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New Inorganic−Organic Hybrid Materials Based on Polyoxovanadates: $[Morp]_6[VO_4 \subset V_{14}O_{32}(OH)_6]\cdot 2H_2O$, $[Morp]VO_3$, $[HMTA\text{-}CH_3]_4[H_2V_{10}O_{28}]\cdot 5H_2O$, and $[HMTA\text{-}H][HMTA\text{-}CH_2OH]_2[H_5V_{10}O_{28}]\cdot 6H_2O$

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Four new organic−inorganic hybrid materials containing oxovanadate clusters have been synthesized from acidified, aqueous vanadate solutions in the presence of organic templates morpholine or hexamethylenetetraamine and their crystal structures are reported. Crystal data: $[Morp]_6[V^VO_4 \subset V^{IV}_3V^V_{11}O_{32}(OH)_6]\cdot 2H_2O$ (**1**) (Morph = morpholinium), monoclinic, space group $C2/c$, $a = 19.2521(9)$, $b = 14.1317(6)$, and $c = 21.3212\ (9)$ Å, $\beta = 92.117(10)°$, $V = 5796.8(4)(Å)^3$, and $Z = 4$; $[Morp]VO_3$ (**2**), monoclinic, space group $P2_1/c$, $a = 6.4775(7)$, $b = 20.099(2)$, and $c = 5.7999(6)$ Å, $\beta = 105.682(2)°$, $V = 726.99(13)$ Å^3, and $Z = 2$; $[HMTA\text{-}CH_3]_4[H_2V_{10}O_{28}]\cdot 5H_2O$ (**3**) (HMTA = hexamethylenetetramine), monoclinic, space group $C2/m$, $a = 20.8504(6)$, $b = 8.6955(3)$, and $c = 13.4096(4)$ Å, $\beta = 124.369(1)°$, $V = 2006.78(11)$ Å^3, and $Z = 2$; and $[HMTA\text{-}H][HMTA\text{-}CH_2OH]_2[H_5V_{10}O_{28}]\cdot 6H_2O$ (**4**), orthorhombic, space group $Pna2_1$, $a = 23.4579(2)$, $b = 19.1436(3)$, and $c = 11.0369(2)$ Å, $V = 4956.33(13)$ Å^3, and $Z = 4$. The formation of novel inorganic−organic hybrid compounds in the presence of organic bases under significantly different reaction conditions such as pH, nature of templates, and starting materials are discussed.

In recent years,[1−6] mixed-valent polyoxovanadate clusters have evoked considerable interest as these molecular fragments encapsulate charged or neutral species that function as structure directors in the self-organization process of the formation of the metal oxide cage; they can also be good model systems in the design of complex materials intermediate between molecular compounds and infinite solids. Although the laws governing this process are still not clear, Muller's work[3] has underscored the significant role played by templates in the formation of unusual structures of polyoxovanadates; several groups have assembled a large number of clusters with varying V^{IV}/V^V through the linking of VO_x^{n+} polyhedra (tetrahedra, square-pyramids, and octahedra), using a variety of organic bases. In most cases, the structure-directing organic molecules are either found inside the cavity of the shell-like cluster or occurred on the outer surface as countercations. N-containing ligands, such as ethylenediamine (en), tetramethylammonium (TMA), 1,4-diazabicyclooctane (DABCO), 2,2′-bipyridine, etc., have been commonly employed as templates;[7−10] the geometry of the guest has been identified as the major influence in the formation of these polyoxovanadates although in many instances the organic molecules merely appear as *countercations*.

It is well-known that under aqueous conditions, a number of vanadate species can exist in equilibrium depending on pH while the optimum synthesis conditions leading to desirable products remain debatable;[8] the two large V^V isopolyanions, $[V_{10}O_{28}]^{6-}$ and $[V_{12}O_{32}]^{4-}$ are the most stable clusters isolated in the presence of different countercations and reveal the combined effect of structure-directing organic molecules and self-assembly process.[11] The role of these countercations can become quite significant, especially if these organic species can act as buffers, have the ability to reduce the vanadate, and can provide suitable centers that can also participate in nonbonding interactions. Our systematic investigation in the assembly of mixed-valent as well as fully oxidized vanadium and molybdenum based polyoxoanions has resulted in the isolation and char-

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Table 1. Crystal Data and Structure Refinement for the Compounds 1−4[a]

crystal data	**1**	**2**	**3**	**4**
chemical formula	$C_{24}H_{64}N_6O_{50}V_{15}$	$C_8H_{20}N_2O_8V_2$	$C_{14}H_{40}N_8O_{33}V_{10}$	$C_{20}H_{56}N_{12}O_{36}V_{10}$
formula weight	2000.91	374.14	1357.94	1550.17
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$C2/c$	$P2_1/c$	$C2/m$	$Pna2_1$
a (Å)	19.2521(9)	6.4775(7)	20.8504(6)	23.4579(2)
b (Å)	14.1317(6)	20.099(2)	8.6955(3)	19.1436(3)
c (Å)	21.3212(9)	5.7999(6)	13.4096(4)	11.0369(3)
α (deg)	90.00	90.00	90.00	90.00
β (deg)	92.117(10)	105.682(2)	124.369(1)	90.00
γ (deg)	90.00	90.00	90.00	90.00
V (Å^3)	5796.8(4)	726.99(13)	2006.78(11)	4956.33
T (K)	296(2)	293(2)	293(2)	293(2)
Z	4	2	2	4
ρ_{calc} (g/cm^3)	2.293	1.709	2.247	2.077
ρ_{expt} (g/cm^3)	2.4	1.9	2.24	2.0
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
R_1 [$I > 2s(I)$]	0.0510	0.0250	0.0358	0.0573
wR_2	0.1543	0.0693	0.0896	0.1052
2θ range (deg)	3.82−58.44	4.06−58.04	3.68−58.68	3.48−58.90
no. of reflections collected	18 318	4565	6505	30 654
F(000)	3980	384	1348	3112
total parameters	439	100	175	761
GOF	1.066	1.058	1.051	1.022
extn coefficient	0.00024(5)	0.005(2)	0.00019	0.0003
absorption coefficient (mm^{-1})	2.419	1.322	2.334	1.910

[a] $R_1 = (||Fo| - |Fc||)/(|Fo|)$; $wR_2 = [w(Fo^2 - Fc^2)/(wFo^4)]^{1/2}$; GOF $= [w(Fo^2 - Fc^2)^2/(n - p)]^{1/2}$ where "n" is the number of reflections and "p" is the number of parameters refined.

acterization of organic−inorganic hybrid solids synthesized in the presence of morpholine, hexamethylenetetramine (HMTA), 1,3,5-triazine, $[(CH_3)_4N]^+$, and triethanolamine.[12−14] In this study, we employed morpholine which contains two basic sites, N and O, and cage-like HMTA as structure directors. While the influence of morpholine in the formation of **1** and **2** mainly depends on pH of the reaction, use of hexamethylenetetramine results in the formation of **3** and **4** under acidic conditions. Herein, we report the synthesis and structural characterization of four novel organic−inorganic hybrid materials based on isopolyvanadates: $[Morp]_6[V^VO_4\subset V^{IV}{}_3V^V{}_{11}O_{32}(OH)_6]\cdot 2H_2O$ (**1**) containing mixed-valent bicapped Keggin anion, $[Morp]VO_3$ (**2**) containing 1D infinite VO_3^- chains, and $[HMTA\text{-}CH_3]_4[H_2V_{10}O_{28}]\cdot 5H_2O$ (**3**) and $[HMTA\text{-}H][HMTA\text{-}CH_2O\ H]_2[H_5V_{10}O_{28}]\cdot 6H_2O$ (**4**), exhibiting discrete decavanadate clusters, $[V_{10}O_{28}]$.$^{6-}$

Experimental Section

General Methods. The chemicals used were of reagent-grade quality and were used without further purification. FTIR spectra were recorded on KBr pellets using Nicolet 5DX spectrophotometer. TG analyses were carried out using Perkin-Elmer TGA7 system on well-ground samples in nitrogen atmosphere with a heating rate of 10 °C/min. The single-crystal X-ray analyses were obtained on a Simens SMART CCD diffractometer with Mo Kα radiation (0.71073 Å).

Synthesis of $[Morp]_6[VO_4\subset V_{14}O_{32}(OH)_6]\cdot 2H_2O$ (1). In a typical preparation, V_2O_5 (0.5 g; 2.75 mmol) was dissolved in morpholine (0.8 mL; 9.2 mmol) in 60 mL of water. The pH of the light brown color solution was adjusted to 4.5 by the addition of HCl. After 2 weeks, dark brown crystals appeared which were filtered off from the solution and washed with water followed by acetone, and dried in air. Yield: 1.1 g, 40% based on vanadium. Thermogram: first loss of water around 200 °C (in this region DTA shows a sharp endothermic peak) and a broad weight loss around 400−550 °C (a broad endothermic peak) corresponding to the decomposition of morpholine molecules. Chemical analysis (cerimetric titration) indicated vanadium to be in a mixed-valent state. Average oxidation state: 4.85. Total vanadium: exp, 37.8; calcd 38.2. Total V^{4+}: exp 7.8; calcd 7.6. $\rho_o(exp) = 2.4$ g/cm^3. Elemental analysis: obsd, C, 4.5; H, 1.0; N, 1.1; calcd, C, 4.5; H, 1.0; N, 1.3. ESR at room temperature showed a broad signal with $g \sim 2.01$ corresponding to the presence of V(IV) species. Scanning electron micrographs showed the formation of cubic blocklike crystals.

Synthesis of $[Morp]VO_3$ (2). An identical procedure employed for the synthesis of **1** was adopted, except the pH of the reaction medium was adjusted to ∼8.0. The colorless crystals obtained were filtered off and washed with water followed by acetone and dried in air. Yield: 1.4 g, 43% based on vanadium. Chemical analysis (cerimetric titration) indicated the total vanadium: exp 27.0; calcd 27.3. $\rho_o(exp) = 1.9$ g/cm^3. Elemental analysis: obsd, C, 4.6; H, 1.0; N, 1.3; calcd, C, 4.8; H, 1.0; N, 1.4. Cerimetric titration and ESR show no evidence of the presence of (V^{IV}) in **2** unlike the case of low pH preparation. Scanning electron micrographs show the formation of rodlike crystals, a habit different from **1**.

Synthesis of $[HMTA\text{-}CH_3]_4[H_2V_{10}O_{28}]\cdot 5H_2O$ (3). The compound **3** was synthesized from a mixture of $NaVO_3$ (0.2 g, 1.64 mmol) and HMTA(0.23 g, 1.64 mmol) dissolved in 60 mL of distilled water. pH of the clear solution was adjusted to 5.3 by HCl (0.4 mL, 6.3 mmol), and the resulting orange color solution was reduced with $NaBH_4$ (0.031 g, 8.0 mmol) and the dark green color solution was kept at room temperature (25 °C) for crystallization. After 30 days orange red color crystals were filtered off from the solution and washed with water followed by acetone and dried in air. Yield: 0.8 g, 48% based on vanadium. Chemical analysis (cerimetric titration) indicated vanadium to be in fully oxidized state. Total vanadium: exp 37.7; calcd 37.5. $\rho_o(expt) = 2.24$ g/cm^3. Elemental analysis: obsd, C, 4.1; H, 2.5; N, 2.0; calcd, C, 4.3; H, 1.0; N, 2.8.

Synthesis of $[HMTA\text{-}H][HMTA\text{-}CH_2OH]_2[H_5V_{10}O_{28}]\cdot 6H_2O$ (4). An aqueous solution of $VOSO_4\cdot 6H_2O$ (0.2 g, 0.74 mmol) in 30 mL of water was added to HMTA(0.1035 g, 0.74 mmol). The resulting turbid, light blue color solution was

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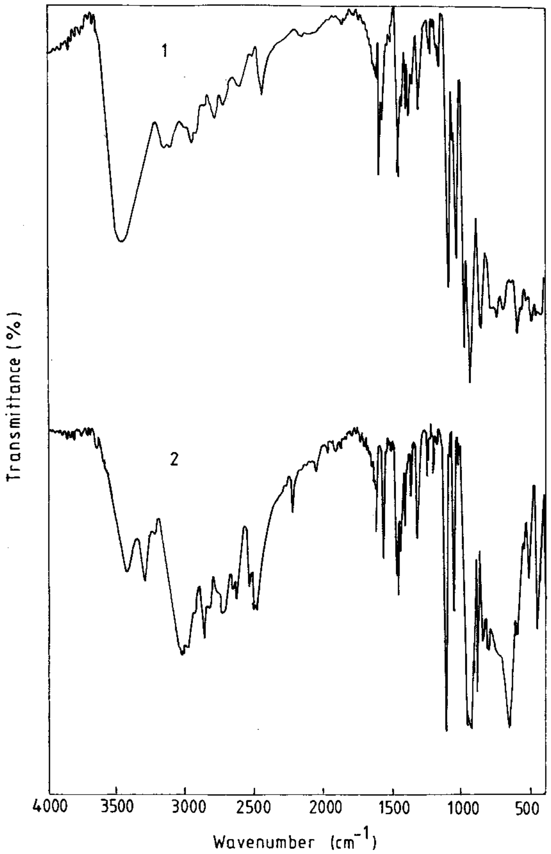

Figure 1. FTIR spectra of compounds **1** and **2**.

adjusted to pH 3.5 by the addition of 0.8 mL of dilute HCl. The clear blue color solution was kept for crystallization at room temperature in air; during the crystallization period the color of the solution changed from blue to green. After 2 weeks brown, platy crystals were filtered off from green color solution. Yield: 0.2 g, 18% based on vanadium. Chemical analysis (cerimetric titration) indicated vanadium to be in a mixed-valent state. Average oxidation state: 4.8. Total vanadium: exp 32.6; calcd 33.0. ρ_o(expt) = 2.0 g/cm^3. Elemental analysis: obsd, C, 4.1; H, 1.0; N, 2.9; calcd, C, 4.3; H, 1.0; N, 3.0.

X-ray Crystallographic Studies. Single-crystal diffraction studies were carried out on a Siemens SMART CCD diffractometer with a Mo Kα sealed tube at 23 °C for all **1**–**4**. The software SADABS was used for absorption correction, and SHELXTL, for space group and structure determination and refinements.[15] All the non-hydrogen atoms were refined anisotropically. Riding models were used to place the H atoms attached to carbon and nitrogen atoms. All the hydrogen atoms of the water molecules were located in the difference Fourier map for all **1**–**4**. A common O–H distance and common isotropic thermal parameters of the oxygen atoms of the water molecules were refined for **1**–**4**. The hydrogen atoms attached to the [$V_{10}O_{28}$] clusters in **3** and **4** could not be located. The least-squares refinement cycles on F^2 were performed until the model converged. The crystallographic data and refinement details are shown in Table 1. Additional details are available as Supporting Information.

Results and Discussion

The title compounds **1**–**4** were synthesized from the reaction of $NaVO_3$/V_2O_5/$VOSO_4$ and morpholine/HMTA in water under controlled pH and appropriate reaction conditions. The materials were characterized by FTIR, TGA/DTA, EPR, chemical analysis, powder X-ray diffraction, and single-crystal X-ray diffraction. While dark brown color crystals of **1** were isolated in 40% yield from an aqueous solution containing V_2O_5 and morpholine at pH 4.5, **2** was obtained in 43% yield as colorless crystals under the same reaction conditions, but at pH ~8.0. The FTIR spectra (Figure 1) of the compounds **1** and **2** showed characteristic vibrational features similar to polyoxovanadates and metavanadates respectively reported in the literature.[16] For **1**, symmetric and asymmetric stretching of the different kinds of V–O bonds are observed in the following regions: The terminal V–O bonds are in the range 990–975 cm^{-1}; the strong bands at 850–740 and 690 cm^{-1} are assigned to the antisymmetric stretching vibrations of V–O–V features. The bands at 3460, 3300, 2930, 2700, 2510, 1610, 1590, 1450, 1300, 1092, and 1040 cm^{-1} indicate the presence of morpholinium cations and water molecules. The FTIR spectra of the compound **2** showed characteristic vibrational features at 960 (m), 925 (sh), 900, 880, 800, 650 (sh), 590 (m), 500 (m) and 450 cm^{-1} corresponding to V–O symmetric stretching and V–O–V antisymmetric vibrational features of the metavanadates. The bands at 3420, 3280, 3000, 2850, 2730, 2520 1615, 1560, 1455, 1400, 1310, 1100, and 1040 cm^{-1} are associated with morpholinium cations.

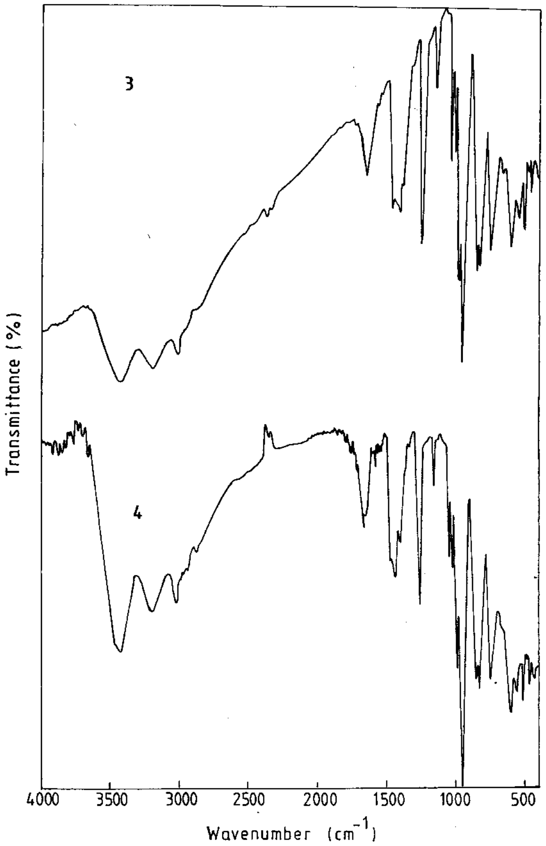

Figure 2. FTIR spectra of compounds **3** and **4**.

Compounds **3** and **4** were isolated from a reaction mixture of acidified, aqueous vanadate solution containing HMTA as template. While the orange red crystals of **3** were isolated in 48% yield from an aqueous solution

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement parameters (Å$^2 \times 10^3$) of 1

atoms	x	y	z	U_{eq}	atoms	x	y	z	U_{eq}
V(1)	5000	2583(1)	2500	35(1)	O(17)	5982(2)	3411(2)	1312(1)	21(1)
V(2)	5000	−120(1)	2500	18(1)	O(18)	4815(2)	1766(2)	1003(1)	20(1)
V(3)	6288(1)	917(1)	2847(1)	17(1)	O(19)	3510(1)	3664(2)	1347(1)	20(1)
V(4)	5450(1)	901(1)	1370(1)	17(1)	O(20)	4702(2)	3659(2)	776(1)	21(1)
V(5)	6545(1)	2563(1)	1681(1)	18(1)	O(21)	5485(1)	4977(2)	3260(1)	19(1)
V(6)	4141(1)	2616(1)	1042(1)	18(1)	O(22)	5745(1)	4746(2)	2134(1)	19(1)
V(7)	5000	5304(1)	2500	19(1)	O(1S)	2041(2)	−132(3)	4603(2)	34(1)
V(8)	6289(1)	4271(1)	2854(1)	17(1)	C(1)	2111(3)	−603(4)	5200(2)	37(1)
V(9)	5261(1)	4282(1)	1318(1)	19(1)	C(2)	2199(3)	104(4)	5729(2)	33(1)
O(1)	5577(1)	1963(2)	2229(1)	17(1)	N(1)	2810(2)	722(3)	5620(2)	29(1)
O(2)	5000	−1258(3)	2500	29(1)	C(3)	2748(3)	1179(3)	4989(2)	33(1)
O(3)	6798(2)	62(2)	3070(2)	25(1)	C(4)	2640(2)	429(3)	4490(2)	30(1)
O(4)	5463(2)	68(2)	848(1)	26(1)	O(2S)	3575(2)	7101(2)	3765(2)	33(1)
O(5)	7280(2)	2737(2)	1353(2)	27(1)	C(5)	3121(3)	7867(4)	3902(2)	32(1)
O(6)	3715(2)	2467(2)	388(2)	27(1)	C(6)	3226(3)	8673(3)	3448(2)	32(1)
O(7)	5000	6446(3)	2500	29(1)	N(2)	3099(2)	8351(3)	2785(2)	30(1)
O(8)	6877(2)	5080(2)	2931(2)	26(1)	C(7)	3520(3)	7479(4)	2650(2)	33(1)
O(9)	5543(2)	5115(2)	879(1)	25(1)	C(8)	3402(3)	6744(3)	3153(2)	33(1)
O(10)	4669(1)	3205(2)	1975(1)	17(1)	O(3S)	6115(2)	7812(2)	3952(2)	32(1)
O(11)	5833(1)	198(2)	2098(1)	19(1)	C(9)	6091(3)	6804(4)	3971(2)	34(1)
O(12)	5423(1)	442(2)	3188(1)	19(1)	C(10)	5749(3)	6451(4)	4557(2)	35(1)
O(13)	6912(1)	1520(2)	2274(1)	21(1)	N(3)	5037(2)	6854(3)	4585(2)	30(1)
O(14)	3636(1)	1773(2)	1581(1)	21(1)	C(11)	5426(3)	8170(4)	3929(2)	35(1)
O(15)	6203(2)	1529(2)	1186(1)	21(1)	C(12)	5046(3)	7909(4)	4517(2)	35(1)
O(16)	6660(1)	3392(2)	2409(1)	20(1)	O(4S)	3976(2)	9734(3)	5335(2)	47(1)

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement parameters (Å$^2 \times 10^3$) of 2

atoms	x	y	z	U_{eq}
V(1)	3281(1)	2916(1)	3385(1)	19(1)
O(1)	5916(2)	2942(1)	4275(2)	30(1)
O(2)	2311(2)	2664(1)	275(2)	28(1)
O(3)	2340(2)	3655(1)	3634(2)	40(1)
N(1)	8754(2)	3512(1)	8203(3)	27(1)
O(4)	6741(2)	4749(1)	8500(3)	48(1)
C(1)	5858(3)	4149(1)	9103(4)	40(1)
C(2)	7560(3)	3639(1)	10033(3)	34(1)
C(3)	9586(3)	4145(1)	7478(4)	38(1)
C(4)	7749(4)	4628(1)	6639(4)	51(1)

containing $NaVO_3$, HMTA, and $NaBH_4$, **4** was obtained in 18% yield as brown platy crystals from an aqueous reaction mixture containing $VOSO_4{\cdot}6H_2O$ and HMTA. The FTIR spectra of the compounds **3** and **4** (Figure 2) showed characteristic features of decavanadate cores reported in the literature.[17,18] The strong bands at 990 (m), 953 (sh) cm^{-1} are associated with the terminal V−O bonds; the features at 848, 830, 747 (s), 600 (m), 548, and 505 cm^{-1} are assigned to the antisymmetric stretching vibrations of V−O−V. The various symmetric and antisymmetric stretching vibrational modes of the templating cations occur at 3420, 3190, 1700, 1420, 1400, and 1150 cm^{-1} and at 3400, 3200, 2950, 1610, 1490, 1450, and 1200 cm^{-1} for **3** and **4**, respectively.

Description of the Structures. The crystallographic data and the experimental details of **1**−**4** are given in Table 1. The atomic positional parameters of **1** and **2** are given in Tables 2 and 3, respectively. The crystal structure of the compound **1** consists of discrete "bicapped Keggin" anions, $[V^{V}O_4{\subset}V^{IV}{}_3V^{V}{}_{11}O_{32}(OH)_6]^{6-}$ and morpholinium cations, $[C_4H_{10}NO]^+$, linked together by means of an extensive network of hydrogen bonds (Figure 3). The three electron reduced oligomeric anion possesses a crystallographic 2-fold symmetry and the atoms V(1), V(2), V(7), O(2), and O(7) are present on the 2-fold axis. The metal oxo−anion cluster (Figure 4) contains 12 VO_6 octahedra, 2 VO_5 square pyramids, and 1 VO_4 tetrahedra where the two square pyramids and the tetrahedra occur along the 2-fold axis of the molecular symmetry like in the "bicapped Keggin" anions reported in the literature.[19−21] The central VO_4 tetrahedron shares its oxygen atoms with four V_3O_{13} units, each of which is made of three edge-sharing VO_6 octahedra. These four V_3O_{13} units are linked to each other by corner sharing. The two VO_5 square pyramids capped along the molecular axis share through edges

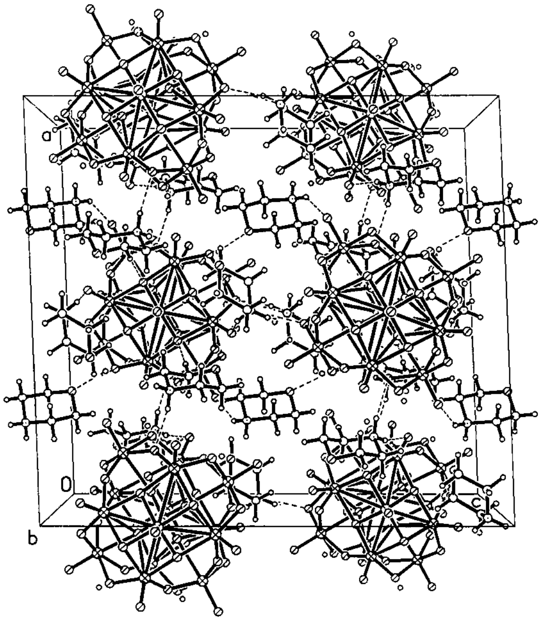

Figure 3. Unit cell packing diagram of the compound **1**. The "bicapped" inorganic anion stacks one over the other is viewed down b axis.

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for 1[a]

V(1)−O(10)	1.542(3)	V(3)−O(1)	2.379(3)	V(5)−O(1)	2.392(3)	V(8)−O(8)	1.612(3)
V(1)−O(1)	1.543(3)	V(4)−O(4)	1.620(3)	V(6)−O(6)	1.604(3)	V(8)−O(16)	1.732(3)
V(2)−O(2)	1.609(5)	V(4)−O(15)	1.756(3)	V(6)−O(18)	1.774(3)	V(8)−O(19)#1	1.932(3)
V(2)−O(12)	1.833(3)	V(4)−O(18)	1.879(3)	V(6)−O(20)	1.926(3)	V(8)−O(22)	1.947(3)
V(2)−O(12)#1	1.833(3)	V(4)−O(11)	1.964(3)	V(6)−O(14)	1.940(3)	V(8)−O(21)	2.058(3)
V(2)−O(11)	1.899(3)	V(4)−O(12)#1	2.063(3)	V(6)−O(19)	2.037(3)	V(8)−O(10)#1	2.420(3)
V(2)−O(11)#1	1.899(3)	V(4)−O(1)	2.374(3)	V(6)−O(10)	2.352(3)	V(9)−O(9)	1.612(3)
V(3)−O(3)	1.618(3)	V(5)−O(5)	1.620(3)	V(7)−O(7)	1.613(4)	V(9)−O(20)	1.782(3)
V(3)−O(14)#1	1.721(3)	V(5)−O(17)	1.780(3)	V(7)−O(22)#1	1.836(3)	V(9)−O(17)	1.856(3)
V(3)−O(13)	1.941(3)	V(5)−O(15)	1.906(3)	V(7)−O(22)	1.836(3)	V(9)−O(21)#1	1.983(3)
V(3)−O(12)	1.960(3)	V(5)−O(16)	1.952(3)	V(7)−O(21)#1	1.897(3)	V(9)−O(22)	2.050(3)
V(3)−O(11)	2.060(3)	V(5)−O(13)	2.051(3)	V(7)−O(21)	1.897(3)	V(9)−O(10)	2.386(3)

O(10)#1-V(1)−O(10)	110.6(2)	O(18)−V(4)−O(11)	151.33(12)	O(6)−V(6)−O(18)	102.8(2)	O(22)−V(8)−O(10)#1	86.70(11)
O(10)#1−V(1)−O(1)#1	109.56(14)	O(4)−V(4)−O(12)#1	96.80(14)	O(6)−V(6)−O(20)	96.8(2)	O(21)−V(8)−O(10)#1	69.47(10)
O(10)−V(1)−O(1)#1	108.15(14)	O(18)−V(4)−O(12)#1	82.30(12)	O(18)−V(6)−O(20)	94.87(13)	O(9)−V(9)−O(17)	102.23(14)
O(10)#1−V(1)−O(1)	108.15(14)	O(11)−V(4)−O(12)#1	76.56(11)	O(6)−V(6)−O(14)	100.6(2)	O(20)−V(9)−O(17)	95.83(13)
O(10)−V(1)−O(1)	109.56(14)	O(4)−V(4)−O(1)	170.18(14)	O(18)−V(6)−O(14)	89.69(13)	O(9)−V(9)−O(21)#1	99.66(14)
O(1)#1−V(1)−O(1)	110.8(2)	O(15)−V(4)−O(1)	77.92(11)	O(20)−V(6)−O(14)	160.56(12)	O(20)−V(9)−O(21)#1	96.28(13)
O(2)−V(2)−O(12)	115.66(9)	O(18)−V(4)−O(1)	87.49(11)	O(6)−V(6)−O(19)	94.74(14)	O(17)−V(9)−O(21)#1	152.38(12)
O(2)−V(2)−O(12)#1	115.66(9)	O(11)−V(4)−O(1)	71.62(10)	O(18)−V(6)−O(19)	162.45(12)	O(9)−V(9)−O(22)	96.13(14)
O(12)−V(2)−O(12)#1	128.7(2)	O(5)−V(5)−O(17)	103.6(2)	O(20)−V(6)−O(19)	83.42(12)	O(20)−V(9)−O(22)	162.32(12)
O(2)−V(2)−O(11)	103.68(9)	O(5)−V(5)−O(15)	99.7(2)	O(14)−V(6)−O(19)	86.55(12)	O(21)#1−V(9)−O(22)	76.73(11)
O(12)−V(2)−O(11)	84.32(12)	O(17)−V(5)−O(15)	94.57(13)	O(6)−V(6)−O(10)	166.46(13)	O(9)−V(9)−O(10)	170.37(13)
O(12)#1−V(2)−O(11)	83.93(12)	O(5)−V(5)−O(16)	100.2(2)	O(18)−V(6)−O(10)	89.09(12)	O(20)−V(9)−O(10)	77.06(11)
O(2)−V(2)-O(11)#1	103.68(9)	O(17)−V(5)−O(16)	89.83(13)	O(20)−V(6)−O(10)	75.43(11)	O(17)−V(9)−O(10)	87.38(11)
O(12)−V(2)−O(11)#1	83.93(12)	O(15)−V(5)−O(16)	158.06(12)	O(14)−V(6)−O(10)	85.77(11)	O(21)#1−V(9)−O(10)	71.35(10)
O(12)#1−V(2)−O(11)#1	84.32(12)	O(5)−V(5)−O(13)	95.08(14)	O(19)−V(6)−O(10)	73.55(10)	O(22)−V(9)−O(10)	85.30(10)
O(11)−V(2)−O(11)#1	152.6(2)	O(17)−V(5)−O(13)	161.20(13)	O(7)−V(7)−O(22)#1	115.47(9)	V(2)−O(11)−V(4)	100.27(12)
O(3)−V(3)−O(14)#1	106.3(2)	O(15)−V(5)−O(13)	83.89(12)	O(7)−V(7)−O(22)	115.47(9)	V(2)−O(11)−V(3)	96.27(12)
O(3)−V(3)−O(13)	97.46(14)	O(16)−V(5)−O(13)	85.07(12)	O(22)#1−V(7)−O(22)	129.1(2)	V(4)−O(11)−V(3)	119.95(14)
O(14)#1−V(3)−O(13)	95.73(13)	O(5)−V(5)−O(1)	166.79(14)	O(7)−V(7)−O(21)#1	104.14(9)	V(2)−O(12)−V(3)	102.09(13)
O(3)−V(3)−O(12)	98.57(14)	O(17)−V(5)−O(1)	88.92(11)	O(22)−V(7)−O(21)#1	84.24(12)	V(2)−O(12)−V(4)#1	99.00(12)
O(14)#1−V(3)−O(12)	91.61(13)	O(15)−V(5)−O(1)	74.87(10)	O(7)−V(7)−O(21)	104.14(9)	V(3)−O(12)−V(4)#1	141.2(2)
O(13)−V(3)−O(12)	159.71(12)	O(16)−V(5)−O(1)	83.76(11)	O(22)#1−V(7)−O(21)	84.24(12)	V(3)−O(13)−V(5)	119.77(14)
O(3)−V(3)−O(11)	95.50(14)	O(13)−V(5)−O(1)	72.56(10)	O(22)−V(7)−O(21)	83.70(12)	V(3)#1−O(14)−V(6)	145.1(2)
O(14)#1−V(3)−O(11)	156.75(13)	V(1)−O(1)−V(4)	126.4(2)	O(21)#1−V(7)−O(21)	151.7(2)	V(4)−O(15)−V(5)	122.4(2)
O(13)−V(3)−O(11)	89.12(12)	V(1)−O(1)−V(3)	123.56(14)	O(8)−V(8)−O(16)	105.2(2)	V(8)−O(16)−V(5)	146.0(2)
O(12)−V(3)−O(11)	77.06(11)	V(4)−O(1)−V(3)	94.29(10)	O(8)−V(8)−O(19)#1	96.23(14)	V(5)−O(17)−V(9)	152.6(2)
O(3)−V(3)−O(1)	163.30(13)	V(1)−O(1)−V(5)	124.5(2)	O(16)−V(8)−O(19)#1	95.25(13)	V(6)−O(18)−V(4)	152.6(2)
O(14)#1−V(3)−O(1)	89.31(12)	V(4)−O(1)−V(5)	84.64(9)	O(8)−V(8)−O(22)	100.98(14)	V(8)#1−O(19)−V(6)	120.15(14)
O(13)−V(3)−O(1)	74.70(11)	V(3)−O(1)−V(5)	92.74(10)	O(16)−V(8)−O(22)	92.09(13)	V(9)−O(20)−V(6)	121.3(2)
O(12)−V(3)−O(1)	86.53(11)	V(1)−O(10)−V(6)	124.5(2)	O(19)#1−V(8)−O(22)	158.82(12)	V(7)−O(21)−V(9)#1	99.58(12)
O(11)−V(3)−O(1)	70.02(10)	V(1)−O(10)−V(9)	126.6(2)	O(16)−V(8)−O(21)	155.38(13)	V(7)−O(21)−V(8)	96.55(12)
O(4)−V(4)−O(15)	100.4(2)	V(6)−O(10)−V(9)	86.00(9)	O(19)#1−V(8)−O(21)	88.50(12)	V(9)#1−O(21)−V(8)	121.26(14)
O(4)−V(4)−O(18)	102.3(2)	V(1)−O(10)−V(8)#1	122.79(14)	O(22)−V(8)−O(21)	76.86(11)	V(7)−O(22)−V(8)	102.66(13)
O(15)−V(4)−O(18)	96.22(13)	V(6)−O(10)−V(8)#1	92.24(9)	O(8)−V(8)−O(10)#1	164.16(13)	V(7)−O(22)−V(9)	99.25(12)
O(4)−V(4)−O(11)	99.24(14)	V(9)−O(10)−V(8)#1	94.26(10)	O(16)−V(8)−O(10)#1	88.20(12)	V(8)−O(22)−V(9)	140.7(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, y, -z + {}^1/_2$.

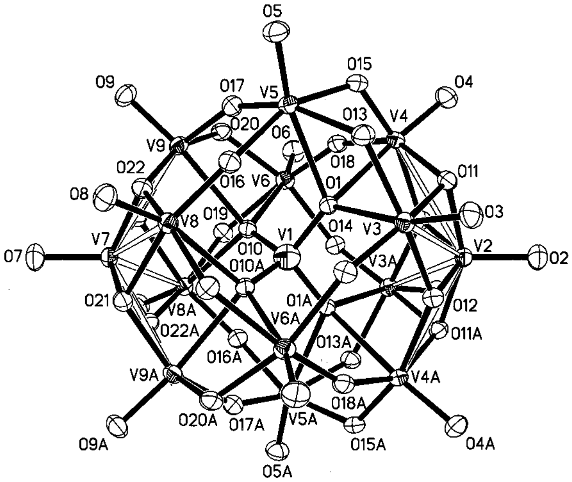

Figure 4. ORTEP view of the anion of **1**.

to the neighboring V_3O_{13}. The results of the X-ray structure analysis reveal that among each of these units, the V(2) of the VO_5 square pyramid show a shorter V−V metal distances in the range 2.950−2.965 Å with the four vanadium (V(3), V(3A), V(4), and V(4A)) of the VO_6; there is no short V···V interaction either between the four VO_6 octahedra occurring on the *xz* plane or the four VO_6 octahedra among the two units. Selected bonding parameters of the anion are listed in Table 4. The V═O, V···O(μ_1), V···O(μ_2), and V···O(μ_3) bond distances are in the range of 1.60−1.62, 1.73−1.94, 1.83−2.05, and 2.35−2.39 Å, respectively, indicating the expected trend of increasing V−O bond length for one- < two- < three- < four-coordinated oxygen as reported earlier.[22−24] The central VO_4 tetrahedral environment involves O−V−O angles ranging from 108.5 to 110.8° and V−O bond distances ~1.54 Å. Surprisingly, the V(1)−O distances were shorter than expected,[18,20−22] except for a report by Hou et al.[24] Also, in the structure of **1**, the isotropic thermal parameter of V(1) is about twice that of the

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Table 5. Nonbonding Interactions [Distances(Å)and Angles (deg)] in 1 and 2

1		2	
O(4S)···H(1C)−N(1)	1.886(6)	N(1)−H(1B)···O(1)	1.884(2)
O(5)···H(1D)−N(1)	2.115(2)	N(1)···O(1)	2.760(2)
O(3)···H(2C)−N(2)	2.164 (2)	N(1)−H(1A)···O(2)	1.970(3)
O(16)···H(2D)−N(2)	1.997 (1)	N(1)···O(2)	2.857(2)
O(22)···H(8B)−C(8)	2.370 (3)		
O(20)···H(3C)−N(3)	1.857 (2)		
O(9)···H(3D)−N(3)	2.204 (1)		
O(4)···H(4S1)−O(4S)	2.015 (1)		
O(18)···H(4S2)−O(4S)	2.230 (1)		
O(3)···H(2B)−C(2)	2.450 (2)		
O(3S)···H(1D)−N(1)	2.447 (1)		

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 2

V(1)−O(3)	1.625(1)	V(1)−O(2)	1.815(1)
V(1)−O(1)	1.645(1)	V(1)−O(2A)	1.824(1)
O(3)−V(1)−O(1)	108.97(7)	O(1)−V(1)−O(2)	111.83(6)
O(3)−V(1)−O(2)	107.84(6)	O(3)−V(1)−O(2A)	109.38(7)

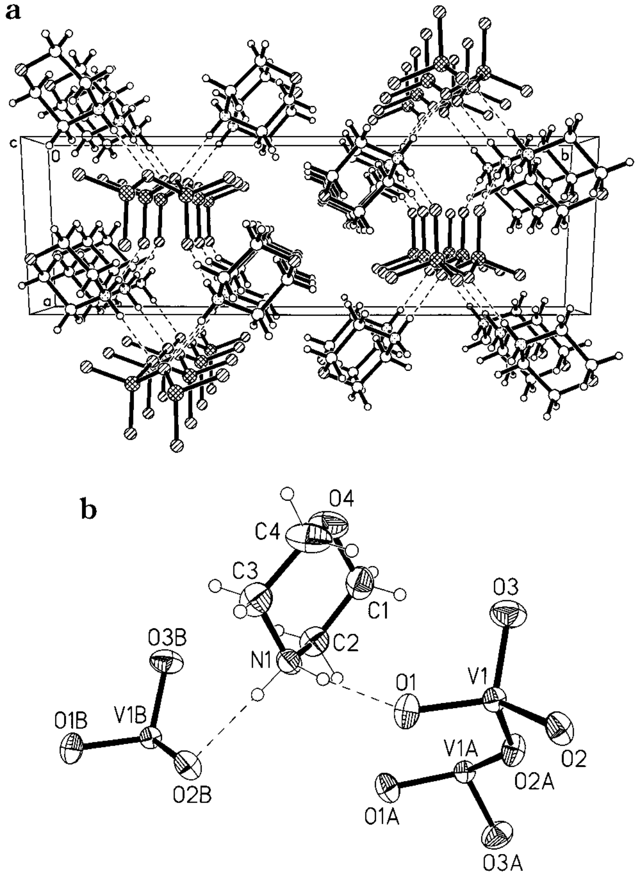

Figure 5. (a) The virtual layer of structure **2** as viewed perpendicular to the *ab* plane. The broken lines show the weak hydrogen contacts between morpholinium ions and V−O of VO_3^- chain. (b) ORTEP view of VO_3^- anion is showed with its cation, $[C_4H_{10}NO]^+$.

Table 7. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement parameters (Å$^2 \times 10^3$) for 3

atoms	*x*	*y*	*z*	U_{eq}
V(1)	−3819(1)	0	4697(1)	24(1)
V(2)	−3594(1)	0	7128(1)	23(1)
V(3)	−4729(1)	−1759(1)	7508(1)	29(1)
V(4)	−5000	−1900(1)	5000	21(1)
O(1)	−2889(2)	0	5349(2)	31(1)
O(2)	−2661(1)	0	7781(2)	30(1)
O(3)	−4650(1)	−3107(3)	8392(2)	42(1)
O(4)	−3913(1)	−1433(2)	5771(2)	22(1)
O(5)	−4145(1)	−1555(2)	3564(2)	30(1)
O(6)	−4896(1)	0	6081(2)	22(1)
O(7)	−4894(1)	−3051(2)	6104(2)	29(1)
O(8)	−3720(1)	−1539(2)	7947(2)	27(1)
O(9)	−4682(2)	0	8292(2)	31(1)
N(1)	−2435(2)	0	1419(3)	24(1)
N(2)	−3329(1)	−1405(3)	1713(2)	33(1)
N(3)	−2243(2)	0	3385(3)	30(1)
C(1)	−1842(2)	0	2789(3)	29(1)
C(2)	−2947(2)	−1424(3)	1084(2)	30(1)
C(3)	−2736(2)	−1385(4)	3024(3)	36(1)
C(4)	−3810(2)	0	1373(4)	39(1)
C(5)	−2031(3)	0	780(4)	37(1)
O(11)	−1123(2)	0	5978(4)	58(1)
O(12)	−1244(3)	−540(6)	8003(5)	59(2)
O(13)	−5000	−3983(11)	10000	74(2)

average U_{eq} of the other vanadium atoms. On the basis of electron density, it appeared that the central atom position may be fully occupied by Si, P, S, Cl, or partially by vanadium itself. Further crystallographic least-squares refinements were carried out to investigate this. The occupancy of this vanadium, V(1) in the special position was refined to 0.346(1) with U_{eq} similar to other vanadium atoms ($R_1 = 0.0032$ and $wR_2 = 0.0864$). When phosphorus atom was substituted in the place of V(1), the model converged at $R_1 = 0.0285$, $wR_2 = 0.0770$ and the U_{eq} of P(1) was similar to other vanadium atoms. To confirm the presence of P or other elements such as Si, S, or Cl atoms, chemical and spectroscopic analyses (AAS, EDAX, and ^{31}P NMR) were carried out and to our surprise none of these elements were detected. On the basis of our chemical and spectroscopic data, we ruled out the presence of these "foreign elements" and retained the present model. However, partial occupancy of vanadium may be a possibility! The influence of the encapsulated fragment, VO_4, on the shape and size of the cage, is comparable to other vanadate anions.[18,20−22] On the basis of close contacts and bond valence calculations[25] we found that H atoms are possibly attached to the doubly bridged O(13) and O(19). Our attempts to refine the protons attached to cluster oxygens were not successful. The location of V(IV) could not be resolved on the basis of bond valence sums.

An interesting feature of this structure is that each anion is surrounded by six morpholinium cations with its N atoms directed toward the O_t atoms of the anion by means of nonbonding interactions (see Figure 3 and Table 5). The shortest nonbonding distance 1.857(6) Å is between O(20) of the anionic cluster and H(3C) of the morpholinium N−H hydrogen atom. The oxygen atoms O(3), O(4), O(5), O(9), O(16), O(18), O(20), and O(22) of the cluster anions are involved in close contacts of the type, X−H···O (X = N, C) and the distances range from 1.857 to 2.370 Å. Of these strong and medium O···H interactions stemmed from N−H hydrogen atoms of the morpholinium cations and the weak interactions are due to C−H···O interactions. All the N−H hydrogen atoms of the morpholinium ions are participating in the weak bonding, mostly to the anionic cluster.

The compound **2** contains the metavanadate anion formed by corner-sharing VO_4 tetrahedra connected via O(2) atoms into infinite chains parallel to *c* axis similar to other metavanadates.[26−28] Selected bonding param-

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Table 8. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 4

atoms	x	y	z	U_{eq}	atoms	x	y	z	U_{eq}	atoms	x	y	z	U_{eq}
V(1)	2322(1)	1604(1)	−793(1)	21(1)	O(18)	2021(2)	894(2)	4501(3)	24(1)	N(8)	4159(2)	2682(3)	−5520(5)	37(2)
V(2)	1317(1)	1145(1)	792(1)	21(1)	O(19)	2004(2)	2009(2)	3140(4)	24(1)	C(8)	3638(3)	2590(3)	−3198(5)	29(2)
V(3)	1398(1)	−171(1)	2424(1)	23(1)	O(20)	2932(1)	10(2)	2099(4)	19(1)	C(9)	3666(3)	1499(3)	−4375(6)	35(2)
V(4)	1398(1)	1297(1)	3583(1)	23(1)	O(21)	2953(2)	1190(2)	3061(3)	21(1)	C(10)	3559(3)	2628(4)	−5438(5)	32(2)
V(5)	3470(1)	2095(1)	365(1)	23(1)	O(22)	3847(2)	1623(2)	1677(3)	24(1)	C(11)	4501(3)	1941(4)	−3409(6)	43(2)
V(6)	3394(1)	660(1)	−885(1)	25(1)	O(23)	3805(2)	358(2)	579(4)	26(1)	C(12)	4382(3)	3036(4)	−4437(6)	40(2)
V(7)	3548(1)	805(1)	2020(1)	23(1)	O(24)	3767(2)	1518(2)	−747(3)	23(1)	C(13)	4408(3)	1976(4)	−5587(6)	42(2)
V(8)	2502(1)	387(1)	3665(1)	22(1)	O(25)	2916(2)	2381(2)	1732(3)	24(1)	C(14)	2746(3)	2142(4)	−4174(6)	36(2)
V(9)	2382(1)	193(1)	695(1)	19(1)	O(26)	2808(2)	1056(2)	−1713(3)	23(1)	O(30)	2506(2)	2790(3)	−3961(5)	51(1)
V(10)	2448(1)	1730(1)	2017(1)	18(1)	O(27)	2844(2)	2305(2)	−633(3)	21(1)	N(9)	4655(2)	−1894(3)	4983(5)	37(1)
O(1)	1883(2)	1909(2)	−1783(4)	31(1)	O(28)	2846(2)	−93(2)	−385(4)	23(1)	N(10)	3745(2)	−1322(3)	5371(6)	39(1)
O(2)	893(2)	1439(2)	−226(4)	29(1)	H(3)	674(10)	−870(4)	2886(5)	57(7)	N(11)	4386(2)	−1580(3)	7037(5)	42(2)
O(3)	023(2)	−858(2)	2557(4)	32(1)	N(1)	1401(2)	−263(3)	−2906(5)	24(1)	N(12)	4620(2)	−676(3)	5597(7)	48(2)
O(4)	1041(2)	1690(2)	4619(4)	36(1)	N(2)	572(2)	−675(3)	−1809(4)	31(1)	C(15)	4066(3)	−1847(4)	4616(7)	46(2)
O(5)	3852(2)	2787(2)	252(4)	34(1)	N(3)	536(2)	447(3)	−2805(5)	28(1)	C(16)	4684(3)	−2086(4)	6257(6)	38(2)
O(6)	3746(2)	264(3)	−1923(4)	39(1)	N(4)	541(2)	−626(3)	−4008(4)	32(1)	C(17)	4917(3)	−1200(4)	4844(7)	47(2)
O(7)	3981(2)	482(2)	3006(4)	31(1)	C(1)	1190(3)	−671(4)	−1832(6)	33(2)	C(18)	3794(3)	−1542(4)	6689(7)	46(2)
O(8)	2933(2)	86(2)	4669(4)	30(1)	C(2)	1161(2)	475(3)	−2837(6)	27(1)	C(19)	4013(3)	−634(4)	5215(7)	44(2)
O(9)	2880(1)	1131(2)	699(4)	19(1)	C(3)	1164(2)	−617(4)	−4056(5)	29(2)	C(20)	4650(3)	−897(4)	6883(7)	52(2)
O(10)	2005(1)	765(2)	2061(4)	20(1)	C(4)	352(3)	26(3)	−1755(6)	31(2)	O(1S)	166(2)	−1747(3)	3775(5)	62(2)
O(11)	1909(2)	723(2)	−309(3)	19(1)	C(5)	359(3)	−1006(4)	−2920(6)	39(2)	O(2S)	2538(2)	−1373(2)	4842(4)	35(1)
O(12)	1935(1)	1884(2)	708(3)	19(1)	C(6)	330(3)	102(3)	−3907(6)	31(2)	O(3S)	3314(2)	−1310(3)	2216(6)	60(2)
O(13)	1036(2)	302(2)	1131(3)	23(1)	C(7)	2046(2)	−229(4)	−2945(6)	32(2)	O(4S)	789(2)	2218(4)	7070(6)	73(2)
O(14)	1062(2)	1556(2)	2177(4)	23(1)	O(29)	2271(2)	−900(3)	−2927(5)	47(1)	O(5S)	2851(2)	−1570(3)	−964(5)	63(2)
O(15)	1078(2)	424(2)	3513(4)	24(1)	N(5)	3391(2)	2211(3)	−4281(5)	28(1)	O(6S)	4616(5)	−577(5)	700(15)	110(6)
O(16)	2016(2)	−375(2)	3447(4)	23(1)	N(6)	4257(2)	2640(3)	−3317(5)	35(1)	O(7S)	4019(6)	−1702(6)	−77(14)	98(5)
O(17)	1957(2)	−476(2)	1029(3)	23(1)	N(7)	4279(2)	1568(3)	−4498(5)	39(1)					

eters of the anion is listed in Table 6. In **2**, the [—O—V(=O)$_2$—O—]$_n$ chains are arranged parallel to the c axis and stacked on each other along a axis (Figure 5a,b). The adjacent strands are hydrogen bonded by morpholinium cations in such a way that neighboring cations are placed alternatively on either side of the stacking of the strands. The H(1A) is bonded to O(2) and the H(2A) is bonded to O(1) of the adjacent anionic polymer strand. Due to the close proximity, there are also some weak interactions between C−H hydrogens and O(3) (the distances are 2.406 and 2.453 Å; refer Table 5). There are also weak interactions between the morpholine O atoms and the C−H hydrogen atoms of the neighboring morpholinium cations (2.548 Å).

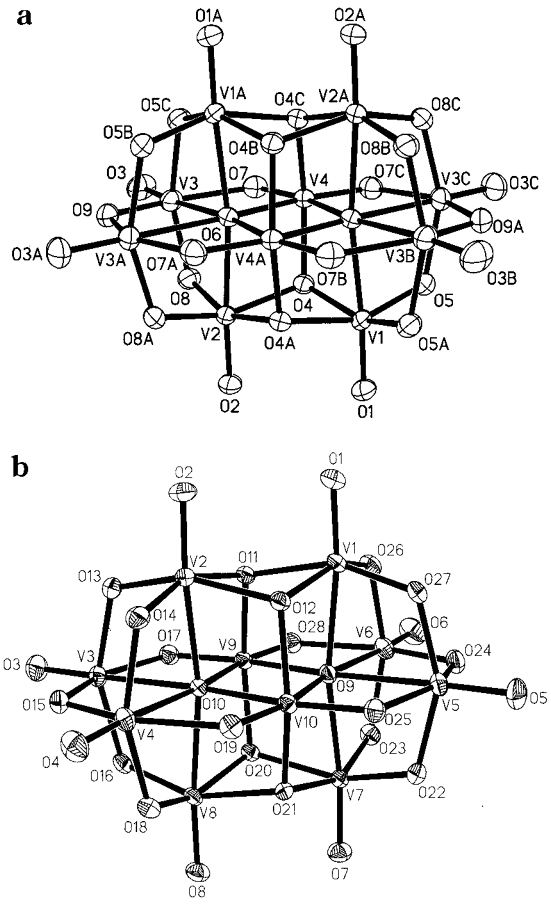

Figure 6. (a) ORTEP view of the decavanadate core present in **3**. (b) ORTEP view of the decavanadate core present in **4**.

The atomic positional parameters of **3** and **4** are given in Tables 7 and 8, respectively. Unlike **1** and **2**, the compounds **3** and **4** contain decavanadate cores. The crystal structure of the molecular anion (Figure 6a,b) possesses gross vanadium−oxygen framework of the prototype, [H$_n$V$_{10}$O$_{28}$]$^{(6-n)-}$ reported in the literature.[29−34] The framework contains a central {V$_6$O$_{12}$} core built of six edge-shared VO$_6$ octahedral units arranged in 2 × 3 rectangular array (V(3), V(3A), V(3B), V(3C), V(4), and V(4A)); two VO$_6$ units from above and two from below share the equatorial oxygens at the apexes of the octahedra in the rectangle. The molecular symmetry of an idealized framework is D_{2h}. Selected bond distances and bond angles of the decavanadate cores of **3** and **4** are listed in Tables 9 and 10, respectively. Compound **3**is a fully oxidized polyoxovanadate cluster, whereas **4** is a mixed-valent cluster although both are protonated. On the basis of the crystallographic studies, we could not establish any of the protonation sites for the anion

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Table 9. Selected Bond Distances(Å) and Angles for 3

V(1)−O(1)	1.615(3)	V(2)−O(8)	1.841(2)	V(3)−O(7)	2.048(2)
V(1)−O(5)	1.853(2)	V(2)−O(4)	1.986(2)	V(3)−O(6)	2.317(2)
V(1)−O(5)#1	1.853(2)	V(2)−O(4)#1	1.986(2)	V(4)−O(7)#3	1.695(2)
V(1)−O(4)#1	1.995(2)	V(2)−O(6)	2.244(2)	V(4)−O(7)	1.695(2)
V(1)−O(4)	1.995(2)	V(3)−O(3)	1.608(2)	V(4)−O(4)	1.931(2)
V(1)−O(6)#2	2.261(2)	V(3)−O(9)	1.828(2)	V(4)−O(4)#3	1.931(2)
V(2)−O(2)	1.622(2)	V(3)−O(8)	1.848(2)	V(4)−O(6)	2.127(2)
V(2)−O(8)#1	1.841(2)	V(3)−O(5)#3	1.949(2)	V(4)−O(6)#2	2.127(2)
O(1)−V(1)−O(5)	102.48(9)	O(9)−V(3)−O(5)#3	89.93(10)	V(4)−O(4)−V(1)	107.99(8)
O(5)−V(1)−O(5)#1	93.72(13)	O(8)−V(3)−O(5)#3	155.08(8)	V(2)−O(4)−V(1)	98.69(8)
O(5)−V(1)−O(4)#1	155.19(8)	O(3)−V(3)−O(7)	99.90(10)	V(1)−O(5)−V(3)#3	113.71(10)
O(1)−V(1)−O(4)	100.71(9)	O(9)−V(3)−O(7)	156.21(9)	V(4)−O(6)−V(4)#2	101.95(10)
O(5)−V(1)−O(4)	89.78(8)	O(8)−V(3)−O(7)	85.37(8)	V(4)−O(6)−V(2)	92.79(7)
O(4)#1-V(1)−O(4)	77.32(10)	O(5)#3−V(3)−O(7)	82.26(8)	V(4)#2−O(6)−V(2)	92.79(7)
O(1)−V(1)−O(6)#2	175.85(12)	O(3)−V(3)−O(6)	174.27(10)	V(4)−O(6)−V(1)#2	92.69(7)
O(5)−V(1)−O(6)#2	80.29(7)	O(9)−V(3)−O(6)	81.78(8)	V(4)#2−O(6)−V(1)#2	92.69(7)
O(4)−V(1)−O(6)#2	76.10(7)	O(8)−V(3)−O(6)	78.91(8)	V(2)−O(6)−V(1)#2	171.29(12)
O(2)−V(2)−O(8)	102.10(9)	O(5)#3−V(3)−O(6)	76.98(8)	V(4)−O(6)−V(3)#1	170.26(9)
O(8)#1−V(2)−O(8)	93.30(12)	O(7)−V(3)−O(6)	74.59(7)	V(4)#2−O(6)−V(3)#1	87.70(2)
O(2)−V(2)−O(4)	99.95(9)	O(7)#3−V(4)−O(7)	107.59(14)	V(2)−O(6)−V(3)#1	85.34(7)
O(8)#1−V(2)−O(4)	156.39(8)	O(7)#3−V(4)−O(4)	97.26(8)	V(1)#2−O(6)−V(3)#1	88.12(7)
O(8)−V(2)−O(4)	90.21(8)	O(7)−V(4)−O(4)	97.01(8)	V(4)−O(6)−V(3)	87.70(2)
O(4)−V(2)−O(4)#1	77.74(10)	O(4)−V(4)−O(4)#3	155.73(11)	V(4)#2−O(6)−V(3)	170.26(9)
O(2)−V(2)−O(6)	175.33(12)	O(7)#3−V(4)−O(6)	165.23(9)	V(2)−O(6)−V(3)	85.34(7)
O(8)−V(2)−O(6)	81.04(7)	O(7)−V(4)−O(6)	87.18(8)	V(1)#2−O(6)−V(3)	88.12(7)
O(4)−V(2)−O(6)	76.47(7)	O(4)−V(4)−O(6)	80.49(8)	V(3)#1−O(6)−V(3)	82.62(8)
O(3)−V(3)−O(9)	103.64(11)	O(7)−V(4)−O(6)#2	165.23(9)	V(4)−O(7)−V(3)	110.49(10)
O(3)−V(3)−O(8)	102.44(10)	O(4)−V(4)−O(6)#2	80.72(8)	V(2)−O(8)−V(3)	113.89(10)
O(9)−V(3)−O(8)	92.80(11)	O(6)−V(4)−O(6)#2	78.05(10)	V(3)−O(9)−V(3)#1	113.65(14)
O(3)−V(3)−O(5)#3	100.95(10)	V(4)−O(4)−V(2)	107.84(8)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x, y, z$; #2, $-x-1, -y, -z+1$; #3, $-x-1, y, -z+1$; #4, $-x-1, -y-1, -z+2$.

in **3**. However, bond-valence calculations[25] indicate that the possible protonation sites are at the doubly bridging oxygens of the vanadium (O(5) and O(8)) as reported in the literature.[31,32]

The structure of **3** (Figure 7a) shows the presence of chains containing the inorganic anion and the organic cations running along [101]. Along the chain each decavanadate anion (A) is surrounded by two methylated HMTA cation (C), forming a sequence ···C—A—C··· C—A—C···C—A—C···. The anions on the *ac* planes are aligned such that their C_2 axes lie parallel to the *b* axis while the C_3 axis of the organic cation lies on the same plane but oriented along [101]. The substituted CH_3 groups at the N are pointed away from the anion. The chains on the adjacent *ac* planes are related by the lattice symmetry of the unit cell. The water molecules lie between the planes containing the chains. There is no appreciable hydrogen bonding between the water molecules and the anions or cations.

In **4**, HMTA-CH$_2$OH and HMTA-H are the countercations. Unlike **3**, in **4** there is no regular arrangement of the cations and anions (Figure 7b). There is medium to weak nonbonding interactions among the cations, the anions, and the space-filling water molecules. We could successfully locate only one proton attached to the cluster oxygen O(3). For several oxidized polyoxovanadates of the types, $[H_nV_{10}O_{28}]^{(6-n)-}$, it has been suggested that doubly and triply bridging oxo groups provide the protonation sites as a consequence of the greater basicity of these in relation to terminal oxo groups, a feature recently confirmed by ab initio SCF calculations.[32] However, we did not succeed in locating the remaining H atoms.

Chemistry of the Formation of Polyoxovanadates. Isolation of the polyoxovanadates **1**−**4** discussed in this paper, and **5**[35] and **6**[36] in our earlier work[13] (refer to Figures 8 and 9), in the presence of organic bases appears to be interesting. A number of metavanadates, decavanadates, and other isopolyvanadates in addition to several fully oxidized and mixed-valent high nuclear polyoxovanadate clusters have been crystallized from acidified, aqueous vanadate solution depending on the pH and oxidation state of vanadium. The role of organic base in dictating the final structure of the solids either in determining the shape and size of the molecular cluster or occurring as a countercation but influence the packing/linking of the inorganic anionic cores is important to understand the self-assembly process taking place in aqueous vanadate solution. In this work, we have investigated the formation of polyoxovanadates by varying pH of the initial solution, the molar ratio of the starting materials, the oxidation state of vanadium, and organic bases with varying geometry—planar to spherical. Attempts were made to grow single crystals either through solution evaporation or by hydrothermal treatment. In all our experiments one of the organic bases,

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(35) Synthesis and crystal data of **5**. A mixture of NaVO$_3$ (0.3 g, 2.5 mmol) and hexamethylenetetramine(0.34 g, 2.5 mmol) was dissolved in 60 mL of distilled water. pH of the clear solution was adjusted to 5.5 by HCl (0.3 mL, 8.0 mmol). Crystal data: crystal system, triclinic; space group, $P\bar{1}$; $a = 9.5759(1)$, $b = 10.4917(1)$, and $c = 11.1943(1)$ Å, $\alpha = 103.27(1)$, $\beta = 98.318(1)$, and $\gamma = 103.329(1)°$; $V = 1037.57(2)$ (Å)^3; $Z = 1$; $\rho_o = 2.329$ g/cm^3. A total of 4248 reflections with $Fo > 4s(Fo)$ and 349 parameters, and $R_1 = 0.03890$ and w$R_2 = 0.1141$ for all 4993 data.

(36) Synthesis and crystal data of **6**: A mixture of NaVO$_3$ (0.5 g, 4.1 mmol) and 1,3,5-triazine (0.03 g, 0.41 mmol) was dissolved in 60 mL of water in a 150-mL beaker. The pH of the clear solution was adjusted to 4.2 by the addition of HCl (0.4 mL, 2.0 mmol). Crystal data: crystal system, monoclinic; space group, $P2_1/n$; $a = 12.0627(2)$, $b = 17.1745(2)$, $c = 18.2094(2)$ Å, and $\beta = 106.34(1)°$; $V = 3620.56(8)$(Å)^3; $Z = 4$; $\rho_o = 2.379$ g/cm^3. A total of 5642 reflections with $Fo > 4s(Fo)$ and 597 parameters, and $R_1 = 0.0402$ and w$R_2 = 0.0902$ for all 8846 data.

Table 10. Selected Bond Distances(Å) and Angles (deg) for 4

V(1)−O(1)	1.610(4)	V(3)−O(13)	1.892(4)	V(6)−O(6)	1.603(4)	V(8)−O(21)	1.982(4)
V(1)−O(27)	1.825(4)	V(3)−O(17)	2.105(4)	V(6)−O(26)	1.816(4)	V(8)−O(20)	2.128(4)
V(1)−O(26)	1.853(4)	V(3)−O(10)	2.323(4)	V(6)−O(24)	1.868(4)	V(8)−O(10)	2.240(4)
V(1)−O(12)	1.963(4)	V(4)−O(4)	1.605(4)	V(6)−O(23)	1.969(4)	V(9)−O(17)	1.665(4)
V(1)−O(11)	2.016(4)	V(4)−O(14)	1.811(4)	V(6)−O(28)	2.008(4)	V(9)−O(28)	1.704(4)
V(1)−O(9)	2.290(4)	V(4)−O(15)	1.834(4)	V(6)−O(9)	2.307(4)	V(9)−O(11)	1.868(4)
V(2)−O(2)	1.604(4)	V(4)−O(18)	1.939(4)	V(7)−O(7)	1.611(4)	V(9)−O(20)	2.047(4)
V(2)−O(13)	1.781(4)	V(4)−O(19)	2.028(4)	V(7)−O(22)	1.758(4)	V(9)−O(10)	2.063(4)
V(2)−O(14)	1.821(4)	V(4)−O(10)	2.425(4)	V(7)−O(23)	1.904(4)	V(9)−O(9)	2.142(4)
V(2)−O(11)	2.014(4)	V(5)−O(5)	1.604(4)	V(7)−O(21)	1.953(4)	V(10)−O(25)	1.692(4)
V(2)−O(12)	2.029(4)	V(5)−O(24)	1.791(4)	V(7)−O(20)	2.101(4)	V(10)−O(19)	1.703(4)
V(2)−O(10)	2.257(4)	V(5)−O(27)	1.879(4)	V(7)−O(9)	2.230(4)	V(10)−O(12)	1.902(4)
V(3)−O(3)	1.590(4)	V(5)−O(22)	1.923(4)	V(8)−O(8)	1.606(4)	V(10)−O(21)	1.949(4)
V(3)−O(15)	1.819(4)	V(5)−O(25)	2.065(4)	V(8)−O(18)	1.751(4)	V(10)−O(9)	2.112(4)
V(3)−O(16)	1.877(4)	V(5)−O(9)	2.335(4)	V(8)−O(16)	1.867(4)	V(10)−O(10)	2.120(4)
O(1)−V(1)−O(27)	103.1(2)	O(14)−V(4)−O(19)	85.2(2)	O(6)−V(6)−O(26)	103.2(2)	O(28)−V(9)−O(10)	162.9(2)
O(1)−V(1)−O(26)	103.1(2)	O(15)−V(4)−O(19)	152.7(2)	O(6)−V(6)−O(24)	103.5(2)	O(11)−V(9)−O(10)	83.7(2)
O(27)−V(1)−O(26)	93.2(2)	O(18)−V(4)−O(19)	82.3(2)	O(26)−V(6)−O(24)	91.6(2)	O(20)−V(9)−O(10)	79.0(2)
O(1)−V(1)−O(12)	100.3(2)	O(4)−V(4)−O(10)	175.2(2)	O(6)−V(6)−O(23)	101.2(2)	O(17)−V(9)−O(9)	166.2(2)
O(27)−V(1)−O(12)	91.6(2)	O(14)−V(4)−O(10)	77.2(2)	O(26)−V(6)−O(23)	155.0(2)	O(28)−V(9)−O(9)	85.6(2)
O(26)−V(1)−O(12)	154.4(2)	O(15)−V(4)−O(10)	80.1(2)	O(24)−V(6)−O(23)	87.8(2)	O(11)−V(9)−O(9)	82.5(2)
O(1)−V(1)−O(11)	100.1(2)	O(18)−V(4)−O(10)	75.7(2)	O(6)−V(6)−O(28)	100.7(2)	O(20)−V(9)−O(9)	78.40(14)
O(27)−V(1)−O(11)	155.7(2)	O(19)−V(4)−O(10)	72.81(14)	O(26)−V(6)−O(28)	87.3(2)	O(10)−V(9)−O(9)	77.75(14)
O(26)−V(1)−O(11)	88.2(2)	O(5)−V(5)−O(24)	103.8(2)	O(24)−V(6)−O(28)	155.3(2)	O(25)−V(10)−O(19)	107.5(2)
O(12)−V(1)−O(11)	77.5(2)	O(5)−V(5)−O(27)	102.5(2)	O(23)−V(6)−O(28)	83.0(2)	O(25)−V(10)−O(12)	98.9(2)
O(1)−V(1)−O(9)	175.2(2)	O(24)−V(5)−O(27)	91.9(2)	O(6)−V(6)−O(9)	174.7(2)	O(19)−V(10)−O(12)	96.8(2)
O(27)−V(1)−O(9)	80.6(2)	O(5)−V(5)−O(22)	100.8(2)	O(26)−V(6)−O(9)	79.8(2)	O(25)−V(10)−O(21)	96.1(2)
O(26)−V(1)−O(9)	79.6(2)	O(24)−V(5)−O(22)	92.7(2)	O(24)−V(6)−O(9)	80.7(2)	O(19)−V(10)−O(21)	96.2(2)
O(12)−V(1)−O(9)	76.43(14)	O(27)−V(5)−O(22)	154.4(2)	O(23)−V(6)−O(9)	75.4(2)	O(12)−V(10)−O(21)	156.2(2)
O(11)−V(1)−O(9)	75.76(14)	O(5)−V(5)−O(25)	100.9(2)	O(28)−V(6)−O(9)	74.83(14)	O(25)−V(10)−O(9)	87.7(2)
O(2)−V(2)−O(13)	103.6(2)	O(24)−V(5)−O(25)	155.3(2)	O(7)−V(7)−O(22)	103.6(2)	O(19)−V(10)−O(9)	164.7(2)
O(2)−V(2)−O(14)	103.4(2)	O(27)−V(5)−O(25)	83.1(2)	O(7)−V(7)−O(23)	101.1(2)	O(12)−V(10)−O(9)	82.2(2)
O(13)−V(2)−O(14)	95.4(2)	O(22)−V(5)−O(25)	82.2(2)	O(22)−V(7)−O(23)	95.4(2)	O(21)−V(10)−O(9)	80.1(2)
O(2)−V(2)−O(11)	98.4(2)	O(5)−V(5)−O(9)	174.6(2)	O(7)−V(7)−O(21)	101.4(2)	O(25)−V(10)−O(10)	164.8(2)
O(13)−V(2)−O(11)	91.1(2)	O(24)−V(5)−O(9)	81.5(2)	O(22)−V(7)−O(21)	94.4(2)	O(19)−V(10)−O(10)	87.6(2)
O(14)−V(2)−O(11)	155.0(2)	O(27)−V(5)−O(9)	78.4(2)	O(23)−V(7)−O(21)	152.5(2)	O(12)−V(10)−O(10)	81.0(2)
O(2)−V(2)−O(12)	99.6(2)	O(22)−V(5)−O(9)	77.5(2)	O(7)−V(7)−O(20)	97.3(2)	O(21)−V(10)−O(10)	79.8(2)
O(13)−V(2)−O(12)	154.9(2)	O(25)−V(5)−O(9)	73.8(2)	O(22)−V(7)−O(20)	158.4(2)	O(9)−V(10)−O(10)	77.20(14)
O(14)−V(2)−O(12)	88.4(2)	V(3)−O(3)−H(3)	124(5)	O(23)−V(7)−O(20)	85.8(2)	V(2)−O(10)−V(4)	82.82(11)
O(11)−V(2)−O(12)	76.0(2)	V(10)−O(9)−V(9)	101.2(2)	O(21)−V(7)−O(20)	76.0(2)	V(3)−O(10)−V(4)	81.12(11)
O(2)−V(2)−O(10)	172.7(2)	V(10)−O(9)−V(7)	92.3(2)	O(7)−V(7)−O(9)	172.6(2)	V(9)−O(11)−V(2)	105.6(2)
O(13)−V(2)−O(10)	81.0(2)	V(9)−O(9)−V(7)	98.6(2)	O(22)−V(7)−O(9)	83.7(2)	V(9)−O(11)−V(1)	109.0(2)
O(14)−V(2)−O(10)	81.6(2)	V(10)−O(9)−V(1)	90.37(13)	O(23)−V(7)−O(9)	78.6(2)	V(2)−O(11)−V(1)	99.0(2)
O(11)−V(2)−O(10)	75.66(14)	V(9)−O(9)−V(1)	91.02(13)	O(21)−V(7)−O(9)	77.06(14)	V(10)−O(12)−V(1)	107.9(2)
O(12)−V(2)−O(10)	75.04(14)	V(7)−O(9)−V(1)	169.3(2)	O(20)−V(7)−O(9)	75.35(14)	V(10)−O(12)−V(2)	108.0(2)
O(3)−V(3)−O(15)	103.2(2)	V(10)−O(9)−V(6)	170.2(2)	O(8)−V(8)−O(18)	103.9(2)	V(1)−O(12)−V(2)	100.3(2)
O(3)−V(3)−O(16)	101.5(2)	V(9)−O(9)−V(6)	87.44(14)	O(8)−V(8)−O(16)	101.1(2)	V(2)−O(13)−V(3)	115.2(2)
O(15)−V(3)−O(16)	92.9(2)	V(7)−O(9)−V(6)	91.08(13)	O(18)−V(8)−O(16)	96.1(2)	V(4)−O(14)−V(2)	117.2(2)
O(3)−V(3)−O(13)	102.5(2)	V(1)−O(9)−V(6)	84.74(13)	O(8)−V(8)−O(21)	100.1(2)	V(3)−O(15)−V(4)	115.5(2)
O(15)−V(3)−O(13)	90.7(2)	V(10)−O(9)−V(5)	87.99(14)	O(18)−V(8)−O(21)	95.2(2)	V(8)−O(16)−V(3)	112.8(2)
O(16)−V(3)−O(13)	154.1(2)	V(9)−O(9)−V(5)	170.0(2)	O(16)−V(8)−O(21)	152.7(2)	V(9)−O(17)−V(3)	108.7(2)
O(3)−V(3)−O(17)	100.6(2)	V(7)−O(9)−V(5)	84.74(12)	O(8)−V(8)−O(20)	98.1(2)	V(8)−O(18)−V(4)	115.5(2)
O(15)−V(3)−O(17)	156.1(2)	V(1)−O(9)−V(5)	85.03(13)	O(18)−V(8)−O(20)	157.2(2)	V(10)−O(19)−V(4)	113.1(2)
O(16)−V(3)−O(17)	84.3(2)	V(6)−O(9)−V(5)	83.10(12)	O(16)−V(8)−O(20)	85.4(2)	V(9)−O(20)−V(7)	106.1(2)
O(13)−V(3)−O(17)	82.0(2)	V(9)−O(10)−V(10)	103.6(2)	O(21)−V(8)−O(20)	74.8(2)	V(9)−O(20)−V(8)	104.9(2)
O(3)−V(3)−O(10)	173.5(2)	V(9)−O(10)−V(8)	100.53(14)	O(8)−V(8)−O(10)	171.3(2)	V(7)−O(20)−V(8)	96.5(2)
O(15)−V(3)−O(10)	83.3(2)	V(10)−O(10)−V(8)	92.56(14)	O(18)−V(8)−O(10)	84.4(2)	V(10)−O(21)−V(7)	106.7(2)
O(16)−V(3)−O(10)	77.9(2)	V(9)−O(10)−V(2)	91.4(2)	O(16)−V(8)−O(10)	80.3(2)	V(10)−O(21)−V(8)	106.6(2)
O(13)−V(3)−O(10)	77.0(2)	V(10)−O(10)−V(2)	93.2(2)	O(21)−V(8)−O(10)	76.17(14)	V(7)−O(21)−V(8)	106.6(2)
O(17)−V(3)−O(10)	72.93(14)	V(8)−O(10)−V(2)	165.2(2)	O(20)−V(8)−O(10)	73.43(13)	V(7)−O(22)−V(5)	113.4(2)
O(4)−V(4)−O(14)	104.7(2)	V(9)−O(10)−V(3)	88.84(14)	O(17)−V(9)−O(28)	106.8(2)	V(7)−O(23)−V(6)	113.5(2)
O(4)−V(4)−O(15)	104.1(2)	V(10)−O(10)−V(3)	167.5(2)	O(17)−V(9)−O(11)	101.2(2)	V(5)−O(24)−V(6)	114.6(2)
O(14)−V(4)−O(15)	92.0(2)	V(8)−O(10)−V(3)	86.19(14)	O(28)−V(9)−O(11)	98.0(2)	V(10)−O(25)−V(5)	110.4(2)
O(4)−V(4)−O(18)	102.0(2)	V(2)−O(10)−V(3)	85.26(12)	O(17)−V(9)−O(20)	94.4(2)	V(6)−O(26)−V(1)	115.2(2)
O(14)−V(4)−O(18)	152.4(2)	V(9)−O(10)−V(4)	168.8(2)	O(28)−V(9)−O(20)	94.1(2)	V(1)−O(27)−V(5)	115.1(2)
O(15)−V(4)−O(18)	88.1(2)	V(10)−O(10)−V(4)	86.38(13)	O(11)−V(9)−O(20)	156.5(2)	V(9)−O(28)−V(6)	111.7(2)
O(4)−V(4)−O(19)	102.9(2)	V(8)−O(10)−V(4)	83.92(13)	O(17)−V(9)−O(10)	89.4(2)		

morpholine, HMTA, 1,3,5-triazine, triethanolamine, or ethylenediamine (en) was employed. Under hydrothermal treatment, only "en" yielded single crystals which were found to be identical to V_4O_{10} clusters reported in the literature.[7] Except for the conditions reported for compounds **1−6**, we invariably obtained materials which were either amorphous precipitates or crystalline powders that are difficult to characterize and hence are not included in this discussion.

The formation of morpholinium metavanadate at pH ∼8 was not surprising, but we did not obtain metavanadate with other bases. For pH <6, only morpholine yielded isopolyvanadate whereas decavanadates were the only species with HMTA and 1,3,5-triazine. When

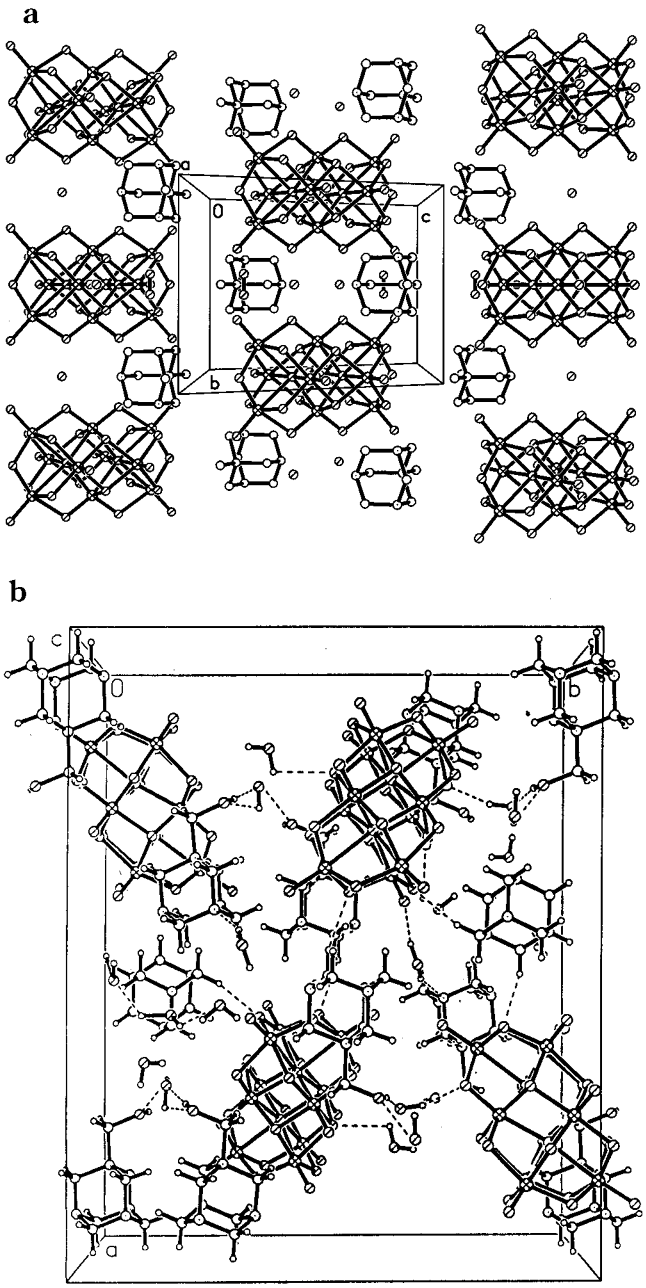

Figure 7. (a) Unit cell of the structure of **3** viewed down the crystallographic *a*-axis. (b) Crystal structure of **4** viewed along the *ab* plane. The hydrogen bonds are indicated by broken lines.

pH <2, we invariably obtained polycrystalline materials similar to vanadia xerogels with most of the bases. The relationship between the reaction conditions and the nature of molecular clusters is still far from understood. It appears that lower pH values in the range 2.0−6.0 are ideal for the formation of self-assembled polyoxoanions.

Use of HMTA has resulted only in the formation of decavanadate clusters; the solids differ in terms of the nature of the countercations and the packaging arrangement of inorganic and organic units. Under acidic conditions N-substituted cations of HMTA such as N−H, N−Me, and N−CH_2OH are present in the solution.[37−39] Compounds **4** and **5** were isolated from similar reaction condition except for the source of vanadium. In both solids HMTA-CH_2OH and HMTA-H were present as countercations. Compound **4** contained discrete mixed-valent decavanadate cores as $VOSO_4$ was used in the synthesis. Compound **5** was synthesized from $NaVO_3$, and hence the decavanadates were fully oxidized but the presence of hydrated sodium cations in the solution were possibly responsible for the linking of the decavanadate clusters to form molecular chains. Alhough linking of oxovanadate clusters through hydrated metal cations are known in the literature,[40] **5** exhibits a unique structure. Formation of **3** is a little surprising, since the initial solution contained sodium hydrates as well as reduced vanadates. Still, in the final solid, the decavanadates occurred as discrete clusters with only organic species as countercations. But the presence of N−Me in **3** is understandable as it is obtained from the reduction of N−CH_2OH by $NaBH_4$. The facile formation of structurally unprecedented **5** and **6** points out that the inorganic fragments of a self-assembled system can be easily linked to metal hydrates toward the formation of an unusual higher order molecular chains and rectangular arrays. The occurrence of an unusual dimer of hydrated sodium, $[Na_2(H_2O)_{10}]^{2+}$ in **6** is difficult to explain. Also, this material is an interesting case wherein the organic molecule 1,3,5-triazine did not figure in the final solid but the solid did not form in its absence.

The crystal topology of the six novel inorganic−organic hybrid salts **1**−**6**, emphasize the criteria caused for the crystallization of such oxo anion cores exhibiting interactions with cations. To maximize the intermolecular contacts the packing of inorganic fragments depend on the organic cations which exhibit specific interactions. In **1**, the morpholinium ions participate in strong nonbonding interactions with the cluster oxygens and hence strongly influence the packing of the hybrid salt. In **3**, the hydrophobic nature of HMTA-Me forces the anionic fragments to stack one over the other. Whereas in **4**, the occurrence of hydrogen bonding between the N-substituted HMTA and lattice water results in a disordered arrangement of the organic and inorganic units. In **5** and **6**, the sodium hydrates link the anionic clusters to form one-dimensional chains and two-dimensional arrays.

Conclusions

The formation of the four novel hybrid salts of polyoxovanadate clusters reported in this paper signifies the richness of the influence of molecules such as morpholine and HMTA and the role of pH in obtaining new vanadates. A pH of >8 seems to favor the formation of metavanadates (V^V) with infinite chains forming layers such as **2** and the morpholinium ions occur between the layers as countercations; on the other hand, acidic conditions (pH <5) are more favorable to form isopolyvanadates or decavanadates. The choice of the countercations depends on the reaction conditions and

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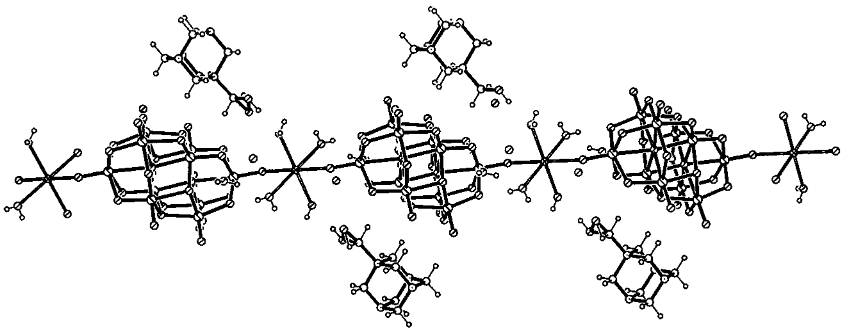

Figure 8. A view of decavanadate chains connected through hydrated sodium cations, $[Na(H_2O)_4]^+$.

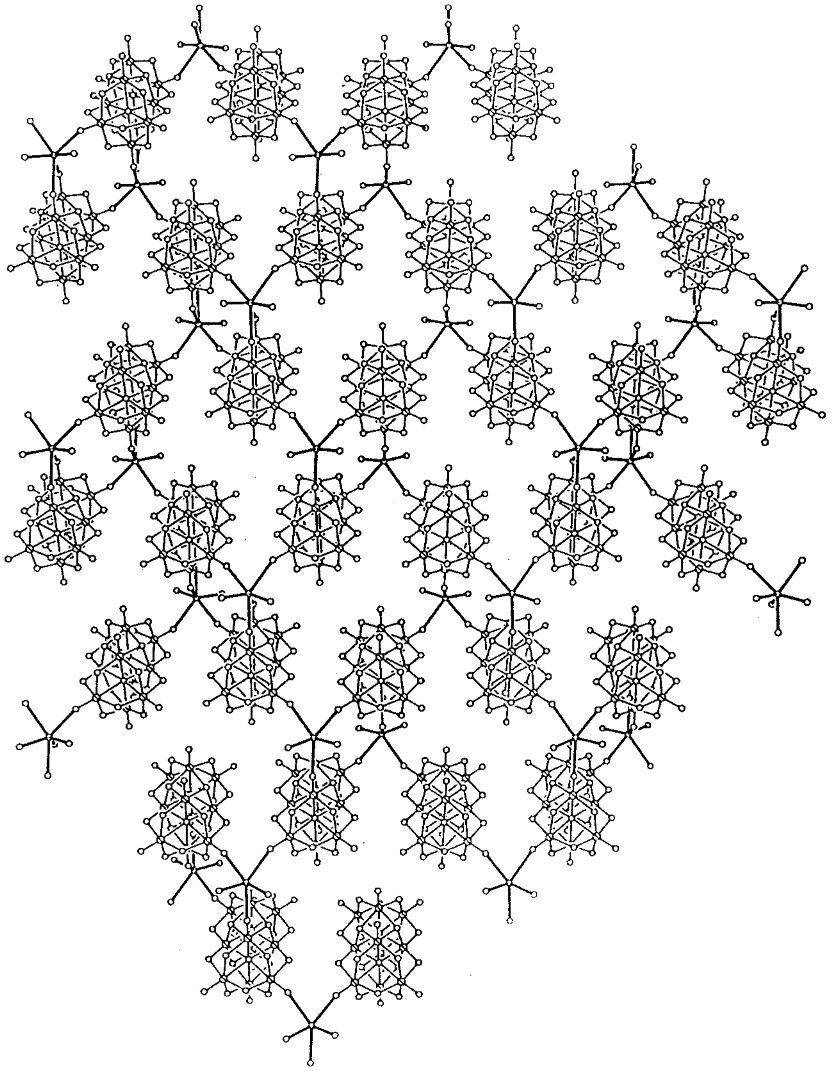

Figure 9. A view of 2D molecular arrays of decavanadate clusters through hydrated sodium cations.

mostly these molecules influence the crystal packing. Controlling the oxidation state of vanadium appears to be difficult at this stage. Our attempts to grow vanadate crystals with average oxidation state < 4.5 have not been successful.

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Supporting Information Available: Complete tables of crystallographic conditions, atomic positional parameters, listings of bond distances and angles and anisotropic temperature factors for compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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