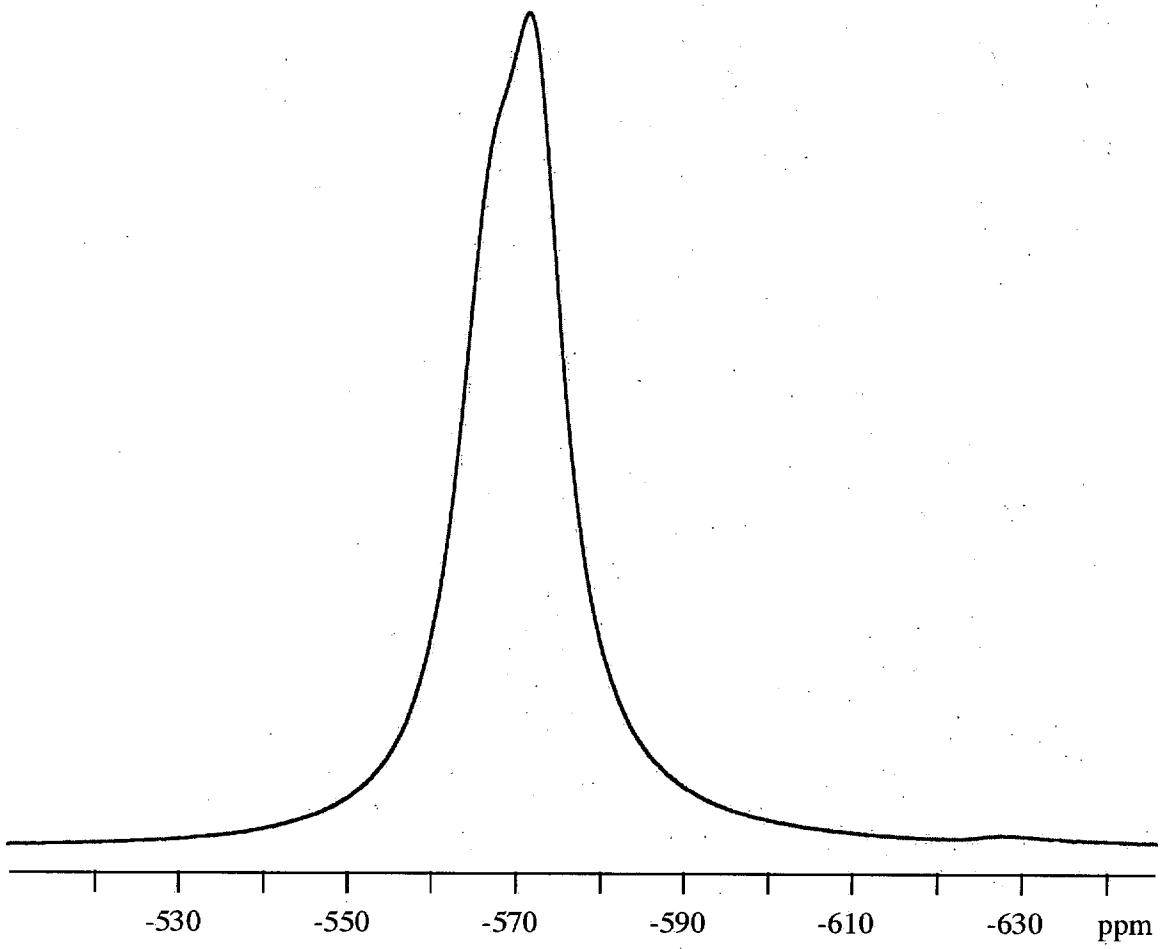

Figure S5. ^{51}V NMR spectrum of 450 mM $[(C_4H_9)_4N]_3(V_3O_9)$ with 380 mM $[(C_2H_5)_4N]Br$ in CD_3CN.

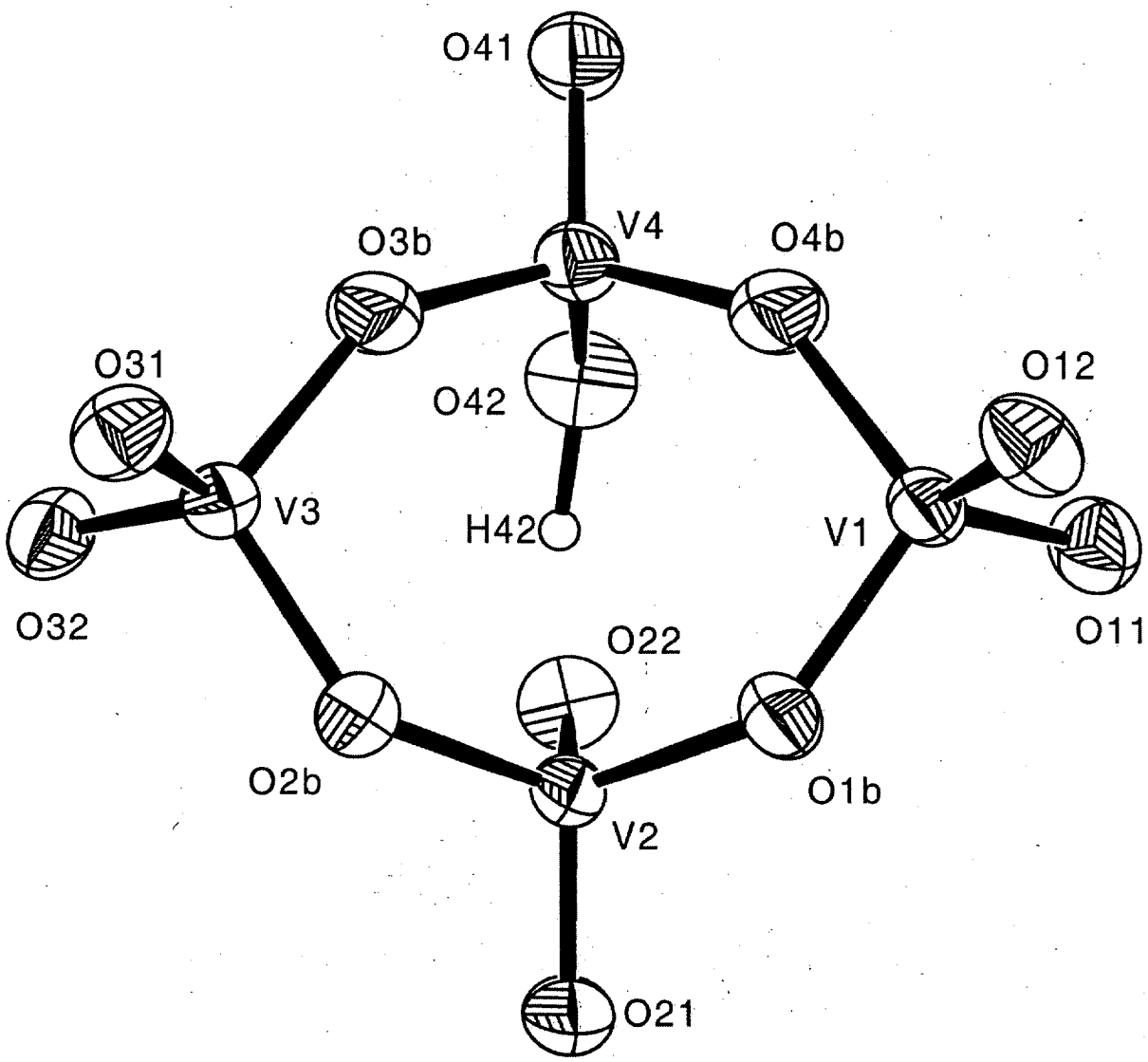

Figure S6. ORTEP representation of the $(HV_4O_{12})^{3-}$ anion with thermal ellipsoids drawn at the 50% probability level.

Table S1. Experimental procedures for X-ray crystal structure determination of $[(C_4H_9)_4N]_3(V_3O_9)\cdot 0.5H_2O$

DATA COLLECTION

A colorless cube of $C_{48}H_{109}N_3O_{9.50}V_3$ having approximate dimensions of 0.50 x 0.47 x 0,47 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo K_α radiation (λ = 0.71073 Å) on a Nonius KappaCCD.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 75615 reflections in the range $4 < \theta < 27°$. The orthorhombic cell parameters and calculated volume are: a = 22.049(1), b = 22.245(1), c = 24.138(0) Å, V = 11839.5 Å^3. For Z = 8 and F.W. = 1033.24 the calculated density is 1.16 g/cm^3. The space group was determined by the program ABSEN(ref1). From the systematic presences of:

h00 h=2n
0k0 k=2n
00l l=2n

and from subsequent least-squares refinement, the space group was determined to be $P2_12_12_1$ (# 19).

The data were collected at a temperature of 173 ± 1 K. Data were collected to a maximum 2θ of 55.0°.

DATA REDUCTION

A total of 75615 reflections were collected, of which 26511 were unique.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 5.0/cm for Mo K_α radiation. An empirical absorption correction using SCALEPACK (ref 2) was applied. Transmission coefficients ranged from 0.584 to 0.790 with an average value of 0.746. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 9.2% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved using the structure solution program SHELXS97 (ref 3). The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ and the weight w is defined as $w = 1/[\sigma^2(F_o^2) + (0.0890P)^2 + 2.3894P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Scattering factors were taken from the "International Tables for Crystallography" (ref 4). 20713 reflections were used in the refinements. However, only reflections with $F_o^2 > 2\sigma(F_o^2)$ were used in calculating R. The final cycle of refinement included 1167 variable parameters and converged (largest parameter shift was 0.10 times its esd) with unweighted and weighted agreement factors of:

$R1 = \Sigma|F_o - F_c|/\Sigma F_o = 0.059$

$R2 = SQRT(\Sigma w(F_o^2 - F_c^2)2/\Sigma w(F_o^2)^2) = 0.142$

The standard deviation of an observation of unit weight was 1.02. The highest peak in the final difference Fourier had a height of 0.49 e/Å^3. The minimum negative peak had a height of -0.44 e/Å^3. The factor for the determination of the absolute structure (ref 5) refined to –0.01.

Table S1. (*Continued*)

Refinement was performed on a AlphaServer 2100 using SHELX-97 (ref 6). Crystallographic drawings were done using program ORTEP (ref 7), and PLUTON (ref 8).

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(4) "International Tables for Crystallography", Vol. C, K1uwer Academic Publishers, Dordrecht, The Netherlands, 1992, Tables 4.2.6.8 and 6.1.1.4.
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(7) Johnson, C. K. ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA (1976).
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Table S2. Crystal data and data collection parameters for $[(C_4H_9)_4N]_3(V_3O_9)\cdot 0.5H_2O$

Formula	$C_{48}H_{109}N_3O_{9.50}V_3$
Formula weight	1033.24
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (No. 19)
Color of crystal	colorless
Dimensions of crystal	0.50 mm x 0.47 mm x 0.47 mm
a	22.0495(5) Å
b	22.2453(5) Å
c	24.1378(3) Å
Z	8
Linear absorption coefficient	0.495 mm^{-1}
Range of transmission factors	0.58 to 0.79
Temperature	173 K
Wavelength of radiation	Mo K_α (0.71073 Å)
2θ range	8.00° to 55.04°
Number of data	75615
Unique data	26511
Data used in refinement	20713
Data with $I > 2.0\sigma(I)$	14107
Cut-off	$F_o^2 > 2.0\sigma(F_o^2)$
Number of parameters refined	1167
$R(F_o)$[a]	0.059
$R_w(F_o^2)$[b]	0.142
Goodness of fit	1.022
Calculated density	1.159 g cm^{-1}

[a] $R = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$ for $F_o^2 > 2.0\sigma(F_o^2)$
[b] $R_w = [\Sigma \, w \, (|F_o^2| - |F_c^2|)^2 / \Sigma \, w \, |F_o^2|^2]^{1/2}$

Table S3. Positional parameters for $[(C_4H_9)_4N]_3(V_3O_9)\cdot 0.5H_2O$

Atom	x	y	z	U (Å^2)
V1	0.19205(4)	0.47941(4)	0.08252(3)	0.0408(2)
V2	0.33978(4)	0.50246(4)	0.08058(3)	0.0419(2)
V3	0.26120(4)	0.51154(4)	-0.03340(3)	0.0468(3)
V4	-0.25841(4)	0.46385(4)	-0.03776(3)	0.0450(2)
V5	-0.23815(4)	0.52116(4)	0.08507(3)	0.0530(3)
V6	-0.18851(4)	0.59156(4)	-0.02375(3)	0.0457(2)
O11	0.14978(15)	0.52459(16)	0.11952(13)	0.0489(10)
O12	0.16277(18)	0.41206(17)	0.08525(18)	0.0673(12)
O1B	0.26853(15)	0.47702(17)	0.10939(12)	0.0509(9)
O21	0.36754(18)	0.5591(2)	0.11520(16)	0.0683(14)
O22	0.38904(18)	0.44725(18)	0.08222(19)	0.0723(14)
O2B	0.32629(16)	0.52589(17)	0.01059(13)	0.0522(10)
O31	0.2710(2)	0.45006(16)	-0.06964(14)	0.0612(12)
O32	0.2527(2)	0.56824(16)	-0.07634(14)	0.0710(14)
O3B	0.19589(16)	0.50419(19)	0.01131(13)	0.0603(11)
O41	-0.22822(19)	0.39831(16)	-0.04794(17)	0.0653(14)
O42	-0.32083(18)	0.47003(19)	-0.07359(15)	0.0680(14)
O4B	-0.27514(15)	0.47365(17)	0.03528(13)	0.0553(10)
O51	-0.18308(17)	0.48365(19)	0.11569(14)	0.0610(12)
O52	-0.28774(19)	0.5418(3)	0.13143(15)	0.0873(18)
O5B	-0.2092(2)	0.58513(18)	0.04849(15)	0.0750(14)
O61	-0.11637(18)	0.60759(18)	-0.0283(2)	0.0783(14)
O62	-0.22563(16)	0.64562(16)	-0.05357(15)	0.0550(10)
O6B	-0.20436(17)	0.52044(16)	-0.05719(13)	0.0553(12)
O900	-0.1670(2)	0.37262(19)	0.0546(2)	0.0830(15)
N4	0.2723(2)	0.28722(19)	0.0363(2)	0.0623(16)
N5	-0.4484(2)	0.5157(2)	0.05952(16)	0.0560(12)
N6	-0.2606(2)	0.5483(2)	-0.22489(16)	0.0583(14)
N7	-0.01128(19)	0.5003(2)	0.04889(19)	0.0537(14)
N8	0.3333(2)	0.71024(18)	-0.01273(17)	0.0477(12)
N9	0.2596(2)	0.4799(2)	-0.23267(14)	0.0527(12)
C1	0.2643	0.4978	0.0432	0.0507
C2	-0.2880	0.5260	0.0079	0.0507
C411	0.2942(3)	0.3254(2)	0.0837(2)	0.0623(17)
C412	0.3412(4)	0.2954(3)	0.1209(3)	0.089(3)
C413	0.3544(4)	0.3333(4)	0.1702(3)	0.098(3)
C414	0.4049(5)	0.3091(5)	0.2051(4)	0.135(4)
C421	0.2342(3)	0.3273(3)	0.0004(2)	0.0670(19)

Table S3. (*Continued*)

Atom	x	y	z	U (Å^2)
C422	0.2049(5)	0.2957(4)	-0.0490(3)	0.105(3)
C423	0.1738(5)	0.3356(5)	-0.0878(4)	0.123(4)
C424	0.1260(6)	0.3600(5)	-0.0611(5)	0.148(5)
C431	0.2352(4)	0.2339(3)	0.0557(3)	0.076(2)
C432	0.1804(4)	0.2465(3)	0.0910(3)	0.083(2)
C433	0.1419(4)	0.1879(4)	0.0918(4)	0.121(4)
C434	0.0944(6)	0.1887(6)	0.1306(5)	0.166(6)
C441	0.3248(4)	0.2621(3)	0.0014(3)	0.092(3)
C442	0.3657(4)	0.3096(4)	-0.0243(3)	0.100(3)
C443	0.4194(5)	0.2786(5)	-0.0538(4)	0.114(3)
C444	0.4662(5)	0.2549(6)	-0.0155(5)	0.148(5)
C511	-0.4008(2)	0.5584(3)	0.0378(2)	0.0573(17)
C512	-0.4212(3)	0.6209(3)	0.0233(3)	0.079(2)
C513	-0.3732(3)	0.6547(3)	-0.0096(3)	0.076(2)
C514	-0.3676(3)	0.6335(3)	-0.0696(3)	0.073(2)
C521	-0.4148(3)	0.4566(3)	0.0715(3)	0.078(2)
C522	-0.4537(4)	0.4061(4)	0.0943(4)	0.104(3)
C523	-0.4054(9)	0.3510(5)	0.1068(8)	0.244(8)
C524	-0.4458(11)	0.2983(10)	0.1282(11)	0.40(2)
C531	-0.5002(3)	0.5056(4)	0.0189(2)	0.084(2)
C532	-0.4800(3)	0.4833(6)	-0.0384(3)	0.144(5)
C533	-0.5350(8)	0.4454(7)	-0.0659(4)	0.270(12)
C534	-0.5596(5)	0.4999(6)	-0.0805(4)	0.144(5)
C541	-0.4783(3)	0.5382(3)	0.1116(2)	0.065(2)
C542	-0.4363(3)	0.5433(5)	0.1611(2)	0.096(3)
C543	-0.4622(5)	0.5765(6)	0.2107(4)	0.127(4)
C544	-0.5185(5)	0.5568(7)	0.2274(5)	0.157(5)
C611	-0.2645(3)	0.5882(3)	-0.2761(2)	0.068(2)
C612	-0.2837(3)	0.6518(3)	-0.2659(2)	0.069(2)
C613	-0.2817(4)	0.6886(4)	-0.3193(3)	0.096(3)
C614	-0.3042(4)	0.7513(4)	-0.3132(3)	0.101(3)
C621	-0.2117(3)	0.5714(3)	-0.1862(2)	0.067(2)
C622	-0.1486(4)	0.5765(4)	-0.2111(3)	0.100(3)
C623	-0.1041(5)	0.5983(5)	-0.1709(4)	0.120(4)
C624	-0.0429(5)	0.6068(5)	-0.1938(5)	0.144(5)
C631	-0.3196(3)	0.5472(3)	-0.1936(2)	0.065(2)
C632	-0.3744(3)	0.5283(4)	-0.2259(3)	0.087(3)

Table S3. (*Continued*)

Atom	x	y	z	U (Å^2)
C633	-0.4316(4)	0.5302(4)	-0.1926(3)	0.096(3)
C634	-0.4863(5)	0.5151(6)	-0.2218(4)	0.145(5)
C641	-0.2455(4)	0.4861(3)	-0.2463(3)	0.080(2)
C642	-0.2365(5)	0.4385(3)	-0.2015(4)	0.111(3)
C643	-0.2204(6)	0.3815(5)	-0.2274(6)	0.169(6)
C644	-0.2552(13)	0.3393(8)	-0.2254(11)	0.449(17)
C711	-0.0525(2)	0.4740(3)	0.0045(2)	0.0527(17)
C712	-0.0248(3)	0.4280(3)	-0.0341(3)	0.073(2)
C713	-0.0726(4)	0.4115(5)	-0.0807(4)	0.125(4)
C714	-0.0517(7)	0.3717(7)	-0.1221(5)	0.186(6)
C721	-0.0517(3)	0.5425(3)	0.0822(2)	0.0627(17)
C722	-0.0205(4)	0.5769(4)	0.1293(4)	0.103(3)
C723	-0.0496(8)	0.6391(5)	0.1379(5)	0.246(12)
C724	-0.1018(7)	0.6213(8)	0.1652(6)	0.226(8)
C731	0.0416(2)	0.5342(3)	0.0234(3)	0.0657(18)
C732	0.0254(3)	0.5873(3)	-0.0115(4)	0.101(3)
C733	0.0825(4)	0.6253(4)	-0.0218(4)	0.106(3)
C734	0.0766(5)	0.6792(5)	-0.0375(11)	0.273(12)
C741	0.0177(3)	0.4517(3)	0.0839(3)	0.0617(17)
C742	-0.0268(3)	0.4120(3)	0.1143(3)	0.071(2)
C743	0.0092(3)	0.3651(4)	0.1484(3)	0.083(2)
C744	-0.0297(4)	0.3240(4)	0.1805(3)	0.102(3)
C811	0.2919(3)	0.6685(2)	0.0206(2)	0.0527(17)
C812	0.2479(3)	0.7016(3)	0.0589(2)	0.0687(19)
C813	0.2107(3)	0.6552(3)	0.0900(2)	0.0610(18)
C814	0.1625(4)	0.6831(4)	0.1268(3)	0.088(3)
C821	0.3716(3)	0.7481(2)	0.0255(2)	0.0517(15)
C822	0.4165(3)	0.7147(3)	0.0615(2)	0.0597(18)
C823	0.4406(3)	0.7564(3)	0.1057(3)	0.076(2)
C824	0.4894(4)	0.7292(4)	0.1406(3)	0.101(3)
C831	0.3717(3)	0.6692(2)	-0.0487(2)	0.0560(17)
C832	0.4158(3)	0.7025(3)	-0.0862(3)	0.068(2)
C833	0.4566(3)	0.6611(3)	-0.1191(3)	0.074(2)
C834	0.4997(4)	0.6964(4)	-0.1549(3)	0.092(3)
C841	0.2959(3)	0.7535(2)	-0.0481(2)	0.0540(17)
C842	0.2542(3)	0.7252(3)	-0.0902(3)	0.070(2)
C843	0.2201(4)	0.7730(4)	-0.1219(3)	0.085(3)
C844	0.1792(4)	0.7469(5)	-0.1655(4)	0.119(4)

Table S3. (*Continued*)

Atom	x	y	z	U (Å^2)
C911	0.3099(3)	0.4472(3)	-0.2004(2)	0.0593(18)
C912	0.3532(3)	0.4111(3)	-0.2365(2)	0.0663(18)
C913	0.4035(3)	0.3847(3)	-0.2022(3)	0.078(2)
C914	0.4454(4)	0.3447(4)	-0.2351(3)	0.098(3)
C921	0.2855(3)	0.5305(3)	-0.2674(2)	0.0557(17)
C922	0.3171(3)	0.5812(3)	-0.2368(2)	0.076(2)
C923	0.3276(4)	0.6338(3)	-0.2747(3)	0.082(2)
C924	0.3586(5)	0.6863(4)	-0.2483(4)	0.115(4)
C931	0.2158(3)	0.5043(3)	-0.1886(2)	0.0630(18)
C932	0.1657(3)	0.5434(3)	-0.2119(3)	0.072(2)
C933	0.1245(3)	0.5630(4)	-0.1653(3)	0.089(3)
C934	0.0944(4)	0.5124(5)	-0.1331(4)	0.118(3)
C941	0.2274(3)	0.4377(3)	-0.2728(2)	0.0587(17)
C942	0.1945(3)	0.3855(3)	-0.2441(2)	0.0657(18)
C943	0.1762(4)	0.3367(3)	-0.2850(3)	0.078(2)
C944	0.1404(4)	0.2872(4)	-0.2565(3)	0.097(3)
H41A	0.2596	0.3366	0.1063	0.0810
H41B	0.3116	0.3620	0.0688	0.0810
H41C	0.3262	0.2565	0.1328	0.1160
H41D	0.3783	0.2890	0.1001	0.1160
H41E	0.3181	0.3362	0.1927	0.1280
H41F	0.3649	0.3735	0.1580	0.1280
H41G	0.4004	0.2664	0.2090	0.1750
H41H	0.4037	0.3276	0.2410	0.1750
H41I	0.4431	0.3178	0.1877	0.1750
H42A	0.2595	0.3598	-0.0133	0.0870
H42B	0.2025	0.3450	0.0230	0.0870
H42C	0.2361	0.2738	-0.0690	0.1360
H42D	0.1760	0.2664	-0.0352	0.1360
H42E	0.2011	0.3670	-0.1002	0.1600
H42F	0.1601	0.3132	-0.1199	0.1600
H42G	0.1117	0.3325	-0.0334	0.1930
H42H	0.0941	0.3678	-0.0872	0.1930
H42I	0.1381	0.3969	-0.0438	0.1930
H43A	0.2219	0.2120	0.0232	0.0990
H43B	0.2619	0.2074	0.0764	0.0990
H43C	0.1571	0.2794	0.0754	0.1080
H43D	0.1926	0.2573	0.1282	0.1080

Table S3. (*Continued*)

Atom	x	y	z	U (Å^2)
H43E	0.1250	0.1814	0.0552	0.1570
H43F	0.1684	0.1543	0.1001	0.1570
H43G	0.1107	0.1846	0.1672	0.2150
H43H	0.0672	0.1559	0.1232	0.2150
H43I	0.0728	0.2260	0.1277	0.2150
H44A	0.3493	0.2361	0.0246	0.1200
H44B	0.3079	0.2375	-0.0281	0.1200
H44C	0.3809	0.3362	0.0044	0.1300
H44D	0.3429	0.3334	-0.0507	0.1300
H44E	0.4038	0.2456	-0.0760	0.1490
H44F	0.4382	0.3072	-0.0788	0.1490
H44G	0.4749	0.2845	0.0124	0.1930
H44H	0.5025	0.2461	-0.0359	0.1930
H44I	0.4516	0.2189	0.0018	0.1930
H51A	-0.3690	0.5616	0.0654	0.0750
H51B	-0.3829	0.5406	0.0049	0.0750
H51C	-0.4301	0.6428	0.0571	0.1020
H51D	-0.4583	0.6186	0.0017	0.1020
H51E	-0.3343	0.6499	0.0086	0.0990
H51F	-0.3831	0.6972	-0.0094	0.0990
H51G	-0.3538	0.5926	-0.0702	0.0950
H51H	-0.3391	0.6585	-0.0888	0.0950
H51I	-0.4065	0.6362	-0.0874	0.0950
H52A	-0.3961	0.4428	0.0374	0.1010
H52B	-0.3825	0.4647	0.0977	0.1010
H52C	-0.4840	0.3937	0.0675	0.1360
H52D	-0.4739	0.4185	0.1281	0.1360
H52E	-0.3840	0.3396	0.0733	0.3200
H52F	-0.3759	0.3628	0.1346	0.3200
H52G	-0.4468	0.2989	0.1680	0.5150
H52H	-0.4292	0.2607	0.1158	0.5150
H52I	-0.4862	0.3028	0.1141	0.5150
H53A	-0.5221	0.5431	0.0144	0.1090
H53B	-0.5280	0.4765	0.0347	0.1090
H53C	-0.4443	0.4580	-0.0347	0.1870
H53D	-0.4697	0.5173	-0.0618	0.1870
H53E	-0.5230	0.4206	-0.0971	0.3500
H53F	-0.5591	0.4228	-0.0395	0.3500

Table S3. (*Continued*)

Atom	x	y	z	U (Å^2)
H53G	-0.5743	0.5200	-0.0480	0.1880
H53H	-0.5925	0.4937	-0.1059	0.1880
H53I	-0.5291	0.5243	-0.0979	0.1880
H54A	-0.5113	0.5113	0.1210	0.0850
H54B	-0.4957	0.5775	0.1042	0.0850
H54C	-0.3995	0.5636	0.1495	0.1250
H54D	-0.4250	0.5031	0.1728	0.1250
H54E	-0.4342	0.5725	0.2415	0.1650
H54F	-0.4649	0.6189	0.2017	0.1650
H54G	-0.5484	0.5688	0.2006	0.2040
H54H	-0.5282	0.5741	0.2627	0.2040
H54I	-0.5183	0.5138	0.2304	0.2040
H61A	-0.2250	0.5888	-0.2939	0.0880
H61B	-0.2928	0.5702	-0.3019	0.0880
H61C	-0.2571	0.6700	-0.2387	0.0900
H61D	-0.3246	0.6522	-0.2511	0.0900
H61E	-0.2402	0.6898	-0.3325	0.1250
H61F	-0.3059	0.6683	-0.3472	0.1250
H61G	-0.3459	0.7507	-0.3018	0.1310
H61H	-0.3008	0.7719	-0.3480	0.1310
H61I	-0.2804	0.7719	-0.2858	0.1310
H62A	-0.2096	0.5449	-0.1544	0.0870
H62B	-0.2238	0.6107	-0.1729	0.0870
H62C	-0.1359	0.5373	-0.2246	0.1310
H62D	-0.1498	0.6037	-0.2425	0.1310
H62E	-0.1019	0.5700	-0.1404	0.1560
H62F	-0.1182	0.6364	-0.1560	0.1560
H62G	-0.0347	0.5759	-0.2205	0.1870
H62H	-0.0136	0.6046	-0.1644	0.1870
H62I	-0.0404	0.6454	-0.2114	0.1870
H63A	-0.3152	0.5201	-0.1623	0.0850
H63B	-0.3269	0.5871	-0.1789	0.0850
H63C	-0.3788	0.5546	-0.2577	0.1130
H63D	-0.3683	0.4878	-0.2395	0.1130
H63E	-0.4272	0.5028	-0.1616	0.1250
H63F	-0.4360	0.5703	-0.1774	0.1250
H63G	-0.4861	0.5340	-0.2575	0.1880
H63H	-0.5208	0.5289	-0.2010	0.1880

Table S3. (*Continued*)

Atom	x	y	z	U (Å^2)
H63I	-0.4887	0.4723	-0.2263	0.1880
H64A	-0.2087	0.4886	-0.2683	0.1050
H64B	-0.2779	0.4731	-0.2707	0.1050
H64C	-0.2044	0.4509	-0.1765	0.1450
H64D	-0.2735	0.4339	-0.1803	0.1450
H64E	-0.2124	0.3895	-0.2662	0.2190
H64F	-0.1824	0.3684	-0.2111	0.2190
H64G	-0.2732	0.3373	-0.1892	0.5860
H64H	-0.2335	0.3027	-0.2326	0.5860
H64I	-0.2864	0.3444	-0.2527	0.5860
H71A	-0.0870	0.4556	0.0228	0.0680
H71B	-0.0679	0.5070	-0.0178	0.0680
H71C	-0.0138	0.3923	-0.0134	0.0950
H71D	0.0116	0.4443	-0.0509	0.0950
H71E	-0.1078	0.3936	-0.0630	0.1620
H71F	-0.0858	0.4484	-0.0984	0.1620
H71G	-0.0105	0.3606	-0.1144	0.2420
H71H	-0.0537	0.3912	-0.1575	0.2420
H71I	-0.0766	0.3364	-0.1225	0.2420
H72A	-0.0847	0.5192	0.0978	0.0810
H72B	-0.0694	0.5715	0.0569	0.0810
H72C	0.0222	0.5818	0.1206	0.1340
H72D	-0.0235	0.5538	0.1632	0.1340
H72E	-0.0245	0.6651	0.1606	0.3210
H72F	-0.0585	0.6589	0.1030	0.3210
H72G	-0.1342	0.6168	0.1389	0.2940
H72H	-0.1127	0.6511	0.1922	0.2940
H72I	-0.0947	0.5836	0.1835	0.2940
H73A	0.0679	0.5478	0.0531	0.0850
H73B	0.0647	0.5063	0.0009	0.0850
H73C	-0.0051	0.6114	0.0071	0.1320
H73D	0.0087	0.5739	-0.0466	0.1320
H73E	0.1058	0.6257	0.0123	0.1370
H73F	0.1068	0.6046	-0.0494	0.1370
H73G	0.0561	0.6801	-0.0726	0.3530
H73H	0.1159	0.6974	-0.0412	0.3530
H73I	0.0533	0.7011	-0.0106	0.3530
H74A	0.0427	0.4266	0.0602	0.0800

Table S3. (*Continued*)

Atom	x	y	z	U (Å^2)
H74B	0.0442	0.4706	0.1109	0.0800
H74C	-0.0531	0.3918	0.0880	0.0920
H74D	-0.0519	0.4362	0.1387	0.0920
H74E	0.0341	0.3416	0.1233	0.1080
H74F	0.0361	0.3861	0.1736	0.1080
H74G	-0.0530	0.3467	0.2068	0.1320
H74H	-0.0048	0.2955	0.1999	0.1320
H74I	-0.0566	0.3030	0.1559	0.1320
H81A	0.2687	0.6439	-0.0049	0.0690
H81B	0.3168	0.6418	0.0427	0.0690
H81C	0.2702	0.7265	0.0848	0.0890
H81D	0.2214	0.7273	0.0373	0.0890
H81E	0.2377	0.6311	0.1127	0.0790
H81F	0.1913	0.6287	0.0635	0.0790
H81G	0.1814	0.7092	0.1534	0.1140
H81H	0.1408	0.6519	0.1459	0.1140
H81I	0.1347	0.7059	0.1045	0.1140
H82A	0.3446	0.7708	0.0494	0.0670
H82B	0.3938	0.7769	0.0031	0.0670
H82C	0.3968	0.6805	0.0787	0.0780
H82D	0.4497	0.6999	0.0390	0.0780
H82E	0.4565	0.7923	0.0880	0.0980
H82F	0.4074	0.7686	0.1295	0.0980
H82G	0.4758	0.6912	0.1547	0.1310
H82H	0.4985	0.7556	0.1709	0.1310
H82I	0.5252	0.7234	0.1186	0.1310
H83A	0.3451	0.6448	-0.0715	0.0730
H83B	0.3946	0.6423	-0.0249	0.0730
H83C	0.3929	0.7274	-0.1117	0.0890
H83D	0.4407	0.7288	-0.0637	0.0890
H83E	0.4795	0.6359	-0.0939	0.0960
H83F	0.4320	0.6352	-0.1423	0.0960
H83G	0.4772	0.7191	-0.1817	0.1200
H83H	0.5267	0.6693	-0.1736	0.1200
H83I	0.5229	0.7234	-0.1321	0.1200
H84A	0.2717	0.7783	-0.0235	0.0700
H84B	0.3237	0.7801	-0.0675	0.0700
H84C	0.2257	0.6989	-0.0716	0.0920

Table S3. (*Continued*)

Atom	x	y	z	U (Å^2)
H84D	0.2778	0.7011	-0.1159	0.0920
H84E	0.1959	0.7964	-0.0961	0.1110
H84F	0.2489	0.8000	-0.1393	0.1110
H84G	0.2020	0.7202	-0.1887	0.1550
H84H	0.1626	0.7788	-0.1876	0.1550
H84I	0.1468	0.7251	-0.1481	0.1550
H91A	0.3331	0.4767	-0.1798	0.0770
H91B	0.2912	0.4203	-0.1738	0.0770
H91C	0.3311	0.3790	-0.2548	0.0860
H91D	0.3702	0.4370	-0.2648	0.0860
H91E	0.3860	0.3615	-0.1722	0.1010
H91F	0.4269	0.4171	-0.1860	0.1010
H91G	0.4234	0.3103	-0.2482	0.1270
H91H	0.4783	0.3317	-0.2119	0.1270
H91I	0.4613	0.3667	-0.2661	0.1270
H92A	0.2527	0.5478	-0.2890	0.0730
H92B	0.3142	0.5133	-0.2934	0.0730
H92C	0.2923	0.5938	-0.2057	0.0990
H92D	0.3556	0.5671	-0.2225	0.0990
H92E	0.3519	0.6204	-0.3059	0.1060
H92F	0.2888	0.6471	-0.2891	0.1060
H92G	0.3427	0.6923	-0.2117	0.1500
H92H	0.3516	0.7217	-0.2701	0.1500
H92I	0.4014	0.6787	-0.2461	0.1500
H93A	0.1976	0.4706	-0.1692	0.0820
H93B	0.2388	0.5275	-0.1618	0.0820
H93C	0.1831	0.5784	-0.2299	0.0930
H93D	0.1426	0.5210	-0.2392	0.0930
H93E	0.0930	0.5886	-0.1805	0.1160
H93F	0.1480	0.5871	-0.1396	0.1160
H93G	0.0763	0.4845	-0.1586	0.1530
H93H	0.0637	0.5287	-0.1093	0.1530
H93I	0.1243	0.4919	-0.1112	0.1530
H94A	0.2570	0.4214	-0.2985	0.0760
H94B	0.1982	0.4606	-0.2942	0.0760
H94C	0.2209	0.3683	-0.2162	0.0850
H94D	0.1586	0.4006	-0.2256	0.0850
H94E	0.2123	0.3197	-0.3018	0.1010

Table S3. (*Continued*)

Atom	x	y	z	U (Å^2)
H94F	0.1518	0.3543	-0.3142	0.1010
H94G	0.1625	0.2732	-0.2247	0.1260
H94H	0.1344	0.2545	-0.2818	0.1260
H94I	0.1018	0.3026	-0.2449	0.1260

Table S4. Thermal parameters for $[(C_4H_9)_4N]_3(V_3O_9)\cdot 0.5H_2O$

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
V1	0.0356(4)	0.0484(5)	0.0385(4)	0.0014(4)	0.0002(4)	-0.0029(4)
V2	0.0354(4)	0.0521(5)	0.0381(4)	0.0041(4)	0.0023(3)	-0.0007(4)
V3	0.0676(6)	0.0432(5)	0.0296(4)	-0.0029(4)	-0.0003(4)	-0.0006(3)
V4	0.0514(5)	0.0386(4)	0.0451(4)	-0.0039(4)	-0.0028(4)	0.0001(4)
V5	0.0484(5)	0.0742(6)	0.0363(4)	0.0079(5)	-0.0025(4)	0.0018(4)
V6	0.0508(5)	0.0331(4)	0.0531(5)	-0.0011(4)	-0.0088(4)	0.0025(4)
O11	0.044(2)	0.054(2)	0.0486(18)	0.0049(18)	0.0009(15)	-0.0049(17)
O12	0.057(2)	0.049(2)	0.096(3)	-0.006(2)	0.011(2)	-0.009(2)
O1B	0.0385(19)	0.074(2)	0.0401(16)	0.0035(19)	0.0040(14)	0.0085(17)
O21	0.055(3)	0.085(3)	0.065(2)	-0.011(2)	-0.005(2)	-0.025(2)
O22	0.046(2)	0.072(3)	0.099(3)	0.023(2)	0.020(2)	0.023(2)
O2B	0.057(2)	0.059(2)	0.0407(17)	-0.0127(19)	0.0038(15)	0.0020(16)
O31	0.094(3)	0.043(2)	0.0466(19)	-0.006(2)	0.014(2)	-0.0076(16)
O32	0.122(4)	0.046(2)	0.0450(18)	-0.014(2)	-0.019(2)	0.0089(16)
O3B	0.049(2)	0.095(3)	0.0368(16)	0.009(2)	-0.0053(15)	0.0043(18)
O41	0.075(3)	0.040(2)	0.081(3)	0.000(2)	0.000(2)	-0.0084(18)
O42	0.065(3)	0.078(3)	0.061(2)	0.000(2)	-0.0159(19)	-0.001(2)
O4B	0.048(2)	0.073(2)	0.0448(17)	-0.0071(19)	0.0009(16)	0.0045(18)
O51	0.048(2)	0.077(3)	0.058(2)	0.003(2)	-0.0060(17)	0.015(2)
O52	0.057(3)	0.163(5)	0.0418(19)	0.026(3)	-0.0027(18)	-0.019(3)
O5B	0.122(4)	0.053(2)	0.050(2)	-0.005(2)	-0.008(2)	-0.0051(18)
O61	0.045(2)	0.058(2)	0.132(4)	-0.005(2)	-0.023(3)	0.024(3)
O62	0.051(2)	0.044(2)	0.070(2)	0.0025(18)	-0.0175(18)	0.0082(17)
O6B	0.071(3)	0.044(2)	0.0508(19)	-0.0102(19)	0.0178(18)	-0.0053(16)
O900	0.079(3)	0.065(3)	0.105(3)	0.008(2)	-0.013(3)	0.020(2)
N4	0.089(4)	0.034(2)	0.064(3)	0.002(2)	0.015(3)	-0.007(2)
N5	0.042(2)	0.081(3)	0.045(2)	0.017(3)	0.0068(19)	-0.005(2)
N6	0.078(3)	0.056(3)	0.041(2)	-0.001(3)	0.007(2)	-0.007(2)
N7	0.039(2)	0.055(3)	0.067(3)	-0.001(2)	-0.006(2)	0.008(2)
N8	0.053(3)	0.039(2)	0.051(2)	0.003(2)	0.000(2)	0.0016(19)
N9	0.049(2)	0.078(3)	0.0310(18)	0.006(3)	-0.0021(18)	-0.004(2)
C411	0.086(4)	0.044(3)	0.057(3)	0.009(3)	0.010(3)	-0.007(3)
C412	0.105(6)	0.076(5)	0.087(5)	0.019(5)	-0.005(4)	-0.009(4)
C413	0.122(7)	0.100(6)	0.073(4)	0.004(5)	-0.012(5)	0.006(4)
C414	0.112(8)	0.176(10)	0.116(7)	0.017(8)	-0.023(6)	0.004(7)
C421	0.090(5)	0.053(3)	0.058(3)	-0.007(3)	-0.002(3)	0.002(3)
C422	0.142(8)	0.101(6)	0.071(5)	-0.022(6)	-0.019(5)	-0.004(4)
C423	0.164(10)	0.113(7)	0.091(6)	-0.051(7)	-0.023(7)	0.019(6)

Table S4. (*Continued*)

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C424	0.159(10)	0.162(10)	0.123(8)	0.077(9)	-0.041(7)	-0.052(7)
C431	0.099(5)	0.046(4)	0.083(4)	0.011(4)	0.009(4)	0.003(3)
C432	0.108(6)	0.059(4)	0.082(4)	0.000(4)	0.011(4)	0.009(3)
C433	0.115(7)	0.096(6)	0.151(8)	0.017(5)	0.061(7)	0.025(6)
C434	0.185(13)	0.153(11)	0.159(10)	0.038(10)	-0.015(10)	-0.018(9)
C441	0.115(7)	0.066(4)	0.095(5)	0.009(4)	0.036(5)	-0.026(4)
C442	0.115(7)	0.101(6)	0.084(5)	-0.003(5)	0.040(5)	0.000(4)
C443	0.115(7)	0.127(7)	0.101(6)	0.014(6)	0.030(6)	-0.027(5)
C444	0.142(10)	0.143(9)	0.158(10)	0.034(8)	-0.001(8)	0.006(8)
C511	0.039(3)	0.077(4)	0.056(3)	0.002(3)	0.001(3)	-0.002(3)
C512	0.082(5)	0.083(5)	0.072(4)	0.027(4)	0.013(4)	-0.004(4)
C513	0.088(5)	0.059(4)	0.080(4)	0.005(4)	0.018(4)	-0.010(3)
C514	0.054(4)	0.093(5)	0.073(4)	0.005(4)	-0.003(3)	0.005(4)
C521	0.055(4)	0.075(4)	0.104(5)	0.004(3)	0.010(4)	0.000(4)
C522	0.095(6)	0.080(5)	0.138(7)	-0.007(5)	0.037(6)	0.007(5)
C523	0.34(2)	0.052(6)	0.34(2)	0.004(9)	0.201(19)	0.057(9)
C524	0.41(4)	0.41(4)	0.37(4)	0.27(4)	-0.02(3)	-0.10(3)
C531	0.037(3)	0.152(7)	0.062(4)	-0.003(4)	-0.006(3)	-0.021(4)
C532	0.073(5)	0.306(15)	0.052(4)	-0.057(7)	0.006(3)	-0.062(7)
C533	0.56(4)	0.174(12)	0.076(7)	0.168(19)	-0.076(12)	-0.053(8)
C534	0.155(9)	0.184(12)	0.094(6)	-0.043(9)	0.040(6)	-0.048(8)
C541	0.057(4)	0.088(5)	0.049(3)	0.014(3)	0.006(3)	0.005(3)
C542	0.082(5)	0.158(8)	0.049(3)	-0.016(5)	0.008(3)	-0.019(4)
C543	0.108(8)	0.183(10)	0.090(6)	0.024(7)	0.010(5)	0.031(6)
C544	0.104(8)	0.245(15)	0.121(8)	0.038(9)	-0.010(7)	-0.007(9)
C611	0.076(4)	0.088(5)	0.040(3)	-0.016(4)	-0.003(3)	0.001(3)
C612	0.071(4)	0.079(5)	0.057(3)	-0.009(3)	-0.004(3)	0.009(3)
C613	0.104(6)	0.121(7)	0.063(4)	0.007(5)	0.003(4)	0.018(4)
C614	0.108(7)	0.095(6)	0.099(5)	0.002(5)	-0.012(5)	0.028(5)
C621	0.088(5)	0.065(4)	0.048(3)	-0.006(3)	-0.007(3)	-0.007(3)
C622	0.102(6)	0.114(7)	0.085(5)	0.009(5)	-0.004(5)	-0.032(5)
C623	0.116(8)	0.125(8)	0.119(7)	-0.003(7)	-0.027(6)	-0.025(6)
C624	0.096(7)	0.158(10)	0.177(10)	-0.001(7)	0.000(7)	-0.051(8)
C631	0.083(5)	0.061(4)	0.051(3)	0.002(3)	0.012(3)	0.002(3)
C632	0.104(6)	0.091(5)	0.065(4)	-0.029(5)	0.014(4)	0.007(4)
C633	0.093(6)	0.117(7)	0.079(5)	-0.002(5)	0.019(4)	0.001(5)
C634	0.123(8)	0.199(12)	0.113(7)	-0.045(9)	0.026(6)	0.008(8)
C641	0.107(6)	0.067(4)	0.067(4)	-0.011(4)	0.021(4)	-0.023(3)

Table S4. (*Continued*)

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C642	0.167(9)	0.045(4)	0.122(6)	-0.002(5)	0.051(6)	-0.009(4)
C643	0.167(12)	0.089(7)	0.250(14)	-0.014(7)	0.088(11)	-0.054(8)
C644	0.57(4)	0.177(15)	0.60(4)	-0.18(2)	0.50(4)	-0.23(2)
C711	0.040(3)	0.064(4)	0.054(3)	0.004(3)	-0.003(2)	0.005(3)
C712	0.064(4)	0.072(4)	0.084(4)	-0.007(3)	0.010(4)	0.002(4)
C713	0.086(6)	0.161(9)	0.127(7)	-0.025(6)	0.026(5)	-0.097(7)
C714	0.193(13)	0.219(14)	0.146(10)	0.037(12)	-0.056(10)	-0.055(10)
C721	0.050(3)	0.076(4)	0.062(3)	0.002(3)	-0.011(3)	-0.004(3)
C722	0.091(6)	0.111(7)	0.106(6)	0.017(5)	-0.041(5)	-0.037(5)
C723	0.53(4)	0.096(8)	0.112(9)	-0.099(16)	-0.108(15)	0.020(7)
C724	0.208(14)	0.31(2)	0.161(12)	-0.177(15)	0.062(11)	-0.106(13)
C731	0.041(3)	0.067(4)	0.089(4)	0.000(3)	-0.008(3)	0.018(3)
C732	0.057(4)	0.083(5)	0.164(8)	0.004(4)	0.015(5)	0.056(5)
C733	0.070(5)	0.083(6)	0.164(8)	-0.011(4)	0.017(5)	0.047(6)
C734	0.089(8)	0.080(7)	0.65(4)	-0.024(6)	-0.016(15)	-0.018(15)
C741	0.047(3)	0.073(4)	0.065(3)	0.000(3)	-0.006(3)	0.018(3)
C742	0.061(4)	0.078(4)	0.074(4)	-0.005(4)	-0.013(3)	0.017(4)
C743	0.074(5)	0.086(5)	0.089(5)	-0.008(4)	-0.020(4)	0.032(4)
C744	0.135(8)	0.091(6)	0.079(5)	-0.032(5)	0.003(5)	0.018(4)
C811	0.072(4)	0.032(3)	0.054(3)	-0.002(3)	0.000(3)	0.004(2)
C812	0.086(5)	0.052(3)	0.068(3)	-0.009(3)	0.019(3)	0.002(3)
C813	0.060(4)	0.065(4)	0.058(3)	-0.009(3)	-0.005(3)	0.013(3)
C814	0.096(6)	0.097(5)	0.070(4)	0.003(5)	0.018(4)	0.017(4)
C821	0.060(3)	0.040(3)	0.055(3)	0.001(3)	-0.003(3)	-0.005(2)
C822	0.059(4)	0.045(3)	0.075(4)	0.013(3)	-0.006(3)	-0.008(3)
C823	0.076(5)	0.079(5)	0.072(4)	0.019(4)	-0.014(3)	-0.021(3)
C824	0.097(6)	0.112(7)	0.093(5)	0.027(5)	-0.029(5)	-0.025(5)
C831	0.063(4)	0.046(3)	0.059(3)	0.011(3)	0.005(3)	-0.008(3)
C832	0.069(4)	0.071(4)	0.065(4)	0.013(3)	0.000(3)	-0.012(3)
C833	0.074(5)	0.083(5)	0.064(4)	0.029(4)	0.004(3)	0.003(3)
C834	0.090(6)	0.102(6)	0.085(5)	0.037(5)	0.019(4)	0.016(4)
C841	0.061(4)	0.046(3)	0.055(3)	0.006(3)	0.001(3)	0.003(2)
C842	0.074(5)	0.069(4)	0.068(4)	0.001(3)	-0.023(3)	0.001(3)
C843	0.090(6)	0.101(6)	0.065(4)	0.007(4)	-0.012(4)	0.016(4)
C844	0.113(7)	0.144(8)	0.100(6)	-0.017(6)	-0.039(6)	0.014(6)
C911	0.065(4)	0.071(4)	0.042(3)	0.004(3)	-0.004(3)	0.001(3)
C912	0.062(4)	0.084(4)	0.053(3)	0.002(4)	-0.001(3)	-0.006(3)
C913	0.060(4)	0.089(5)	0.084(4)	-0.001(4)	-0.011(3)	-0.008(4)

Table S4. (*Continued*)

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C914	0.075(5)	0.103(6)	0.115(6)	0.011(5)	0.015(5)	-0.005(5)
C921	0.061(4)	0.069(4)	0.037(2)	-0.008(3)	0.002(2)	0.001(3)
C922	0.087(5)	0.086(5)	0.055(3)	-0.018(4)	-0.003(3)	0.004(3)
C923	0.090(5)	0.088(5)	0.067(4)	-0.021(4)	0.007(4)	0.010(4)
C924	0.135(8)	0.116(7)	0.095(6)	-0.039(6)	-0.022(5)	0.020(5)
C931	0.064(4)	0.080(4)	0.045(3)	0.001(3)	0.006(3)	-0.003(3)
C932	0.067(4)	0.085(5)	0.063(4)	0.008(4)	0.001(3)	0.017(3)
C933	0.074(5)	0.108(6)	0.085(5)	0.011(4)	0.022(4)	0.016(4)
C934	0.094(6)	0.143(8)	0.116(6)	0.003(6)	0.030(5)	0.009(6)
C941	0.066(4)	0.073(4)	0.037(2)	-0.009(3)	-0.004(3)	-0.002(3)
C942	0.069(4)	0.077(4)	0.051(3)	-0.007(4)	-0.011(3)	0.001(3)
C943	0.093(5)	0.077(5)	0.063(4)	-0.002(4)	-0.018(4)	-0.001(3)
C944	0.121(7)	0.076(5)	0.093(5)	-0.027(5)	-0.021(5)	0.009(4)

Table S5. Crystal data and data collection parameters for $[(C_4H_9)_4N]_3(HV_4O_{12})\cdot CH_2Cl_2$

Formula	$C_{49}H_{111}Cl_2N_3O_{12}V_4$
Formula weight	1209.12
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Color of crystal	pale purple
Dimensions of crystal	0.50 mm x 0.45 mm x 0.35 mm
a	12.2145(3) Å
b	24.0931(6) Å
c	23.0509(4) Å
β	93.9631(14)°
Z	4
Linear absorption coefficient	0.646 mm^{-1}
Range of transmission factors	0.54 to 0.80
Temperature	173 K
Wavelength of radiation	Mo K_α (0.71073 Å)
2θ range	8.00° to 55.01°
Number of data	49808
Unique data	26639
Data used in refinement	11808
Data with $I > 2.0\sigma(I)$	8965
Cut-off	$F_o^2 > 2.0\sigma(F_o^2)$
Number of parameters refined	647
$R(F_o)$[a]	0.064
$R_w(F_o^2)$[b]	0.180
Goodness of fit	1.024
Calculated density	1.187 g cm^{-1}

[a] $R = \Sigma \| |F_o| - |F_c| \| / \Sigma |F_o|$ for $F_o^2 > 2.0\sigma(F_o^2)$

[b] $R_w = [\Sigma w (|F_o^2| - |F_c^2|)^2 / \Sigma w |F_o^2|^2]^{1/2}$

Table S6. Positional parameters for $[(C_4H_9)_4N]_3(HV_4O_{12})\cdot CH_2Cl_2$

Atom	x	y	z	U (Å^2)
V(1)	0.26998(5)	-0.32971(3)	-0.23224(3)	0.03297(17)
V(2)	0.00180(5)	-0.32871(2)	-0.22032(3)	0.03188(15)
V(3)	-0.02914(5)	-0.19463(2)	-0.24015(3)	0.03204(15)
V(4)	0.15943(5)	-0.23870(3)	-0.33316(3)	0.03764(19)
Cl(91)	0.2108(3)	-0.06148(12)	0.05941(12)	0.1629(12)
Cl(92)	0.3859(3)	-0.13976(14)	0.07968(14)	0.1723(14)
O(11)	0.3070(2)	-0.38750(12)	-0.26228(13)	0.0500(8)
O(12)	0.3659(2)	-0.31121(12)	-0.18352(11)	0.0458(8)
O(1B)	0.1437(2)	-0.33959(11)	-0.19738(11)	0.0402(7)
O(21)	-0.0740(2)	-0.37301(11)	-0.18752(13)	0.0470(8)
O(22)	-0.0178(3)	-0.33752(12)	-0.29135(12)	0.0512(9)
O(2B)	-0.0345(2)	-0.25918(10)	-0.20068(11)	0.0398(7)
O(31)	0.0022(2)	-0.14553(11)	-0.19382(11)	0.0421(8)
O(32)	-0.1474(2)	-0.18091(11)	-0.27420(13)	0.0464(8)
O(3B)	0.0772(2)	-0.19721(11)	-0.29265(12)	0.0474(8)
O(41)	0.2217(2)	-0.20141(12)	-0.37808(12)	0.0498(8)
O(42)	0.0782(3)	-0.28619(14)	-0.37623(12)	0.0591(9)
O(4B)	0.2541(2)	-0.27517(13)	-0.28832(13)	0.0518(9)
N(1)	0.1686(3)	-0.24612(15)	-0.05121(13)	0.0471(9)
N(2)	0.0950(3)	0.01359(13)	0.27395(14)	0.0462(9)
N(3)	0.6314(3)	-0.20091(14)	0.23320(15)	0.0441(10)
C(111)	0.2020(4)	-0.22544(18)	-0.11002(16)	0.0480(13)
C(112)	0.2607(6)	-0.1721(2)	-0.1107(2)	0.084(2)
C(113)	0.2959(6)	-0.1594(2)	-0.1711(2)	0.077(2)
C(114)	0.3290(11)	-0.1040(4)	-0.1798(4)	0.159(5)
C(121)	0.2690(4)	-0.2611(2)	-0.01187(17)	0.0540(14)
C(122)	0.3413(5)	-0.3061(2)	-0.0325(2)	0.0649(15)
C(123)	0.4432(5)	-0.3127(3)	0.0094(3)	0.091(2)
C(124)	0.5218(6)	-0.3546(3)	-0.0087(4)	0.108(3)
C(131)	0.1063(4)	-0.2012(2)	-0.02023(18)	0.0569(14)
C(132)	0.0011(5)	-0.1828(2)	-0.0513(2)	0.0692(17)
C(133)	-0.0362(6)	-0.1273(3)	-0.0251(3)	0.098(3)
C(134)	-0.1309(9)	-0.1017(4)	-0.0549(4)	0.146(4)
C(141)	0.0965(4)	-0.2962(2)	-0.06391(17)	0.0543(14)
C(142)	0.0537(5)	-0.3253(2)	-0.0115(2)	0.0678(19)
C(143)	-0.0160(7)	-0.3742(4)	-0.0311(3)	0.118(3)

Table S6. (*Continued*)

Atom	x	y	z	U (Å^2)
C(144)	-0.0755(8)	-0.3998(4)	0.0168(4)	0.136(4)
C(211)	0.0145(4)	0.05170(16)	0.30221(19)	0.0486(12)
C(212)	-0.0609(4)	0.02403(18)	0.34260(19)	0.0544(12)
C(213)	-0.1462(4)	0.0667(2)	0.3598(2)	0.0651(15)
C(214)	-0.2139(5)	0.0463(3)	0.4077(2)	0.082(2)
C(221)	0.1579(4)	-0.02267(16)	0.31907(18)	0.0489(12)
C(222)	0.2265(4)	0.00789(18)	0.36528(19)	0.0540(14)
C(223)	0.2729(4)	-0.0316(2)	0.4120(2)	0.0664(15)
C(224)	0.3489(5)	-0.0020(3)	0.4580(2)	0.0808(19)
C(231)	0.1729(4)	0.05107(16)	0.24286(19)	0.0517(12)
C(232)	0.2558(5)	0.0212(2)	0.2090(3)	0.0718(17)
C(233)	0.3322(5)	0.0616(3)	0.1814(3)	0.0838(19)
C(234)	0.4062(9)	0.0362(5)	0.1398(5)	0.168(5)
C(241)	0.0332(4)	-0.02572(17)	0.23128(18)	0.0547(12)
C(242)	-0.0290(7)	0.0013(2)	0.1806(3)	0.107(3)
C(243)	-0.0906(6)	-0.0393(2)	0.1422(2)	0.0822(19)
C(244)	-0.1563(11)	-0.0168(3)	0.0921(4)	0.192(6)
C(311)	0.5789(3)	-0.14472(17)	0.24391(19)	0.0448(10)
C(312)	0.6582(4)	-0.0981(2)	0.2609(3)	0.0640(17)
C(313)	0.5952(5)	-0.0472(2)	0.2788(3)	0.0745(17)
C(314)	0.5378(7)	-0.0536(3)	0.3332(4)	0.121(3)
C(321)	0.6912(3)	-0.2224(2)	0.2882(2)	0.0515(14)
C(322)	0.6209(4)	-0.2373(3)	0.3374(2)	0.0776(19)
C(323)	0.6918(6)	-0.2538(4)	0.3901(3)	0.116(3)
C(324)	0.6267(18)	-0.2869(7)	0.4280(7)	0.274(11)
C(331)	0.5374(3)	-0.23948(17)	0.21258(19)	0.0458(10)
C(332)	0.5716(4)	-0.29804(19)	0.1957(2)	0.0570(14)
C(333)	0.4728(4)	-0.3333(2)	0.1832(2)	0.0602(15)
C(334)	0.5001(5)	-0.3916(2)	0.1636(3)	0.0750(19)
C(341)	0.7171(4)	-0.1977(2)	0.1891(2)	0.0550(14)
C(342)	0.6778(5)	-0.1773(3)	0.1305(2)	0.0697(17)
C(343)	0.7716(5)	-0.1825(3)	0.0894(2)	0.0760(17)
C(344)	0.8028(6)	-0.2418(3)	0.0747(3)	0.106(3)
C(901)	0.2621(7)	-0.1141(3)	0.1025(3)	0.100(3)
H(42)	0.004(4)	-0.319(2)	-0.364(2)	0.066(14)
H(11A)	0.2480	-0.2535	-0.1261	0.0620
H(11B)	0.1361	-0.2223	-0.1359	0.0620

Table S6. (*Continued*)

Atom	x	y	z	U (Å^2)
H(11C)	0.3249	-0.1735	-0.0835	0.1100
H(11D)	0.2133	-0.1427	-0.0984	0.1100
H(11E)	0.3562	-0.1838	-0.1790	0.1000
H(11F)	0.2353	-0.1679	-0.1991	0.1000
H(11G)	0.2753	-0.0791	-0.1660	0.2070
H(11H)	0.3359	-0.0977	-0.2205	0.2070
H(11I)	0.3985	-0.0975	-0.1588	0.2070
H(12A)	0.3131	-0.2278	-0.0057	0.0700
H(12B)	0.2445	-0.2720	0.0256	0.0700
H(12C)	0.3633	-0.2971	-0.0710	0.0850
H(12D)	0.3010	-0.3408	-0.0349	0.0850
H(12E)	0.4804	-0.2772	0.0132	0.1180
H(12F)	0.4201	-0.3228	0.0474	0.1180
H(12G)	0.4855	-0.3898	-0.0135	0.1400
H(12H)	0.5815	-0.3578	0.0204	0.1400
H(12I)	0.5497	-0.3436	-0.0449	0.1400
H(13A)	0.0904	-0.2150	0.0178	0.0740
H(13B)	0.1538	-0.1691	-0.0143	0.0740
H(13C)	-0.0549	-0.2108	-0.0475	0.0900
H(13D)	0.0114	-0.1779	-0.0923	0.0900
H(13E)	-0.0523	-0.1338	0.0150	0.1280
H(13F)	0.0245	-0.1013	-0.0247	0.1280
H(13G)	-0.1238	-0.1031	-0.0961	0.1890
H(13H)	-0.1359	-0.0637	-0.0428	0.1890
H(13I)	-0.1959	-0.1213	-0.0458	0.1890
H(14A)	0.1377	-0.3230	-0.0851	0.0700
H(14B)	0.0341	-0.2848	-0.0894	0.0700
H(14C)	0.1148	-0.3378	0.0143	0.0880
H(14D)	0.0104	-0.2995	0.0097	0.0880
H(14E)	-0.0692	-0.3624	-0.0618	0.1530
H(14F)	0.0304	-0.4021	-0.0472	0.1530
H(14G)	-0.0265	-0.4236	0.0396	0.1770
H(14H)	-0.1365	-0.4211	0.0004	0.1770
H(14I)	-0.1018	-0.3710	0.0411	0.1770
H(21A)	0.0561	0.0801	0.3239	0.0630
H(21B)	-0.0302	0.0702	0.2716	0.0630
H(21C)	-0.0190	0.0106	0.3770	0.0710

Table S6. (*Continued*)

Atom	x	y	z	U (Å^2)
H(21D)	-0.0974	-0.0073	0.3233	0.0710
H(21E)	-0.1087	0.1006	0.3724	0.0850
H(21F)	-0.1946	0.0755	0.3259	0.0850
H(21G)	-0.2494	0.0122	0.3960	0.1070
H(21H)	-0.2685	0.0736	0.4152	0.1070
H(21I)	-0.1672	0.0403	0.4423	0.1070
H(22A)	0.1056	-0.0456	0.3379	0.0630
H(22B)	0.2055	-0.0473	0.2990	0.0630
H(22C)	0.1820	0.0358	0.3828	0.0700
H(22D)	0.2863	0.0267	0.3478	0.0700
H(22E)	0.3137	-0.0608	0.3940	0.0860
H(22F)	0.2129	-0.0488	0.4308	0.0860
H(22G)	0.4082	0.0152	0.4396	0.1050
H(22H)	0.3777	-0.0286	0.4861	0.1050
H(22I)	0.3081	0.0258	0.4771	0.1050
H(23A)	0.1295	0.0751	0.2165	0.0670
H(23B)	0.2118	0.0746	0.2716	0.0670
H(23C)	0.2179	-0.0011	0.1788	0.0930
H(23D)	0.2986	-0.0036	0.2347	0.0930
H(23E)	0.2881	0.0900	0.1610	0.1090
H(23F)	0.3770	0.0799	0.2121	0.1090
H(23G)	0.4488	0.0073	0.1591	0.2180
H(23H)	0.4545	0.0641	0.1263	0.2180
H(23I)	0.3630	0.0209	0.1073	0.2180
H(24A)	0.0856	-0.0515	0.2165	0.0710
H(24B)	-0.0180	-0.0472	0.2525	0.0710
H(24C)	-0.0802	0.0279	0.1949	0.1380
H(24D)	0.0220	0.0214	0.1580	0.1380
H(24E)	-0.0383	-0.0654	0.1280	0.1070
H(24F)	-0.1391	-0.0601	0.1658	0.1070
H(24G)	-0.2008	0.0132	0.1046	0.2500
H(24H)	-0.2026	-0.0454	0.0749	0.2500
H(24I)	-0.1084	-0.0033	0.0639	0.2500
H(31A)	0.5357	-0.1338	0.2089	0.0580
H(31B)	0.5288	-0.1490	0.2745	0.0580
H(31C)	0.7009	-0.0890	0.2283	0.0830
H(31D)	0.7084	-0.1100	0.2929	0.0830

Table S6. (*Continued*)

Atom	x	y	z	U (Å^2)
H(31E)	0.6462	-0.0163	0.2837	0.0970
H(31F)	0.5415	-0.0376	0.2475	0.0970
H(31G)	0.4729	-0.0756	0.3255	0.1580
H(31H)	0.5177	-0.0177	0.3471	0.1580
H(31I)	0.5856	-0.0716	0.3621	0.1580
H(32A)	0.7438	-0.1945	0.3022	0.0670
H(32B)	0.7323	-0.2552	0.2784	0.0670
H(32C)	0.5760	-0.2057	0.3466	0.1010
H(32D)	0.5723	-0.2678	0.3256	0.1010
H(32E)	0.7540	-0.2753	0.3787	0.1500
H(32F)	0.7194	-0.2210	0.4106	0.1500
H(32G)	0.5896	-0.2628	0.4534	0.3570
H(32H)	0.6740	-0.3116	0.4508	0.3570
H(32I)	0.5735	-0.3081	0.4048	0.3570
H(33A)	0.4975	-0.2226	0.1792	0.0600
H(33B)	0.4872	-0.2424	0.2433	0.0600
H(33C)	0.6137	-0.2963	0.1616	0.0740
H(33D)	0.6177	-0.3143	0.2272	0.0740
H(33E)	0.4254	-0.3157	0.1531	0.0780
H(33F)	0.4326	-0.3357	0.2180	0.0780
H(33G)	0.5357	-0.3897	0.1278	0.0970
H(33H)	0.4338	-0.4128	0.1578	0.0970
H(33I)	0.5482	-0.4091	0.1928	0.0970
H(34A)	0.7756	-0.1734	0.2043	0.0720
H(34B)	0.7483	-0.2343	0.1849	0.0720
H(34C)	0.6550	-0.1389	0.1328	0.0910
H(34D)	0.6153	-0.1991	0.1156	0.0910
H(34E)	0.7501	-0.1631	0.0534	0.0990
H(34F)	0.8359	-0.1639	0.1071	0.0990
H(34G)	0.8268	-0.2610	0.1098	0.1380
H(34H)	0.8610	-0.2413	0.0488	0.1380
H(34I)	0.7402	-0.2605	0.0564	0.1380
H(90A)	0.2088	-0.1439	0.1021	0.1300
H(90B)	0.2737	-0.1008	0.1422	0.1300

Table S7. Thermal parameters for $[(C_4H_9)_4N]_3(HV_4O_{12})\cdot CH_2Cl_2$

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
V(1)	0.0270(3)	0.0378(4)	0.0342(3)	0.0009(2)	0.0027(2)	0.0019(2)
V(2)	0.0268(3)	0.0305(3)	0.0385(3)	-0.0015(2)	0.0034(2)	0.0011(2)
V(3)	0.0319(3)	0.0299(3)	0.0346(3)	-0.0006(2)	0.0044(2)	0.0001(2)
V(4)	0.0393(4)	0.0432(4)	0.0309(3)	0.0017(3)	0.0059(3)	0.0022(3)
Cl(91)	0.187(3)	0.147(2)	0.146(2)	0.011(2)	-0.052(2)	0.0195(17)
Cl(92)	0.149(2)	0.186(3)	0.177(3)	0.023(2)	-0.023(2)	-0.061(2)
O(11)	0.0476(17)	0.0457(16)	0.0576(17)	0.0042(13)	0.0105(13)	-0.0068(13)
O(12)	0.0324(15)	0.0642(18)	0.0405(14)	-0.0026(13)	0.0006(11)	-0.0035(13)
O(1B)	0.0295(13)	0.0476(15)	0.0440(14)	0.0027(11)	0.0051(11)	0.0051(12)
O(21)	0.0403(16)	0.0383(15)	0.0636(18)	-0.0056(12)	0.0125(13)	0.0051(13)
O(22)	0.0558(18)	0.0527(17)	0.0444(16)	-0.0046(14)	-0.0009(13)	-0.0042(13)
O(2B)	0.0403(15)	0.0334(13)	0.0465(15)	0.0016(11)	0.0077(12)	0.0017(11)
O(31)	0.0515(17)	0.0355(14)	0.0394(14)	-0.0019(12)	0.0028(12)	-0.0026(11)
O(32)	0.0404(16)	0.0363(14)	0.0610(18)	-0.0003(12)	-0.0074(13)	0.0029(12)
O(3B)	0.0521(18)	0.0431(15)	0.0492(16)	-0.0005(13)	0.0195(13)	0.0017(12)
O(41)	0.0532(18)	0.0581(18)	0.0395(14)	0.0046(14)	0.0141(13)	0.0111(13)
O(42)	0.067(2)	0.067(2)	0.0427(16)	-0.0102(17)	0.0001(14)	-0.0088(14)
O(4B)	0.0453(17)	0.0581(18)	0.0522(16)	-0.0010(14)	0.0041(13)	0.0195(14)
N(1)	0.057(2)	0.058(2)	0.0264(15)	-0.0059(17)	0.0027(14)	-0.0019(14)
N(2)	0.063(2)	0.0288(16)	0.0472(19)	0.0000(15)	0.0057(16)	0.0001(14)
N(3)	0.0264(17)	0.050(2)	0.057(2)	0.0030(14)	0.0102(14)	-0.0022(16)
C(111)	0.059(3)	0.061(3)	0.0252(18)	-0.004(2)	0.0109(17)	0.0001(17)
C(112)	0.125(5)	0.087(4)	0.043(3)	-0.044(4)	0.020(3)	-0.007(3)
C(113)	0.102(5)	0.076(4)	0.055(3)	-0.019(3)	0.024(3)	0.004(3)
C(114)	0.275(14)	0.103(6)	0.109(6)	-0.029(7)	0.082(8)	0.009(5)
C(121)	0.061(3)	0.070(3)	0.030(2)	-0.007(2)	-0.0050(18)	0.0033(19)
C(122)	0.071(3)	0.073(3)	0.050(3)	-0.002(3)	0.000(2)	0.009(2)
C(123)	0.078(4)	0.129(6)	0.064(3)	0.024(4)	-0.001(3)	0.016(3)
C(124)	0.092(5)	0.110(5)	0.120(6)	0.008(4)	-0.003(4)	0.032(5)
C(131)	0.072(3)	0.067(3)	0.033(2)	0.003(2)	0.014(2)	-0.009(2)
C(132)	0.075(4)	0.094(4)	0.040(2)	0.014(3)	0.013(2)	0.004(2)
C(133)	0.105(5)	0.121(6)	0.071(4)	0.041(4)	0.022(3)	-0.003(4)
C(134)	0.163(9)	0.163(9)	0.113(6)	0.071(7)	0.026(6)	0.010(6)
C(141)	0.056(3)	0.072(3)	0.035(2)	-0.010(2)	0.0045(19)	-0.001(2)
C(142)	0.074(4)	0.080(4)	0.050(3)	-0.018(3)	0.008(2)	0.008(2)
C(143)	0.132(6)	0.140(7)	0.081(4)	-0.083(6)	0.010(4)	0.007(4)

Table S7. (*Continued*)

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
C(144)	0.124(7)	0.172(9)	0.112(6)	-0.063(6)	0.006(5)	0.042(6)
C(211)	0.061(3)	0.031(2)	0.054(2)	0.0059(19)	0.006(2)	-0.0011(17)
C(212)	0.071(3)	0.041(2)	0.052(2)	-0.001(2)	0.009(2)	-0.0020(19)
C(213)	0.062(3)	0.066(3)	0.068(3)	0.009(2)	0.010(2)	0.009(2)
C(214)	0.068(4)	0.106(5)	0.074(3)	0.005(3)	0.021(3)	0.007(3)
C(221)	0.066(3)	0.0311(19)	0.050(2)	0.0070(19)	0.007(2)	0.0052(17)
C(222)	0.058(3)	0.045(2)	0.059(3)	0.004(2)	0.003(2)	0.001(2)
C(223)	0.066(3)	0.067(3)	0.066(3)	0.002(3)	0.004(2)	0.015(2)
C(224)	0.070(4)	0.102(4)	0.069(3)	0.003(3)	-0.005(3)	0.014(3)
C(231)	0.068(3)	0.032(2)	0.056(2)	-0.003(2)	0.011(2)	0.0058(18)
C(232)	0.090(4)	0.046(3)	0.083(3)	0.007(3)	0.031(3)	0.007(2)
C(233)	0.086(4)	0.096(4)	0.072(3)	-0.014(3)	0.024(3)	0.001(3)
C(234)	0.144(9)	0.205(11)	0.163(9)	-0.016(8)	0.073(7)	-0.014(8)
C(241)	0.085(3)	0.031(2)	0.048(2)	0.000(2)	0.003(2)	-0.0027(17)
C(242)	0.187(8)	0.047(3)	0.076(4)	0.003(4)	-0.061(4)	-0.008(3)
C(243)	0.117(5)	0.061(3)	0.065(3)	-0.010(3)	-0.020(3)	0.004(3)
C(244)	0.338(17)	0.089(5)	0.126(7)	0.033(7)	-0.146(9)	-0.022(5)
C(311)	0.034(2)	0.045(2)	0.056(2)	0.0031(17)	0.0084(17)	-0.0018(18)
C(312)	0.045(3)	0.054(3)	0.095(4)	-0.007(2)	0.019(2)	-0.004(3)
C(313)	0.069(3)	0.050(3)	0.104(4)	-0.002(3)	0.003(3)	-0.009(3)
C(314)	0.116(6)	0.088(5)	0.169(7)	-0.036(4)	0.074(6)	-0.062(5)
C(321)	0.031(2)	0.058(3)	0.065(3)	0.0112(19)	-0.0004(19)	-0.002(2)
C(322)	0.048(3)	0.113(5)	0.072(3)	0.015(3)	0.005(2)	0.028(3)
C(323)	0.089(5)	0.183(8)	0.076(4)	0.042(5)	0.005(4)	0.057(5)
C(324)	0.36(3)	0.249(18)	0.195(15)	0.095(18)	-0.118(17)	-0.025(13)
C(331)	0.028(2)	0.053(2)	0.057(2)	0.0013(18)	0.0062(17)	-0.0036(19)
C(332)	0.041(2)	0.054(3)	0.076(3)	0.007(2)	0.005(2)	-0.010(2)
C(333)	0.053(3)	0.061(3)	0.067(3)	-0.003(2)	0.006(2)	-0.008(2)
C(334)	0.078(4)	0.062(3)	0.083(4)	0.005(3)	-0.009(3)	-0.019(3)
C(341)	0.036(2)	0.067(3)	0.064(3)	-0.001(2)	0.018(2)	-0.005(2)
C(342)	0.061(3)	0.086(4)	0.064(3)	0.000(3)	0.019(3)	0.000(3)
C(343)	0.066(3)	0.101(4)	0.063(3)	-0.008(3)	0.019(3)	0.001(3)
C(344)	0.090(5)	0.149(7)	0.081(4)	0.000(5)	0.027(4)	-0.041(4)
C(901)	0.140(7)	0.089(4)	0.067(4)	-0.025(4)	-0.014(4)	0.006(3)