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The crystal structure of bis tetrabutylammonium bis(μ_3 -2,2,2-tri(hydroxymethyl)ethyl-4-((3-methoxy-3-oxopropyl)amino)-4-oxobutanoato)-(μ_6 -oxido)-hexakis(μ_2 -oxido)-hexaoxido-hexavanadium(V), $C_{58}H_{112}N_4O_{29}V_6$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.07 × 0.05 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.83 mm ⁻¹
Diffractometer, scan mode:	Xcalibur, ω
$\theta_{\max}$, completeness:	26.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	22710, 7071, 0.058
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 5268
$N(\text{param})_{\text{refined}}$:	444
Programs:	SHELX [1], CrysAlis ^{PRO} [2]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2691(3)	1.1274(3)	−0.0492(3)	0.0238(9)
H1A	0.2214	1.1240	−0.1068	0.029*
H1B	0.2701	1.1855	−0.0274	0.029*
C2	0.3182(3)	1.0723(3)	0.1081(3)	0.0247(9)
H2A	0.3186	1.1302	0.1302	0.030*
H2B	0.3008	1.0340	0.1478	0.030*
C3	0.2413(3)	0.9730(3)	−0.0189(3)	0.0239(9)
H3A	0.2236	0.9357	0.0214	0.029*
H3B	0.1941	0.9689	−0.0767	0.029*
C4	0.2461(3)	1.0659(3)	0.0146(3)	0.0236(9)
C5	0.1533(3)	1.0900(3)	0.0262(3)	0.0277(10)
H5A	0.1385	1.0492	0.0654	0.033*
H5B	0.1577	1.1464	0.0526	0.033*
C6	−0.0055(3)	1.0972(3)	−0.0570(3)	0.0312(10)
C7	−0.0760(3)	1.1024(3)	−0.1493(3)	0.0361(11)
H7A	−0.0834	1.0459	−0.1759	0.043*
H7B	−0.1350	1.1191	−0.1441	0.043*
C8	−0.0517(3)	1.1642(3)	−0.2104(3)	0.0379(11)
H8A	−0.0025	1.1399	−0.2286	0.045*
H8B	−0.1050	1.1719	−0.2633	0.045*
C9	−0.0216(3)	1.2500(3)	−0.1684(3)	0.0348(11)
C10	0.0455(3)	1.3878(3)	−0.1807(3)	0.0390(12)
H10A	0.0302	1.4077	−0.1297	0.047*
H10B	0.0339	1.4340	−0.2237	0.047*
C11	0.1485(3)	1.3612(3)	−0.1519(3)	0.0422(12)
H11A	0.1535	1.3017	−0.1335	0.051*
H11B	0.1693	1.3653	−0.2031	0.051*
C12	0.2102(4)	1.4120(3)	−0.0801(3)	0.0402(12)
C13	0.3597(4)	1.4183(4)	0.0272(4)	0.0631(17)

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Abstract

$C_{58}H_{112}N_4O_{29}V_6$, $P2_1/n$ (no. 14), $a = 15.3310(5)$ Å, $b = 15.6093(4)$ Å, $c = 15.9394(5)$ Å, $\beta = 109.132(4)^\circ$, $V = 3603.7(2)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0579$, $wR_{\text{ref}}(F^2) = 0.1450$, $T = 104.0$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized by dissolving a mixture of 0.732 g (0.5 mmol) $(Bu_4N)_2[V_6O_{13}\{(OCH_2)_3CCH_2OOCCH_2CH_2COOH\}_2]$, which was prepared according to a previously reported synthetic protocol [3], 0.140 g (1.0 mmol)

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H13A	0.3819	1.4670	0.0034	0.095*
H13B	0.4104	1.3808	0.0557	0.095*
H13C	0.3317	1.4372	0.0697	0.095*
C14	0.2091(3)	0.6677(3)	−0.1486(3)	0.0268(9)
H14A	0.1814	0.6506	−0.2101	0.032*
H14B	0.2280	0.6159	−0.1137	0.032*
C15	0.2952(3)	0.7206(3)	−0.1405(3)	0.0414(12)
H15A	0.2770	0.7755	−0.1696	0.050*
H15B	0.3286	0.7313	−0.0783	0.050*
C16	0.3569(3)	0.6754(3)	−0.1817(3)	0.0416(12)
H16A	0.3233	0.6673	−0.2443	0.050*
H16B	0.4091	0.7123	−0.1773	0.050*
C17	0.3923(4)	0.5917(4)	−0.1429(4)	0.062(17)
H17A	0.4356	0.5705	−0.1698	0.094*
H17B	0.3419	0.5521	−0.1536	0.094*
H17C	0.4224	0.5979	−0.0801	0.094*
C18	0.0561(3)	0.6496(3)	−0.1373(3)	0.0285(10)
H18A	0.0770	0.6000	−0.0993	0.034*
H18B	0.0404	0.6301	−0.1983	0.034*
C19	−0.0315(3)	0.6837(3)	−0.1233(3)	0.0371(11)
H19A	−0.0593	0.7274	−0.1672	0.045*
H19B	−0.0163	0.7094	−0.0648	0.045*
C20	−0.0997(3)	0.6101(4)	−0.1320(3)	0.0445(13)
H20A	−0.1040	0.5768	−0.1846	0.053*
H20B	−0.0771	0.5727	−0.0808	0.053*
C21	−0.1936(4)	0.6424(5)	−0.1383(5)	0.075(2)
H21A	−0.2161	0.6796	−0.1888	0.113*
H21B	−0.1899	0.6736	−0.0853	0.113*
H21C	−0.2350	0.5949	−0.1448	0.113*
C22	0.1740(3)	0.7365(3)	−0.0205(3)	0.0310(10)
H22A	0.2270	0.7736	−0.0118	0.037*
H22B	0.1273	0.7695	−0.0059	0.037*
C23	0.2026(3)	0.6629(3)	0.0440(3)	0.0369(11)
H23A	0.2442	0.6257	0.0264	0.044*
H23B	0.1485	0.6298	0.0423	0.044*
C24	0.2504(3)	0.6953(3)	0.1382(3)	0.0396(12)
H24A	0.3049	0.7276	0.1396	0.048*
H24B	0.2090	0.7338	0.1547	0.048*
C25	0.2784(5)	0.6237(4)	0.2054(3)	0.0643(18)
H25A	0.3212	0.5865	0.1908	0.096*
H25B	0.2247	0.5916	0.2046	0.096*
H25C	0.3071	0.6474	0.2636	0.096*
C26	0.1054(3)	0.7950(3)	−0.1688(3)	0.0384(11)
H26A	0.1584	0.8329	−0.1556	0.046*
H26B	0.0604	0.8220	−0.1466	0.046*
C27	0.0638(4)	0.7867(3)	−0.2685(3)	0.0439(12)
H27A	0.0066	0.7546	−0.2836	0.053*
H27B	0.1060	0.7563	−0.2919	0.053*
C28	0.0454(5)	0.8765(4)	−0.3089(4)	0.0633(17)
H28A	0.0120	0.9098	−0.2780	0.076*
H28B	0.1037	0.9051	−0.3014	0.076*
C29	−0.0076(5)	0.8723(5)	−0.4020(4)	0.087(2)
H29A	0.0239	0.8367	−0.4320	0.130*
H29B	−0.0148	0.9288	−0.4269	0.130*
H29C	−0.0674	0.8484	−0.4091	0.130*
N1	−0.0108(3)	1.3141(3)	−0.2198(2)	0.0362(9)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
H1	−0.0375	1.3116	−0.2764	0.043*
N2	0.1359(2)	0.7122(2)	−0.1191(2)	0.0282(8)
O1	0.3806(2)	0.88591(18)	0.14657(18)	0.0286(7)
O2	0.27345(19)	0.99738(18)	−0.19673(18)	0.0291(7)
O3	0.43820(18)	1.21769(17)	0.07675(18)	0.0242(6)
O4	0.5000	1.0000	0.0000	0.0175(8)
O5	0.55113(18)	0.93989(17)	0.16600(16)	0.0220(6)
O6	0.41936(17)	0.89574(17)	−0.13574(16)	0.0201(6)
O7	0.46929(18)	0.83568(16)	0.02994(17)	0.0217(6)
O8	0.35679(17)	1.10805(16)	−0.05881(16)	0.0197(6)
O9	0.40932(17)	1.05070(17)	0.10863(16)	0.0199(6)
O10	0.32758(17)	0.94452(17)	−0.02553(16)	0.0202(6)
O11	0.08114(19)	1.08934(19)	−0.06035(19)	0.0307(7)
O12	−0.0232(2)	1.0962(2)	0.0123(2)	0.0353(7)
O13	−0.0028(2)	1.2598(2)	−0.0872(2)	0.0449(9)
O14	0.1932(3)	1.4801(2)	−0.0541(3)	0.0601(11)
O15	0.2921(2)	1.3728(2)	−0.0441(2)	0.0527(10)
V1	0.43876(5)	0.93057(4)	0.09116(4)	0.02038(18)
V2	0.47060(4)	1.13146(4)	0.03985(4)	0.01861(17)
V3	0.37102(4)	0.99308(4)	−0.11887(4)	0.01928(17)

β-alanine methyl ester hydrochloride, 0.192 g (1.0 mmol) 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) and 0.135 g (1.0 mmol) 1-hydroxybenzotriazole (HOBt) into 30 mL anhydrous acetonitrile. The solution was stirred and heated at 50 °C for 48 h. The mixture was cooled down to room temperature and the deposits were removed by filtration. The filtrate was dropped into 20 mL deionized water and stood in the air for 2 days. The bulky yellow crystals suitable for X-ray diffraction were acquired by filtration. IR spectrum (cm^{−1}, KBr pellets): 2959 (*m*), 2873 (*m*), 1736 (*s*), 1674 (*s*), 1536 (*m*), 1069 (*m*), 949 (*vs*), 812 (*s*), 723 (*s*).

Experimental details

The hydrogen atoms were generated geometrically and refined using the riding model.

Comment

Polyoxometalates (POMs) are inorganic clusters consisting of transition metal atoms in their highest oxidation state and oxygen atoms [4]. Among the various POMs, the organic derivatives of polyoxovanadates (POVs) have attracted increasing attentions due to their fascinating catalytic, magnetic properties as well as bioactivities [5–8]. The combination of POVs and amino acids may improve the bioactivities of the POVs and reduce their toxicity [9, 10].

However, very few examples of POV hybrids with amino acid species were reported to date.

Herein, we report a new POV hybrid incorporating a β -alanine ester. The title compound consisted of a polyoxo anion $[V_6O_{13}\{(OCH_2)_3CCH_2OOCCH_2CH_2CONHCH_2CH_2COOCH_3\}_2]^{2-}$ and two tetrabutyl ammonium cations. The polyoxoanion exhibited a Lindqvist-type structure which consists of a slightly distorted $\{V_6O_{19}\}$ cluster. The bond lengths of the terminal V—O bonds and central V—O bonds were around 1.60 Å and 2.25 Å, respectively, while the distances between the vanadium and the doubly oxygen were in the range of 1.73 Å and 1.92 Å, which were similar to literature examples [3]. Two trimethylol ligands occupied the opposite sides of the polyoxo anion and linked to the $\{V_6\}$ cluster through μ_2 -O—V bonds, the bond lengths of which were between 1.96 Å and 2.09 Å. The succinyl group is covalently attached to the trimethylol ligand *via* an ester group with the C6—O11 bond length of 1.352 Å and connected to the β -alanine methyl ester at the other end through an amido group in which the distance of C9—N1 was 1.337 Å. No hydrogen bonding interactions were found in the packing structure. The IR spectrum of title compound not only showed the characteristic bands of the hexavanadate cluster at the 949, 812 and 723 cm^{-1} , but also exhibited strong absorption bands at 1736 and 1668 cm^{-1} , which corresponded to the stretching vibration of the C=O bond in the ester group and amido group, respectively.

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References

1. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
2. Agilent Technologies: CrysAlis^{PRO} Software system. Agilent Technologies UK Ltd, Oxford, UK (2015).
3. Xiao, Z.; Chen, K.; Wu, B.; Li, W.; Wu, P.; Wei, Y.: An easy way to construct polyoxovanadate-based organic-inorganic hybrids by stepwise functionalization. *Eur. J. Inorg. Chem.* **2016** (2016) 808–811.
4. Cronin, L.; Müller, A.: From serendipity to design of polyoxometalates at the nanoscale, aesthetic beauty and applications. *Chem. Soc. Rev.* **41** (2012) 7333–7334.
5. Hayashi, Y.: Hetero and lacunary polyoxovanadate chemistry: synthesis, reactivity and structural aspects. *Coord. Chem. Rev.* **255** (2011) 2270–2280.
6. Bayaguud, A.; Chen, K.; Wei, Y.: Facile synthesis of an organically-derivatized hexavanadate containing the remote amino group, $TBA_2[V_6O_{13}\{(OCH_2)_3CNH_2\}_2]$. *CrystEngComm* **18** (2016) 4042–4045.
7. Yin, P.; Wang, J.; Xiao, Z.; Wu, P.; Wei, Y.; Liu, T.: Polyoxometalate-organic hybrid molecules as amphiphilic emulsion catalysts for deep desulfurization. *Chem. Eur. J.* **18** (2012) 9174–9178.
8. Hu, X.; Huang, B.; Xiao, Z.; Wu, P.: Crystal structure of bis(3-(3-ethylureido)-*N,N*-dimethylpropan-1-aminium)bis(μ_3 -2-(hydroxymethyl)-2-(oxidomethyl)propane-1,3-bis(olato))-(μ_6 -oxo)-hexakis(μ_2 -oxo)-hexa-oxo-hexavanadium(V)-dichloromethane (1/1), $C_{27}H_{60}Cl_2N_6O_{23}V_6$. *Z. Kristallogr. NCS* **232** (2017) 849–850.
9. Pessoa, J. C.; Etcheverry, S.; Gambino, D.: Vanadium compounds in medicine. *Coord. Chem. Rev.* **301–302** (2015) 24–48.
10. Yvon, C.; Surman, A. J.; Hutin, M.; Alex, J.; Smith, B. O.; Long, D.; Cronin, L.: Polyoxometalate clusters integrated into peptide chains and as inorganic amino acids: solution and solid-phase approaches. *Angew. Chem. Int. Ed.* **53** (2014) 3336–3341.