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A NEW POLYOXOVANADIUM SUPRAMOLECULAR COMPLEX [(N(CH$_2$CH$_2$NH$_3$)$_3$)$_2$(V$_6$O$_{18}$)]·3H$_2$O: SYNTHESIS, STRUCTURE, AND THERMAL PROPERTIES

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A new polyoxovanadium supramolecular complex, [(N(CH$_2$CH$_2$NH$_3$)$_3$)$_2$(V$_6$O$_{18}$)]·3H$_2$O (**1**), was synthesized as a crystalline product from aqueous solution at room temperature. From single crystal X-ray structural analysis, the complex is monoclinic, space group *P*2$_1$/*n*, with *a* = 15.878(2), *b* = 11.3309(15), *c* = 19.469(3) Å, β = 102.244(2)°, *V* = 3423.0(8) Å^3, *Z* = 4, final *R* = 0.0469. The crystal structure comprises 1D spiral vanadate chain as the oxide moiety, doubly protonated cations of tris(2-aminoethyl)amine (tren) and three lattice molecules of water. There are numerous H bonds in the structure connecting the polyoxovanadium anion moiety, protonated tren cation and lattice water molecules; the average O…O and N…O distances are 2.753 Å for O—H…O and 2.879 Å for N—H…O, respectively.

K e y w o r d s: polyoxovanadate complex, hydrogen bonds, tris(2-aminoethyl)amine, tren, crystal structure.

The past few years have witnessed rapidly growing interest in vanadium chemistry and its potential applications for anode and cathode materials in advanced lithium batteries [1—3] and industrial oxidative catalysts [4]. Recently, the hydrothermal process in combination with organic templates has been used to synthesize a number of vanadium oxides with discrete clusters [5—11]. Muller′s work has underscored the significant role played by templates in the formation of unusual structures of polyoxovanadates [12—15]. Up to the present, three classes of polyoxovanadium complexes have been reported: (i) Organic subunit incorporated as organoammonium cation. Examples are [C$_5$H$_6$N][V$_3$O$_7$] [16], [C$_6$H$_{14}$N]$_5$[V$_5$O$_{15}$] [17], [CH$_3$NH$_3$]$_2$[V$_3$O$_{10}$] [18], [HN(C$_2$H$_4$)$_3$NH][V$_6$O$_{14}$] [19], [H$_3$N(CH$_2$)$_4$NH$_3$][V$_4$O$_9$] [20], [H$_3$N(CH$_2$)$_3$NH$_3$][V$_4$O$_{10}$] [21], [NMe$_4$]$_5$[V$_{18}$O$_{46}$] [22], [HMTA—CH$_3$]$_4$[H$_2$V$_{10}$O$_{28}$] [23], [H$_3$N(CH$_2$)$_3$NH$_3$]$_{0.5}$[V$_2$O$_5$] [24]. (ii) Organodiamine as ligand coordinated to vanadium oxide skeleton. [V$_9$O$_{21}$(2,2′-bipy)$_4$] [25], [V$_9$O$_{22}$(Terpy)$_3$] [26], [{VO$_2$(2,2′-bipy)}$_2$(tp)] (tp = terephthalate) [27], K$_8$[V$_{24}$O$_{24}$(C$_4$O$_4$)$_{12}$(OCH$_3$)$_{32}$] [28], [V$_2$O$_4$(Terpy)$_2$]$_3$[V$_{10}$O$_{28}$] [26]. (iii) Organodiamines as ligands coordinated to heterometals. [Co$_3$(bpypr)$_4$(H$_2$O)$_4$V$_6$O$_{18}$] [29], Co(dien)$_2$(VO$_3$)$_3$·H$_2$O [30], [{Cd(phen)$_2$}$_2$V$_4$O$_{12}$]·5H$_2$O [31], [Cd(enMe)$_2$][V$_8$O$_{20}$] [32], [Cu(pyz)$_2$(V$_6$O$_{16}$)]·0.22H$_2$O [33], [Cu$_3$(tpytrz)$_2$(H$_2$O)$_2$V$_8$O$_{23}$] [34], [Zn(2,2′-bipy)$_2$]$_2$[V$_6$O$_{17}$] [35]. In these complexes, ammonia derivatives (N(CH$_3$)$_4^+$, CH$_3$NH$_2$) or diamines H$_2$N—(CH$_2$)$_n$—NH$_2$ (*n* = = 2, 3, 4) are used as organic templates, and an organic constituent is present as a charge compensating, space filling and structure directing subunit. To our knowledge, complexes containing infinite chains [V$_6$O$_{18}^{6-}$]$_\infty$ of VO$_4$ tetrahedra with tris(2-aminoethyl)amine as organic constituent have not been reported up to now.

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Tris(2-aminoethyl)amine (tren) is extensively used as a ligand [36, 37] due to its ability to achieve various open framework structures and its strong basic properties. We adopted a simple method to obtain the title polyoxovanadium complex with tren as organic constituent in aqueous system under room temperature conditions, the method being different from that reported in the literature. Here, we report synthesis, structure, and thermal properties of $[(N(CH_2CH_2NH_3)_3)_2(V_6O_{18})] \cdot 3H_2O$ (**1**).

EXPERIMENTAL

Reagents and measurements. All chemicals purchased were of reagent grade and used as such. CHN analyses were performed on a Perkin Elmer 240C automatic analyzer. Analysis for vanadium was performed on plasma-Spec(I)-AES spectrometer (ICP). The infrared spectra were recorded on a JASCO FT/IR-480 PLUS Fourier Transform spectrometer with pressed KBr pellets in the range of 200—4000 cm^{-1}. Thermogravimetric analysis (TGA) experiments were carried out on a Perkin Elmer Diamond TG—DTG—DTA instrument.

Synthesis. The complex $[(N(CH_2CH_2NH_3)_3)_2(V_6O_{18})] \cdot 3H_2O$ was prepared by adding tren (0.4 ml, ~2.8 mmol) into a stirring solution of $VOSO_4 \cdot nH_2O$ (71 % of $VOSO_4$) (0.230 g, 1 mmol) in water (10 ml). The components reacted for about 2 h and the color of solution changed from light—blue to yellow, with a small amount of precipitate formed. The precipitate was filtered and discarded; the filtrate was kept in air for 4 days. Light yellow crystals were obtained, dried under vacuum to afford 0.10 g of the product, with the yield of 63.55 % (based on V). Calcd for $C_{12}H_{48}N_8O_{21}V_6$ (%): C 15.22, H 5.07, N 11.84, V 32.28. Found (%): C 15.25, H 4.87, N 11.86, V 32.39.

X-ray structural analysis. A crystal of **1** was mounted on a glass fiber. Data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite—monochromated MoK_α radiation ($\lambda = 0.71073$ Å) in multi-scan mode. Absorption corrections were introduced using SADABS [38]. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. H atoms were positioned geometrically and refined using a riding model except for water molecules and one hydrogen atom of each amino group from the protonated tren which were located from the difference Fourier maps and refined isotropically. Hydrogen atoms of one of lattice water molecule (O20) could not be located from the difference Fourier map. All calculations were performed using SHELX-97 [39].

The crystal data, data collection, and refinement details are summarized in Table 1. Selected bond distances and angles are given in Table 2. Full crystallographic data have been deposited with the

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Summary of crystallographic data for complex **1**

Formula	$C_{12}H_{48}N_8O_{21}V_6$	$\mu(MoK_\alpha)/cm^{-1}$	16.60
M	946.22	θ, deg.	1.86 to 25.00
Crystal system, space group	Monoclinic, $P2_1/n$	Reflections collected	16700
		Independent reflections ($I > 2\sigma(I)$)	4642
a, b, c, Å	9.4772(2), 16.853(3), 12.031(2)	Parameters	449
β, deg.	107.25(3)	Residuals, e·Å^{-3}	0.814 and −0.629
V, Å^3	1835.1(6)	GOOF	1.092
Z	4	R^a	0.0469 (0.0629)^b
D_{calc}, g/cm^3	1.836	$wR_2{}^a$	0.1243 (0.1337)^b
Crystal size, mm	0.22×0.15×0.29		

[a] $R = \sum||Fo| - |Fc||/\sum|Fo|$, $wR_2 = [\sum(w(Fo^2 - Fc^2)^2/[\sum(w(Fo^2)^2)^{1/2}$; $[Fo > 4\sigma(Fo)]$.
[b] Based on all data.

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Selected bond distances (Å) *and angles* (deg.) *for complex* **1**

V(1)—O(3)	1.622(3)	V(3)—O(9)	1.627(3)	V(5)—O(15)	1.637(4)
V(1)—O(1)	1.628(4)	V(3)—O(8)	1.656(3)	V(5)—O(16)	1.784(3)
V(1)—O(2)	1.789(4)	V(3)—O(10)	1.777(3)	V(5)—O(13)	1.786(4)
V(1)—O(4)	1.799(3)	V(3)—O(7)	1.785(3)	V(6)—O(17)	1.622(4)
V(2)—O(6)	1.626(3)	V(4)—O(12)	1.636(3)	V(6)—O(18)	1.658(3)
V(2)—O(5)	1.647(3)	V(4)—O(11)	1.655(4)	V(6)—O(16)	1.762(3)
V(2)—O(4)	1.773(3)	V(4)—O(13)	1.753(3)	V(6)—O(2)[#1]	1.777(4)
V(2)—O(7)	1.798(3)	V(4)—O(10)	1.789(3)	O(2)—V(6)[#2]	1.777(4)
		V(5)—O(14)	1.609(4)		
O(18)—V(6)—O(2)[#1]	110.73(17)	O(6)—V(2)—O(5)	108.46(18)	O(11)—V(4)—O(13)	108.9(2)
O(16)—V(6)—O(2)[#1]	111.63(19)	O(6)—V(2)—O(4)	109.28(19)	O(12)—V(4)—O(10)	110.91(17)
V(6)[#2]—O(2)—V(1)	134.0(2)	O(5)—V(2)—O(4)	110.48(18)	O(11)—V(4)—O(10)	106.77(19)
V(2)—O(4)—V(1)	143.3(2)	O(6)—V(2)—O(7)	106.12(17)	O(13)—V(4)—O(10)	112.54(18)
V(3)—O(7)—V(2)	151.2(2)	O(5)—V(2)—O(7)	110.63(16)	O(14)—V(5)—O(15)	107.7(2)
V(3)—O(10)—V(4)	131.09(18)	O(4)—V(2)—O(7)	111.72(17)	O(14)—V(5)—O(16)	111.3(2)
V(4)—O(13)—V(5)	152.5(3)	O(9)—V(3)—O(8)	109.51(17)	O(15)—V(5)—O(16)	111.68(18)
V(6)—O(16)—V(5)	162.6(2)	O(9)—V(3)—O(10)	108.91(17)	O(14)—V(5)—O(13)	112.1(3)
O(3)—V(1)—O(1)	109.4(2)	O(8)—V(3)—O(10)	110.80(15)	O(15)—V(5)—O(13)	109.0(2)
O(3)—V(1)—O(2)	107.88(17)	O(9)—V(3)—O(7)	109.65(17)	O(16)—V(5)—O(13)	105.03(17)
O(1)—V(1)—O(2)	108.8(2)	O(8)—V(3)—O(7)	109.11(16)	O(17)—V(6)—O(18)	107.45(19)
O(3)—V(1)—O(4)	109.03(18)	O(10)—V(3)—O(7)	108.85(16)	O(17)—V(6)—O(16)	106.60(19)
O(1)—V(1)—O(4)	112.5(2)	O(12)—V(4)—O(11)	105.53(19)	O(18)—V(6)—O(16)	111.13(17)
O(2)—V(1)—O(4)	109.2(2)	O(12)—V(4)—O(13)	111.79(19)	O(17)—V(6)—O(2)#1	109.1(2)

N o t e : Symmetry transformations used to generate equivalent atoms: #1 *x*+1, *y*, *z*; #2 *x*–1, *y*, *z*.

RESULTS AND DISCUSSION

Crystal structure. Recent papers and reviews have emphasized the predominance of hydrothermal synthesis for polyoxovanadate complexes and demonstrated great flexibility of polyoxovanadates to adopt a wide range of clusters, chains and frameworks [40, 41]. However, the method used in this work to synthesize the title complex under room temperature conditions is different and reported here for the first time. In addition, the title complex was also obtained from NH_4VO_3, Na_3VO_4 and V_2O_5 as starting materials replacing $VOSO_4$.

The introduction of tren as organic constituent results in a unique complex **1**. IR spectrum of the title complex showed a band at 3396 cm^{-1} attributed to N—H stretching of the NH_3 from protonated tren groups and band at 2923 cm^{-1} can be assigned to the aliphatic C—H stretching vibration of CH_2 from protonated tren groups. The bands at 955, 921 and 653 cm^{-1} were associated with the stretching vibrations of V=O$_t$ and V—O—V.

The asymmetric unit of the title structure $[(N(CH_2CH_2NH_3)_3)_2(V_6O_{18})]\cdot 3H_2O$ (Fig. 1) consists of anionic cluster $[V_6O_{18}]^{6-}$ that is a zigzag chain of {VO$_4$} corner-sharing tetrahedra, and cations $[N(CH_2CH_2NH_3)_3]^{3+}$ which acts as space filling and charge—compensating species. Vanadate chains
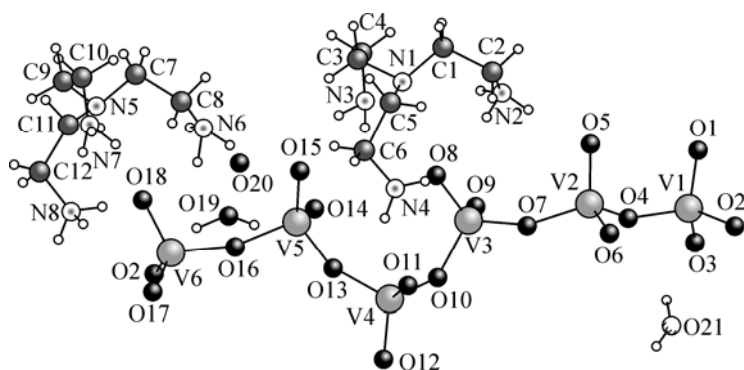
Fig. 1. Complex **1** (asymmetric unit) with the hydrogen atoms

linked by corner-sharing {VO$_4$} tetrahedra are a common feature of organobimetallic vanadates, and the chains can display very distinctive structural roles in the presence of ligand components but the title complex does not contain a secondary metal. Each vanadium from infinite chains [V$_6$O$_{18}^{6-}$]$_\infty$ of VO$_4$ tetrahedra is surrounded by two terminal oxygen atoms with distances in the range of 1.609(4)—1.799(3) Å (average V—O$_t$ = 1.635(3) Å) and two bridging oxygen atoms with distances in the range of 1.753(3)—1.799(3) Å (average V—O$_b$ = 1.781(3) Å). O—V—O angles in the infinite chains [V$_6$O$_{18}^{6-}$]$_\infty$ are in the range of 105.0(2)—112.5(1)° (average O—V—O = 109.4(1)°) and V—O—V angles in the range of 131.1(2)—162.6(2)° (average V—O—V = 145.8 (5)°). For complexes **1—8** (see Table 3 for designations), the average distances V—O$_t$ fall into three classes: the range of 1.602(2)—1.635(5) Å for complexes **1**, **3**, **5** and **6**; shorter bonds 1.573(6)—1.589(2) Å for complexes **7** and **8**; longer bonds 1.637(2)—1.660(2) Å for complexes **2** and **4**. The distances V—O$_b$(M) (M = Zn, Co, Mn, Ni, etc.) (average V—O(M) = 1.7280(2) Å) are shorter than the distances V—O$_b$(V) (average V—O(V) = 1.8014(2) Å). The angles O—V—O in **1** (105.0(3)—111.8(1)°) are similar to those in the complexes **3**, **4**, **7** and **8** (106.8(2)—111.9(1)°).

Numerous hydrogen bonds are found in **1**, as shown in Fig. 2. A hydrogen—bonding network is formed by polyoxovanadium infinite chains [V$_6$O$_{18}^{6-}$]$_\infty$ of VO$_4$ tetrahedra and molecules of lattice water along *c* axis (Fig. 2, *a*). In the hydrogen-bonding packing of the molecules, three lattice water molecules play different roles: (i) O19 forms an intra-chain bridging hydrogen bonds with oxygen atoms (O14B, O9B) from infinite chains [V$_6$O$_{18}^{6-}$]$_\infty$. (ii) O20 forms an inter-chain bridging hydrogen bond with oxygen atoms (O14A, O3) from different infinite chains [V$_6$O$_{18}^{6-}$]$_\infty$ of VO$_4$ tetrahedra. (iii) O21 forms a terminal hydrogen bonding with oxygen atom (O12D) from infinite chains [V$_6$O$_{18}^{6-}$]$_\infty$. The 3D supramolecular network made by the intra- and inter-hydrogen bonds between the protonated tren groups and oxygen atoms from infinite chains [V$_6$O$_{18}^{6-}$]$_\infty$ of VO$_4$ tetrahedra is shown in Fig. 2, *b*.
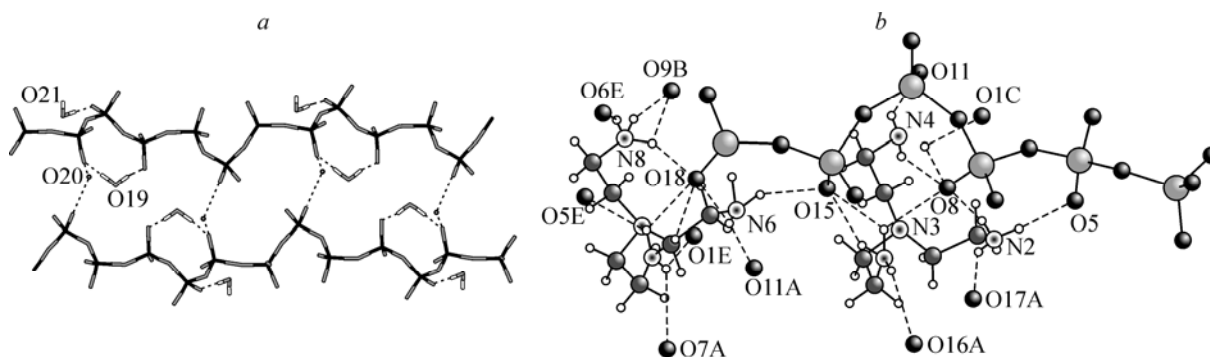

Fig. 2. H bonds between the water molecules and infinite chains [V$_6$O$_{18}^{6-}$]$_\infty$ of VO$_4$ tetrahedra in **1** — *a*; H bonds between protonated tren groups and infinite chains [V$_6$O$_{18}^{6-}$]$_\infty$ of VO$_4$ tetrahedra in **1** — *b*

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Selected distances (Å) *and angles* (deg.) *for complex* **1** *and similar complexes**

	V—O_t	V—O_b(V)	V—O_b(M)	O—V—O	V—O—V	Refs
1	1.635(3)	1.781(3)	—	109.4(1)	145.8(5)	this work
2	1.673(2)	1.794(2)	—	111.1(1); 109.1(1)	135.2(1); 155.7(1)	42
3	1.618(4)	1.791(4)	1.662(4)	109.5(3)	123.9(2); 150.9(2)	43
4	1.660(2)	1.772(3)	1.662(2)	109.4(1); 109.5(1)	147.5(1); 129.1(1)	44
5	1.602(2); 1.617(2)	1.786(2)	1.639(2)	107.3(1); 111.9(1)	129.9(1); 154.2(2)	45
6	1.616(3)	1.787(4)	1.687(3)	106.8(2); 111.3(2)	118.2(2); 152.8(2)	45
7	1.589(2)	1.735(2); 2.059(2)	—	—	—	46
8	1.573(6)		1.962(5)	87.7(2); 129.1(3)	—	47

* **1**: [(N(CH₂CH₂NH₃)₃)₂]₂(V₆O₁₈)]·3H₂O; **2**: [{Zn(2,2′-bipy)₃}₂V₄O₁₂]·11H₂O; **3**: [{Zn(phen)₂}(V₄O₁₂)]·H₂O; **4**: Co₂(4,4′-bipy)₂(V₄O₁₂); **5**: Ni(dien)V₂O₆; **6**: Cu(dien)V₂O₆; **7**: [V^{IV}V$_2^V$O₇(phen)]ₙ; **8**: (VO)₄(4,4′-bipy)₂(HPO₃)₄.

V—O_b(V), oxygen atom bridging two vanadium atoms. V—O_b(M), oxygen atoms bridging a vanadium atom and an M atom.

Remarkably, there is a number hydrogen bonds between protonated tren groups and infinite chains [V₆O₁₈$^{6-}$]∞. While the average distance of the intra-hydrogen bonds (N—H…O) between N2, N3, N4, N6, N7, N8 of the protonated tren groups and O5, O8, O11, O15, O18 of the infinite chains [V₆O₁₈$^{6-}$]∞ is 2.826 Å, the inter-hydrogen bonds between N2, N3, N4, N6, N7, N8 of protonated tren groups and oxygen atoms of infinite chains [V₆O₁₈$^{6-}$]∞ (N2—H…O17A, N3—H…O16A, N6—H…O11A, N7—H7B…O7A, N8—H…O9B, N4—H…O1C, N7—H…O5E, N7—H…O1E and N8—H…O6E) have average distance of 2.952(2) Å (Table 4). This complicated system of hydrogen

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Hydrogen bond distances (Å) *and angles* (deg.) *for complex* **1**

D—H…A	D—H	H…A	D…A	D—H…A	D—H…A	D—H	H…A	D…A	D—H…A
N2—H2A…O17A	0.860	2.098	2.868	148.83	N6—H6B…O19	0.860	2.276	2.828	122.01
N2—H2B…O5	0.860	1.922	2.775	170.96	N6—H6C…O19	1.056	1.916	2.828	142.59
N2—H2C…O8	0.775	2.214	2.959	160.41	N7—H7A…O5E	0.860	2.246	2.855	127.80
N3—H3A…O8	0.860	2.332	2.885	122.37	N7—H7A…O18	0.860	2.248	2.800	122.00
N3—H3A…O15	0.860	2.203	2.793	125.62	N7—H7B…O1E	0.860	2.405	3.036	130.58
N3—H3B…O16A	0.860	2.472	3.154	136.74	N7—H7B…O7A	0.860	2.566	3.152	126.29
N3—H3B…O19A	0.860	2.337	3.043	139.48	N7—H7C…O18	0.910	1.985	2.800	148.21
N3—H3C…O15	0.838	2.036	2.793	149.73	N8—H8A…O18	0.860	2.197	2.797	126.68
N4—H4A…O1C	0.860	2.390	2.955	123.72	N8—H8B…O6E	0.860	2.076	2.810	142.85
N4—H4A…O8	0.860	2.392	2.879	116.37	N8—H8A…O9B	0.8593	2.4952	2.814	102.85
N4—H4B…O11	0.860	2.008	2.726	140.36	N8—H8C…O9B	0.841	2.031	2.812	154.21
N4—H4C…O8	1.021	2.007	2.879	141.74	O19—H19…O14B	1.055	1.609	2.657	171.70
N6—H6A…O11A	0.860	2.239	2.970	142.86	O19—H19B…O9B	1.049	1.844	2.863	162.72
N6—H6A…O18	0.860	2.400	2.893	116.94	O21—H21…O12D	0.797	1.966	2.739	163.53
N6—H6B…O15	0.860	2.188	2.939	145.75					

N o t e . Symmetry transformations used to generate equivalent atoms: A = –x+3/2, y+1/2, –z+1/2; B = –x+ +3/2, y–1/2, –z+1/2; C = –x+1/2, y–1/2, –z+1/2; D = –x+1, –y+1, –z+1; E = x+1, y, z; F = 1–x, 1–y, –z.
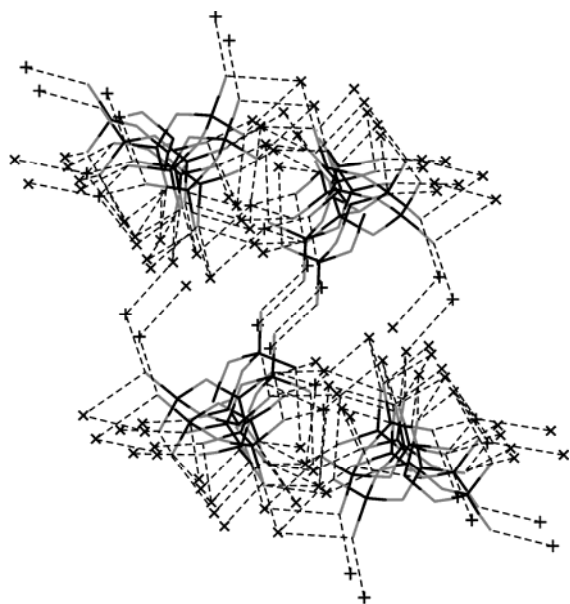
Fig. 3. A view of infinite 3D network formed by H-bonds in complex **1**. ($A = -x+3/2,\ y+1/2,\ -z+1/2;\quad B = -x+3/2,\ y-1/2,\ -z+1/2;\quad C = -x+1/2,\ y-1/2,\ -z+1/2;\quad E = x+1,\ y,\ z$)

bonds among protonated tren groups, water molecules and infinite chains $[V_6O_{18}^{6-}]_\infty$ of VO_4 tetrahedra forms a 3D framework as shown in Fig. 3.

Thermal properties. The thermal stability of complex **1** was examined by TG, DTG and DTA techniques in the temperature range of 50—1000 °C in N_2 with the heating rate of 10 °C/min. Four distinct stages were observed for complex **1**. The first stage is likely a release of three H_2O molecules and three NH_3 molecules with the weight loss of 11.05 % (calculated value 11.12 %), between 99 °C and 201 °C. The second stage, with the weight loss of 5.47 %, was observed in the temperature range from 201 °C to 272 °C and attributed to the release of three NH_3 molecules (calculated value 5.50 %). The third stage occurs within the temperature range of 202—274 °C with the mass loss of 11.28 %, and the last stage in the temperature range of 726—886 °C with the mass loss of 10.59 %. The last two stages should correspond to the release of residual organics (each $[N(CH_2CH_2)_3]^{3+}$ cation would form 10.38 % of initial mass of the sample).

CONCLUSION

Polyoxovanadate complex was prepared for the first time by a simple method that involves an aqueous system and room temperature conditions. The title complex displays hydrogen bonds which definitely play an important role in the formation of the crystal structure linking the discrete subunits or low-dimensional entities into a high-dimensional supramolecular network.

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