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The crystal structure of tris(2,3,4,6,7,8,9,10-octahydro-1*H*-pyrimido[1,2-*a*]azepin-5-ium) trihydrodecavanadate(V), C₂₇H₅₄N₆O₂₈V₁₀

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Abstract

C₂₇H₅₄N₆O₂₈V₁₀, triclinic, $P\bar{1}$ (no. 2), $a = 11.3803(3)$ Å, $b = 14.0832(4)$ Å, $c = 16.2352(7)$ Å, $\alpha = 91.784(3)^\circ$, $\beta = 104.264(3)^\circ$, $\gamma = 107.112(2)^\circ$, $V = 2395.04(14)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0291$, $wR_{ref}(F^2) = 0.0810$, $T = 293(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.30 × 0.26 × 0.23 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.95 mm ⁻¹
Diffractometer, scan mode:	D8, φ and ω
θ_{max} , completeness:	25.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	19494, 8468, 0.021
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 6898
$N(param)_{refined}$:	641
Programs:	Bruker [1], SHELX [2]

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The asymmetric unit of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Vanadium pentoxide (0.453 g; 2.5 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (1.522 g; 10 mmol) were dissolved in 30 mL deionized water. The mixture was stirred for 12 h at room temperature, the resulting solution was stirred at 80 °C for 4 h and then filtered. The filtrate was set to standby

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
V1	0.19317 (4)	0.73835 (3)	0.93744 (3)	0.01919 (11)
V2	0.17734 (4)	0.95560 (3)	0.92230 (3)	0.02003 (11)
V3	0.10097 (4)	1.02294 (3)	0.74243 (3)	0.02194 (11)
V4	0.38385 (4)	1.10791 (3)	0.83842 (3)	0.02159 (11)
V5	0.30449 (4)	0.95834 (3)	0.67754 (3)	0.01934 (11)
V6	0.32366 (4)	0.74662 (3)	0.69509 (3)	0.02024 (11)
V7	0.41903 (4)	0.68271 (3)	0.87273 (3)	0.02226 (12)
V8	0.13640 (4)	0.59398 (3)	0.77324 (3)	0.02250 (12)
V9	0.11018 (3)	0.80615 (3)	0.75800 (3)	0.01663 (11)
V10	0.41043 (4)	0.89898 (3)	0.85916 (3)	0.01743 (11)
O1	0.09629 (14)	0.81682 (12)	0.87495 (11)	0.0185 (4)
O2	0.36767 (17)	0.74912 (14)	0.60925 (12)	0.0287 (4)
O3	0.42176 (14)	0.88946 (12)	0.74913 (10)	0.0177 (4)
O4	0.10128 (15)	0.62357 (13)	0.88124 (11)	0.0229 (4)
O5	0.44413 (15)	0.70338 (13)	0.76890 (12)	0.0238 (4)
O6	0.26772 (14)	0.76291 (12)	0.82108 (10)	0.0178 (4)
O7	0.19921 (15)	0.62806 (13)	0.68026 (11)	0.0233 (4)
O8	0.28003 (16)	0.57074 (13)	0.83226 (12)	0.0251 (4)
O9	0.19436 (14)	0.81856 (12)	0.66772 (10)	0.0185 (4)
O10	0.02708 (15)	0.68427 (13)	0.73186 (11)	0.0221 (4)
O11	0.32235 (14)	0.88640 (12)	0.95837 (11)	0.0185 (4)
H11	0.3718	0.9050	1.0085	0.022*
O12	0.49443 (14)	1.02164 (13)	0.89216 (11)	0.0212 (4)
O13	0.01184 (15)	0.87262 (13)	0.71859 (11)	0.0223 (4)
O14	0.16822 (15)	1.00189 (13)	0.65300 (11)	0.0226 (4)
O15	0.34592 (15)	0.69718 (13)	0.97054 (11)	0.0223 (4)
H15	0.4019	0.7406	1.0092	0.027*
O16	0.23501 (15)	1.13302 (13)	0.78882 (11)	0.0233 (4)
O17	0.50843 (14)	0.83351 (12)	0.90655 (11)	0.0204 (4)
O18	0.25426 (14)	0.94585 (12)	0.80853 (10)	0.0176 (4)
O19	0.34503 (16)	0.96079 (14)	0.59023 (12)	0.0279 (4)
O20	0.15663 (17)	0.73762 (14)	1.02614 (12)	0.0299 (4)
O21	0.48589 (17)	1.21555 (14)	0.87576 (12)	0.0311 (4)
O22	0.06886 (15)	0.99988 (13)	0.85355 (11)	0.0238 (4)
O23	0.31609 (15)	1.07955 (13)	0.94142 (11)	0.0232 (4)
H23	0.3763	1.0764	0.9832	0.028*
O24	0.53030 (17)	0.64074 (15)	0.92003 (13)	0.0333 (5)
O25	0.14492 (17)	0.95660 (15)	1.01285 (12)	0.0304 (4)
O26	-0.01078 (17)	1.06570 (15)	0.69683 (13)	0.0340 (5)
O27	0.03670 (17)	0.48558 (14)	0.74122 (13)	0.0359 (5)
O28	0.41317 (15)	1.07918 (13)	0.73903 (11)	0.0218 (4)
C1	0.7152 (4)	0.5701 (3)	0.3744 (2)	0.0567 (10)
H1A	0.7725	0.5370	0.3603	0.068*
H1B	0.6563	0.5749	0.3214	0.068*
C2	0.6416 (4)	0.5082 (3)	0.4292 (3)	0.0716 (13)
H2A	0.5740	0.4528	0.3932	0.086*
H2B	0.6020	0.5487	0.4555	0.086*
C3	0.7238 (5)	0.4665 (3)	0.5002 (3)	0.0815 (14)
H3A	0.6704	0.4326	0.5353	0.098*
H3B	0.7497	0.4165	0.4731	0.098*
C4	0.8398 (4)	0.5391 (3)	0.5574 (3)	0.0639 (11)
H4A	0.8832	0.5030	0.5977	0.077*
H4B	0.8139	0.5845	0.5899	0.077*
C5	0.9345 (3)	0.6008 (3)	0.5117 (3)	0.0580 (10)
H5A	1.0189	0.6249	0.5512	0.070*

Table 2: (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
H5B	0.9384	0.5590	0.4645	0.070*
C6	0.8952 (3)	0.6868 (2)	0.4791 (2)	0.0386 (7)
C7	0.9224 (4)	0.8642 (3)	0.4967 (2)	0.0693 (13)
H7A	0.9572	0.8954	0.4518	0.083*
H7B	0.9531	0.9126	0.5471	0.083*
C8	0.7808 (4)	0.8317 (3)	0.4685 (3)	0.0621 (11)
H8A	0.7518	0.8883	0.4517	0.075*
H8B	0.7465	0.8064	0.5154	0.075*
C9	0.7342 (3)	0.7522 (3)	0.3951 (2)	0.0494 (9)
H9A	0.6419	0.7256	0.3811	0.059*
H9B	0.7576	0.7804	0.3455	0.059*
C21	0.3238 (4)	0.5084 (3)	0.2395 (3)	0.0644 (11)
H21A	0.4030	0.5412	0.2827	0.077*
H21B	0.2547	0.5180	0.2603	0.077*
C20	0.3067 (3)	0.3977 (3)	0.2285 (2)	0.0465 (8)
H20A	0.3774	0.3881	0.2097	0.056*
H20B	0.3096	0.3722	0.2835	0.056*
C19	0.1831 (3)	0.3379 (2)	0.16505 (19)	0.0326 (7)
H19A	0.1618	0.2691	0.1781	0.039*
H19B	0.1159	0.3636	0.1729	0.039*
C24	0.1993 (3)	0.4213 (2)	0.0382 (2)	0.0412 (8)
C23	0.2048 (4)	0.5149 (3)	0.0857 (3)	0.0632 (11)
H23A	0.1320	0.5017	0.1093	0.076*
H23B	0.1983	0.5643	0.0459	0.076*
C22	0.3265 (4)	0.5581 (3)	0.1579 (3)	0.0786 (14)
H22A	0.3981	0.5514	0.1387	0.094*
H22B	0.3403	0.6290	0.1707	0.094*
C25	0.2077 (4)	0.3376 (3)	-0.0931 (2)	0.0646 (11)
H25A	0.2931	0.3329	-0.0846	0.078*
H25B	0.1744	0.3438	-0.1530	0.078*
C26	0.1241 (3)	0.2468 (3)	-0.0681 (2)	0.0526 (9)
H26A	0.1276	0.1875	-0.0982	0.063*
H26B	0.0365	0.2477	-0.0839	0.063*
C27	0.1669 (3)	0.2434 (2)	0.0268 (2)	0.0376 (7)
H27A	0.1039	0.1906	0.0438	0.045*
H27B	0.2468	0.2281	0.0407	0.045*
C17	0.2833 (3)	1.1163 (2)	0.3174 (2)	0.0472 (9)
H17A	0.3187	1.1876	0.3353	0.057*
H17B	0.1984	1.0940	0.3260	0.057*
C16	0.2735 (3)	1.0975 (3)	0.2241 (2)	0.0494 (9)
H16A	0.2026	1.1164	0.1903	0.059*
H16B	0.3510	1.1381	0.2118	0.059*
C18	0.3647 (3)	1.0638 (2)	0.3721 (2)	0.0366 (7)
H18A	0.4537	1.0994	0.3774	0.044*
H18B	0.3516	1.0648	0.4289	0.044*
C15	0.2850 (3)	0.9310 (2)	0.25513 (19)	0.0327 (7)
C14	0.2582 (3)	0.8257 (2)	0.2209 (2)	0.0480 (9)
H14A	0.3362	0.8079	0.2377	0.058*
H14B	0.2324	0.8202	0.1589	0.058*
C13	0.1549 (3)	0.7515 (3)	0.2514 (2)	0.0509 (9)
H13A	0.0865	0.7797	0.2503	0.061*
H13B	0.1201	0.6910	0.2116	0.061*
C12	0.2004 (4)	0.7240 (3)	0.3404 (2)	0.0615 (11)
H12A	0.1295	0.6752	0.3539	0.074*
H12B	0.2656	0.6925	0.3407	0.074*
C11	0.2539 (3)	0.8115 (2)	0.4098 (2)	0.0491 (9)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
H11A	0.2773	0.7869	0.4647	0.059*
H11B	0.1879	0.8417	0.4111	0.059*
C10	0.3698 (3)	0.8911 (2)	0.39777 (19)	0.0375 (7)
H10A	0.4189	0.9290	0.4527	0.045*
H10B	0.4233	0.8588	0.3774	0.045*
N1	0.7899 (2)	0.67144 (19)	0.41649 (16)	0.0373 (6)
N2	0.9630 (3)	0.7766 (2)	0.51602 (18)	0.0546 (8)
H2	1.0344	0.7843	0.5533	0.065*
N3	0.3363 (2)	0.96030 (17)	0.33712 (15)	0.0278 (5)
N4	0.2546 (2)	0.9933 (2)	0.20121 (17)	0.0429 (7)
H4	0.2208	0.9701	0.1483	0.051*
N5	0.1842 (2)	0.33866 (17)	0.07441 (15)	0.0287 (5)
N6	0.2112 (3)	0.4236 (2)	−0.0407 (2)	0.0624 (9)
H6	0.2216	0.4796	−0.0622	0.075*

at ambient temperature for five days, orange crystals of the title compound suited for X-ray diffraction were obtained.

Yield: 35%, and **elemental analysis**: calc. for $C_{27}H_{54}N_6O_{28}V_{10}$: C 22.84, H 3.83, N 5.92; found: C 22.95, H 3.71, N 6.03. The elemental analyses were performed with PERKIN ELMER MODEL 2400 SERIES II.

Experimental details

All hydrogen atomic positions were taken from a difference Fourier map. Hydrogen atoms were assigned with common isotropic displacement factors $U_{iso}(H) = 1.2$ times $U_{eq}(C, O, N)$. All the H atoms were refined as riding on their parent atom.

Comment

Polyoxovanadates (POVs), are a class of vanadium-oxide clusters with reversible multi-electron redox transformations under mild conditions, which allow them to act as multi-functional catalysts in homogeneous or heterogeneous catalytic systems [3–6]. The functionalization of the POVs cluster can endow them more properties and thus exploration of new functionalized POVs structure is an interesting aspect in recent POVs chemistry [7, 8]. Therefore, a lot of studies on functionalized POVs structure, including organic-inorganic hybrid POVs, organic functionalized POVs, etc. have been widely reported [9]. In addition, as a class of versatile N-ligands, 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) can be used not only as a base

but also as solvent in the synthesis of metal complexes. However, the examples of DBU-based polyoxovanadates are still rare.

The molecular structure of title DBU-based decavanadate is displayed in the figure. Single crystal diffraction analysis shows that the title compound consists of three mono-protonated DBU molecules and a threefold-protonated decavanadate cluster. Accordingly, the title compound is formulated as $(HDBU)_3H_3V_{10}O_{28}$. The protonated HDBU balanced the negative charge of the threefold-protonated decavanadate polyanions. Each DBU ligand has one protonated hydrogen atom on the nitrogen atom, the C–N bond distances of DBU ligand are in the range of 1.306(4) and 1.472(4) Å, which is similar with those of a reported compound [10].

Additionally, the 3D supramolecular structure of the DBU-based decavanadate is stabilized by intermolecular strong C–H...O, N–H...O and O–H...O hydrogen-bonding interactions with the distances 2.733–2.763 Å (O–O), 2.969–3.044 Å (N–O) and 3.126–3.502 Å (C–O) between $H_3V_{10}O_{28}^{3-}$ and three $HDBU^+$ cations.

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