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The crystal structure of hexakis(2-(pyridin-2-ylamino)pyridin-1-ium) decavanadate(V) dihydrate, $C_{60}H_{64}N_{18}O_{30}V_{10}$

Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.21 × 0.20 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.28 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART APEX II, φ and ω
$\theta_{\max}$, completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	36474, 6612, 0.100
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3700
$N(\text{param})_{\text{refined}}$:	532
Programs:	Bruker [1], SHELX [2]

Source of material

In a 50 ml round-bottom flask, dipyrindylamine (0.513 g; 3 mmol), vanadium pentoxide (0.730 g; 4 mmol) and tetramethylammonium hydroxide 25% in solution (1.461 g; 4 mmol) were added successively to 20 ml water and acetic acid. The mixture was stirred for 24 h and then heated to 60 °C for 1 h, resulting in an orange coloured solution. The resulting mixture was filtrated and the filtrate stood for seven days. Crystals of the title compound suited for X-ray diffraction were obtained.

Yield: 38%, and elemental analysis: calc. for $C_{60}H_{64}N_{18}O_{30}V_{10}$: C 35.56, H 3.18, N 12.44; found: C 35.52, H 3.23, N 12.36. The elemental analyses were performed with PERKIN ELMER MODEL 2400 SERIES II.

Experimental details

In the title compound all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned with common isotropic displacement factors $U_{\text{iso}}(\text{H}) = 1.2$ times $U_{\text{eq}}(\text{C}, \text{pyridine ring}; \text{O}, \text{water molecule}; \text{N}, \text{pyridine ring and secondary amine})$. All the H atoms were refined as riding on their parent atom.

Comment

Polyoxovanadates, as an outstanding large important branch of anionic metal-oxo clusters, have led to a rapid

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Abstract

$C_{60}H_{64}N_{18}O_{30}V_{10}$, orthorhombic, *Pbca* (no. 61), $a = 21.1781(19)$ Å, $b = 14.4198(13)$ Å, $c = 24.543(2)$ Å, $V = 7495.2(12)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0538$, $wR_{\text{ref}}(F^2) = 0.1482$, $T = 298$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
V1	0.52679 (4)	0.53877 (6)	0.55746 (3)	0.0288 (2)
V2	0.52096 (4)	0.31753 (6)	0.52849 (3)	0.0312 (2)
V3	0.39234 (4)	0.42508 (6)	0.54553 (3)	0.0314 (2)
V4	0.64689 (4)	0.42315 (7)	0.53863 (4)	0.0375 (3)
V5	0.39827 (4)	0.63499 (7)	0.57529 (4)	0.0373 (3)
N1	0.6719 (4)	0.7049 (5)	0.7444 (3)	0.0944 (18)
H1	0.693539	0.725374	0.771496	0.113*
N2	0.6706 (4)	0.6739 (4)	0.6542 (3)	0.0869 (17)
H2	0.631676	0.658681	0.658440	0.104*
N3	0.5788 (4)	0.6500 (4)	0.7172 (3)	0.0801 (16)
N4	0.3933 (2)	0.4446 (4)	0.70445 (19)	0.0505 (14)
H4	0.393908	0.460337	0.670657	0.061*
N5	0.4949 (2)	0.4052 (3)	0.68603 (18)	0.0432 (13)
H5	0.486181	0.417076	0.652518	0.052*
N6	0.3290 (3)	0.4363 (4)	0.7820 (2)	0.0637 (16)
N7	0.4607 (2)	0.9031 (3)	0.56359 (18)	0.0433 (12)
H7	0.455484	0.844083	0.561012	0.052*
N8	0.5331 (2)	1.0230 (3)	0.56975 (19)	0.0436 (13)
N9	0.4109 (2)	1.0467 (4)	0.56521 (19)	0.0470 (13)
H9	0.447202	1.073263	0.566522	0.056*
O1	0.48319 (15)	0.4183 (2)	0.57893 (12)	0.0270 (8)
O2	0.55522 (15)	0.6341 (2)	0.51112 (12)	0.0297 (8)
O3	0.59535 (15)	0.5104 (2)	0.58771 (13)	0.0319 (9)
O4	0.59482 (16)	0.3299 (3)	0.56519 (13)	0.0376 (9)
O5	0.66384 (16)	0.3593 (3)	0.47582 (15)	0.0410 (10)
O6	0.70892 (17)	0.4112 (3)	0.57418 (15)	0.0495 (11)
O7	0.48929 (17)	0.2266 (2)	0.55512 (14)	0.0403 (9)
O8	0.55496 (17)	0.2757 (3)	0.46677 (13)	0.0368 (9)
O9	0.33504 (15)	0.4624 (3)	0.49910 (14)	0.0375 (9)
O10	0.36195 (17)	0.3366 (3)	0.57587 (14)	0.0446 (10)
O11	0.44704 (14)	0.5451 (2)	0.50725 (12)	0.0264 (8)
O12	0.37769 (16)	0.5175 (3)	0.59634 (13)	0.0357 (9)
O13	0.3725 (2)	0.6978 (3)	0.62410 (15)	0.0536 (11)
O14	0.48669 (17)	0.6031 (2)	0.60323 (12)	0.0347 (9)
O15	0.2441 (4)	0.7544 (5)	0.6625 (3)	0.150 (3)
H15A	0.281592	0.760796	0.674294	0.181*
H15B	0.258568	0.725415	0.635063	0.181*
C1	0.7073 (5)	0.7022 (5)	0.6969 (4)	0.0784 (18)
C2	0.7695 (5)	0.7259 (6)	0.6924 (5)	0.098 (3)
H2A	0.793083	0.742889	0.722777	0.118*
C3	0.7954 (5)	0.7239 (6)	0.6421 (5)	0.104 (3)
H3	0.837377	0.741118	0.637659	0.125*
C4	0.7613 (5)	0.6971 (6)	0.5980 (4)	0.092 (3)
H4A	0.779753	0.696330	0.563643	0.110*
C5	0.6993 (4)	0.6713 (5)	0.6044 (3)	0.081 (2)
H5A	0.676443	0.651507	0.574228	0.097*
C6	0.6111 (4)	0.6834 (5)	0.7593 (3)	0.0735 (17)
C7	0.5858 (5)	0.6944 (5)	0.8105 (3)	0.085 (3)
H7A	0.609692	0.718849	0.838867	0.102*
C8	0.5242 (5)	0.6680 (6)	0.8185 (3)	0.083 (3)
H8	0.505809	0.673664	0.852794	0.100*
C9	0.4904 (4)	0.6338 (5)	0.7762 (3)	0.080 (2)
H9A	0.448548	0.616012	0.781104	0.096*
C10	0.5180 (4)	0.6257 (5)	0.7266 (3)	0.072 (2)
H10	0.494275	0.602378	0.697826	0.087*

Table 2: (continued)

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.4494 (3)	0.4131 (4)	0.7238 (2)	0.0427 (15)
C12	0.4630 (3)	0.3896 (5)	0.7781 (2)	0.0580 (19)
H12	0.431892	0.392915	0.804713	0.070*
C13	0.5231 (3)	0.3617 (5)	0.7911 (3)	0.064 (2)
H13	0.532673	0.345997	0.826883	0.077*
C14	0.5688 (3)	0.3568 (5)	0.7524 (3)	0.066 (2)
H14	0.609661	0.338762	0.761318	0.079*
C15	0.5532 (3)	0.3793 (5)	0.6995 (3)	0.0571 (18)
H15	0.584009	0.376285	0.672549	0.068*
C16	0.3349 (3)	0.4558 (4)	0.7297 (2)	0.0459 (16)
C17	0.2850 (3)	0.4863 (5)	0.6980 (3)	0.063 (2)
H17	0.290982	0.499851	0.661350	0.075*
C18	0.2265 (3)	0.4962 (5)	0.7217 (3)	0.067 (2)
H18	0.192224	0.516156	0.701102	0.081*
C19	0.2195 (3)	0.4763 (5)	0.7757 (3)	0.062 (2)
H19	0.180438	0.481659	0.792707	0.075*
C20	0.2713 (4)	0.4485 (5)	0.8038 (3)	0.068 (2)
H20	0.266543	0.436891	0.840802	0.081*
C21	0.5233 (3)	0.9323 (4)	0.5670 (2)	0.0383 (14)
C22	0.5713 (3)	0.8675 (4)	0.5673 (2)	0.0442 (15)
H22	0.562575	0.804366	0.565341	0.053*
C23	0.6325 (3)	0.8993 (5)	0.5706 (3)	0.0531 (17)
H23	0.666037	0.857700	0.571160	0.064*
C24	0.6434 (3)	0.9925 (5)	0.5730 (3)	0.0552 (17)
H24	0.684356	1.015343	0.575034	0.066*
C25	0.5926 (3)	1.0519 (5)	0.5723 (2)	0.0509 (17)
H25	0.600245	1.115334	0.573683	0.061*
C26	0.4080 (3)	0.9530 (5)	0.5637 (2)	0.0391 (14)
C27	0.3478 (3)	0.9109 (5)	0.5618 (3)	0.0552 (18)
H27	0.343831	0.846719	0.560610	0.066*
C28	0.2961 (3)	0.9659 (6)	0.5617 (3)	0.063 (2)
H28	0.256290	0.938761	0.560292	0.076*
C29	0.3010 (3)	1.0613 (6)	0.5637 (3)	0.066 (2)
H29	0.264941	1.098092	0.564236	0.079*
C30	0.3581 (3)	1.0997 (5)	0.5647 (3)	0.0540 (17)
H30	0.361892	1.163992	0.565115	0.065*

growth due to their structural features and promising applications in diverse areas, such as catalysis, electricity, medicine and functional materials [3–6]. The design and synthesis of new polyoxovanadates architectures with well-defined structures expand the range of polyoxovanadates-inspired hybrid materials [7, 8]. Thus, a lot of hybrid polyoxovanadates have been presented [9]. In addition, as a class of versatile tridentate N-ligands, dipyrldylamine (dpa) can be used in the synthesis of metal complexes, and some of them have been reported [10, 11]. Nevertheless, to the best of our knowledge, examples of dpa-based polyoxovanadates are still rare.

The structure of title hybrid dipyrldylamine-polyoxovanadates is shown in the figure. Single crystal diffraction analysis of the title compound revealed that it

consists of six protonated dipyridylamine ligands, one decavanadate polyanion cluster and two free lattice water molecules, formulated as $(Hdpa)_6V_{10}O_{28} \cdot 2H_2O$. For the polyanion, the decavanadate cluster is composed of ten analogous VO_6 units, which bridged by edge- and corner-sharing oxygen atoms and each vanadium atom of VO_6 subunit exhibited the distorted octahedral geometry, located around a center of inversion. There are four distinct types of oxygen coordination, namely terminal O_t , bridging μ_6-O , μ_3-O and μ_2-O oxygen atoms. The bond lengths and angles found in the decavanadate anion are as expected for those in the previously reported decavanadate structures [12–14]. Each dpa ligand has a protonated hydrogen atom on the nitrogen of pyridinyl moiety. The C–N bond average distance in the pyridine ring of dpa ligands is 1.351 Å, which is larger than that of the unprotonated pyridine.

In addition, the supramolecular structure of the title structure was stabilized by intermolecular electrostatic interactions and strong hydrogen-bonding interactions between $V_{10}O_{28}^{6-}$, $Hdpa^+$ subunits and water molecules. All subunits are connected to the adjacent ones through various intermolecular C–H $\cdots$ O, N–H $\cdots$ O and O–H $\cdots$ O hydrogen-bonding interaction, thus leading to a three-dimensional network.

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References

1. Bruker. APEX2, SAINT and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2004.
2. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, C71, 3–8.
3. Zhang M., Zhang A. M., Chen Y., Xie J., Xin Z. F., Chen Y. J., Kan Y. H., Li S. L., Lan Y. Q., Zhang Q. Polyoxovanadate-polymer hybrid electrolyte in solid state batteries. *Energy Storage Mater.* 2020, 29, 172–181.
4. Petel B. E., Meyer R. L., Maiola M. L., Brennessel W. W., Müller A. M., Matson E. M. Site-selective halogenation of polyoxovanadate clusters: atomically precise models for electronic effects of anion doping in VO_2 . *J. Am. Chem. Soc.* 2020, 142, 1049–1056.
5. Dong J., Hu J., Chi Y., Lin Z., Zou B., Yang S., Hill C. L., Hu C. A polyoxoniobate-polyoxovanadate double-anion catalyst for simultaneous oxidative and hydrolytic decontamination of chemical warfare agent simulants. *Angew. Chem. Int. Ed.* 2017, 56, 4473–4477.
6. Cao J. P., Xue Y. S., Li N. F., Gong J. J., Kang R. K., Xu Y. Lewis acid dominant windmill-shaped V8 clusters: a bifunctional heterogeneous catalyst for CO_2 cycloaddition and oxidation of sulfides. *J. Am. Chem. Soc.* 2019, 141, 19487–19497.
7. Li C., Zhong D., Huang X., Shen G., Li Q., Du J., Li Q., Wang S., Li J., Dou J. Two organic–inorganic hybrid polyoxovanadates as reusable catalysts for Knoevenagel condensation. *New J. Chem.* 2019, 43, 5813–5819.
8. Huang X., Li J., Shen G., Xin N., Lin Z., Chi Y., Dou J., Li D., Hu C. Three Pd-decavanadates with a controllable molar ratio of Pd to decavanadate and their heterogeneous aerobic oxidation of benzylic C–H bonds. *Dalton Trans.* 2018, 47, 726–733.
9. VanGelder L. E., Forrestel P. L., Brennessel W. W., Matson E. M. Site-selectivity in the halogenation of titanium-functionalized polyoxovanadate-alkoxide clusters. *Chem. Commun.* 2018, 54, 6839–6842.
10. Yan B., Xu Y., Bu X., Goh N. K., Chia L. S., Stucky G. D. Hydrothermal syntheses and structures of three one-dimensional heteropolytungstates formed by Dawson or Keggin cluster units. *J. Chem. Soc. Dalton Trans.* 2001, 2009–2014. <https://doi.org/10.1039/b103024h>.
11. Zianna A., Psomas G., Hatzidimitriou A., Lalia-Kantouri M. Synthesis, structural, thermal characterization and interaction with calf-thymus DNA and albumins of cationic Ni(II) complexes with dipyridylamine and salicylaldehydes. *Polyhedron* 2017, 124, 104–116.
12. Huang X., Qi Y., Gu Y., Gong S., Shen G., Li Q., Li J. Imidazole-directed fabrication of three polyoxovanadates-based copper frameworks as efficient catalysts for constructing of C–N bonds. *Dalton Trans.* 2020, 49, 10970–10976.
13. An H., Zhang J., Chang S., Hou Y., Zhu Q. 2D hybrid architectures constructed from two kinds of polyoxovanadates as efficient heterogeneous catalysts for cyanosilylation and Knoevenagel condensation. *Inorg. Chem.* 2020, 59, 10578–10590.
14. Kiyota Y., Taira M., Otake S., Hanyuda K., Naruke H., Ito T. Compositional introduction of lithium ions into conductive polyoxovanadate-surfactant hybrid crystals. *CrystEngComm* 2017, 19, 3037–3043.