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Tetrakis(tetramethylammonium) Dihydrogendecavanadate Acetic Acid 2.8-Hydrate, $[N(CH_3)_4]_4[H_2V_{10}O_{28}].CH_3COOH.2.8H_2O$

Brigitte Pecquenard, Peter Y. Zavalij and
M. Stanley Whittingham

Materials Research Center, State University of New York at Binghamton, Binghamton, NY 13902-6016, USA. E-mail: zavalij@binghamton.edu

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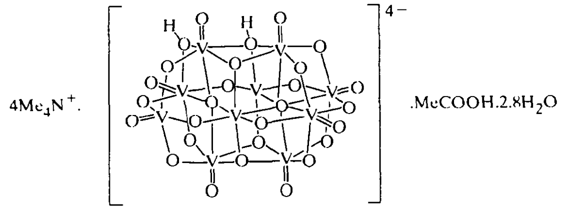
Abstract

The title compound was synthesized and found to crystallize in the triclinic space group $P\bar{1}$. The decavanadate cluster with two H atoms, $[H_2V_{10}O_{28}]^{4-}$, forms layers by hydrogen bonding with acetic acid and water of crystallization. The tetramethylammonium cations fill space between the layers.

Comment

Exploring the synthesis and crystal structures of the vanadium oxides, we have found that mild hydrothermal synthesis leads to the formation of the following metastable structures with open frameworks: $(TMA)V_4O_{10}$ (where TMA is the tetramethylammonium ion; Zavalij *et al.*, 1996), $Li_xV_2O_4.H_2O$ (Chirayil *et al.*, 1996), $(TMA)V_3O_7$ (Zavalij *et al.*, 1997*a*), $(TMA)V_8O_{20}$ (Chirayil *et al.*, 1997), $(CH_3NH_3)V_3O_7$, and $(CH_3NH_3)V_4O_{10}$ (Chen *et al.*, 1998). Nevertheless, often the decavanadate cluster can be formed as well. We have reported the structures of decavanadate compounds with mixed cations, namely, $[Li(H_2O)]_2(TMA)_4[V_{10}O_{28}].4H_2O$ (Zavalij *et al.*, 1997) and $Na_4(TMA)_2[V_{10}O_{28}].20H_2O$ (Zavalij *et al.*, 1997*b*), and also a decavanadate with a long-chain template, $[CH_3(CH_2)_{11}N(CH_3)_3]_4[H_2V_{10}O_{28}].4H_2O$ (Janauer *et al.*, 1997). This work presents a new compound, (I), built by the dihydrogendecavanadate cluster $[H_2V_{10}O_{28}]^{4-}$ (Fig. 1*a*), tetramethylammonium cations, molecular acetic acid (Fig. 1*b*) and water of crystallization.



(I)

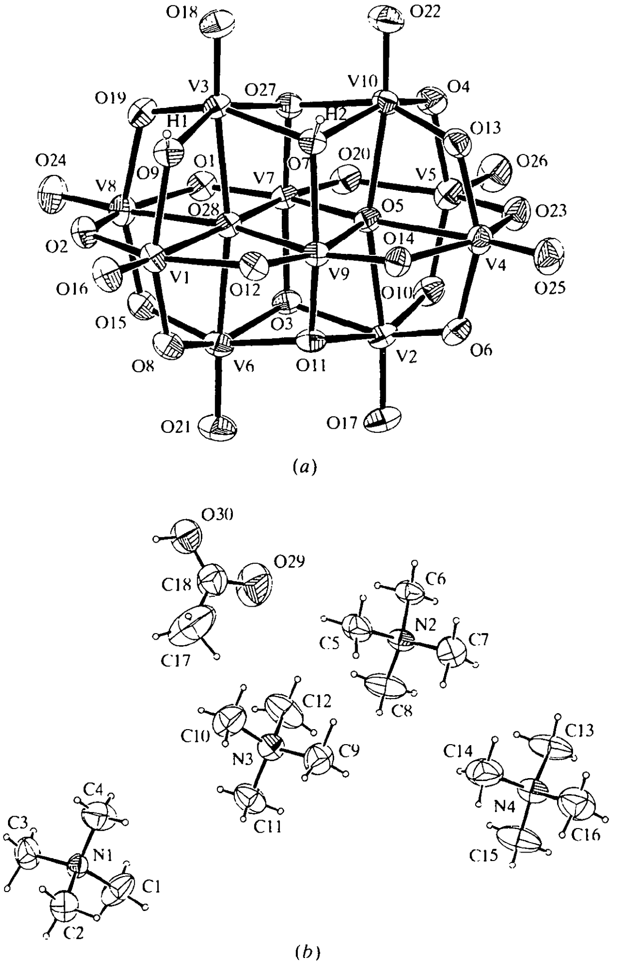


Fig. 1. Displacement ellipsoid plots (50% probability) of (*a*) $[H_2V_{10}O_{28}]^{4-}$ and (*b*) tetramethylammonium and acetic acid.

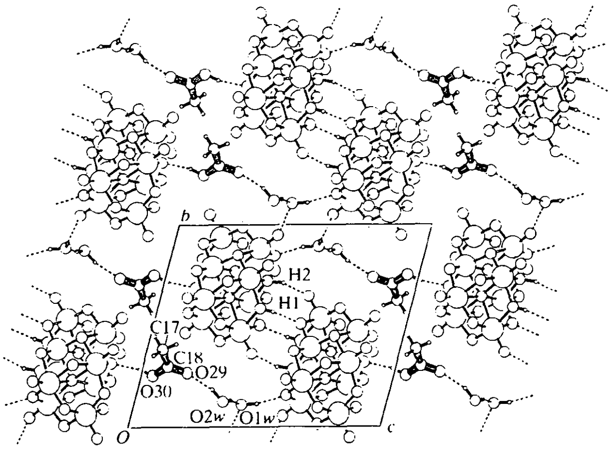


Fig. 2. Hydrogen bonding of the dihydrogendecavanadate cluster, acetic acid and water of crystallization, shown along the *a* axis. Tetramethylammonium cations and disordered water molecules are not shown.

The geometry of the decavanadate cluster (Table 1) is very close to that found in other decavanadate structures. Using their H atoms, decavanadate clusters are linked in centrosymmetric pairs by means of four hydrogen bonds (Fig. 2). Acetic acid and two water molecules (O1*w* and O2*w*) are also linked together by hydrogen bonds, forming an interesting chain, $CH_3C(OH)O\cdots H—O—H\cdots OH_2$. Its three external OH groups form hydrogen bonds with O atoms of the decavanadate pairs, joining them into a two-dimensional sheet in the *bc* plane (Fig. 2). Two disordered water molecules [O3*w* and O4*w*, with occupation factors of 0.43 (2) and 0.36 (2), respectively] form hydrogen bonds (Table 2) with the same pair of O atoms (O21 and O17), which belong to decavanadate clusters of different sheets.

Experimental

The title compound was prepared hydrothermally by mixing V_2O_5 and $Al(NO_3)_3.9H_2O$ powder with an aqueous 25% tetramethylammonium solution in a 1:2:4 molar ratio. Acetic acid (3 *M*, 30 ml) were then added; the initial pH of the resulting solution was 2.94. Then the solution was transferred to a 125 ml Teflon-lined autoclave (Parr bomb), sealed and reacted hydrothermally for 4 d at 473 K. The pH of the solution after reaction was 4.78. The resulting mixture was filtered, washed with distilled water and dried in air. It gave dark-orange crystals of the title compound and a light-green powder, which is still under investigation.

Crystal data

$(C_4H_{12}N)_4[H_2V_{10}O_{28}].$-
$C_2H_4O_2.2.8H_2O$
$M_r = 1366.6$
Triclinic
$P\bar{1}$
$a = 12.6690\,(4)$ Å
$b = 12.6905\,(4)$ Å
$c = 15.8223\,(5)$ Å
$\alpha = 73.092\,(1)°$
$\beta = 78.875\,(1)°$
$\gamma = 78.849\,(1)°$
$V = 2362.5\,(3)$ Å^3
$Z = 2$
$D_x = 1.921$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 2012 reflections
$\theta = 3–28°$
$\mu = 1.98$ mm^{-1}
$T = 295$ K
Prism
0.36 × 0.32 × 0.29 mm
Dark orange

Data collection

Siemens Smart CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.511$, $T_{\max} = 0.563$
14 948 measured reflections
10 265 independent reflections

9335 reflections with $F_o > 4\sigma(F_o)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 28.5°$
$h = -16 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -20 \rightarrow 20$

Refinement

Refinement on F
$R = 0.046$
$wR = 0.071$
$S = 1.82$
9335 reflections
609 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o) + 0.002F_o^2]$

$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.79$ e Å^{-3}
$\Delta\rho_{\min} = -0.66$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

V1—O16	1.614 (2)	V3—O28	2.250 (2)
V1—O8	1.794 (2)	V7—O20	1.679 (2)
V1—O2	1.831 (2)	V7—O1	1.691 (2)
V1—O9	2.008 (2)	V7—O27	1.933 (2)
V1—O12	2.045 (2)	V7—O3	1.955 (2)
V1—O28	2.241 (2)	V7—O5	2.065 (2)
V3—O18	1.605 (3)	V7—O28	2.179 (2)
V3—O19	1.735 (2)	C17—C18	1.450 (11)
V3—O27	1.918 (2)	C18—O30	1.253 (6)
V3—O9	1.942 (2)	C18—O29	1.255 (6)
V3—O7	2.129 (2)		
O30—C18—O29	118.7 (5)	O29—C18—C17	120.4 (6)
O30—C18—C17	120.7 (6)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9—H1···O12^{i}	0.83 (4)	1.92 (4)	2.745 (3)	171 (4)
O7—H2···O16^{i}	1.01 (4)	1.78 (4)	2.752 (3)	160 (3)
O30—H54···O3^{ii}	0.92	1.80	2.662 (4)	156
O1*w*—H55···O22^{iii}	0.95	2.08	2.869 (4)	140
O1*w*—H56···O13^{iv}	0.95	1.87	2.798 (4)	166
O2*w*—H57···O29	0.96	1.84	2.761 (7)	159
O2*w*—H58···O1*w*	0.96	1.88	2.822 (7)	167
O3*w*—H59···O21	1.00	1.96	2.96 (2)	175
O3*w*—H60···O17^{ii}	0.98	1.98	2.96 (2)	175
O4*w*—H61···O21	1.00	1.86	2.86 (2)	179
O4*w*—H62···O17^{ii}	0.99	1.92	2.91 (2)	179

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, -z$; (iii) $1+x, y-1, z$; (iv) $1-x, 1-y, 1-z$.

The crystal structure was solved by direct methods. All V atoms and most of the O atoms were located from the *E* map. The rest of the non-H atoms and all H atoms, except those of disordered water molecules, were found from the subsequent difference Fourier syntheses. The positions of the H atoms of the disordered water molecules were calculated, taking into consideration hydrogen bonding with the closest atoms, O17 and O29. Parameters of the decavanadate H atoms were refined. Positions of the H atoms of the four TMA ions were calculated, but a single U value for all 12 H atoms in each of the four cations was refined. The water molecule H-atom parameters were not refined. The ellipsoid for O4*w* is very eccentric, probably due to the disorder, and therefore O4*w* is not well localized.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *CSD* (Akselrud *et al.* 1993). Program(s) used to refine structure: *CSD*. Molecular graphics: *PLATON*97 and *PLUTON*97 (Spek, 1990). Software used to prepare material for publication: *CSD*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1385). Services for accessing these data are described at the back of the journal.

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An Exopolyhedral Cyclized Platinaundecaborane: $[(PPh_3)(PhCOS)PtB_{10}H_9(PPh_3)]$.$1.5CHCl_3$

Chun-Hua Hu,[a] Jian-Min Dou,[a] Hai-Jun Yao,[b] Jing-De Wei,[b] Ruo-Shui Jin,[b] Jie Sun[c] and Pei-Ju Zheng[a]

[a]*Research Center of Analysis and Measurement, Fudan University, Shanghai 200433, People's Republic of China,* [b]*Department of Chemistry, Fudan University, Shanghai 200433, People's Republic of China, and* [c]*Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China. E-mail: pjzheng@fudan.edu.cn*

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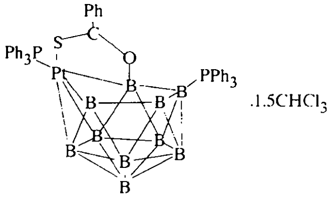
Abstract

The title platinaundecaborane species, 7,11-(μ-thiobenzoato-*S*:*O*)-7,10-bis(triphenylphosphine-*P*)-8:9-μH-7-platina-*nido*-undecaborane–chloroform (1/1.5), has a *nido*-type $\{PtB_{10}\}$ cage with a five-membered Pt—S—C—O—B ring. Of the two PPh_3 ligands, one is bound to the Pt atom and the other to a B atom.

Comment

We have developed an interest in exopolyhedral cyclization of metal ligands to clusters, especially sulfur-containing ligands. Beckett *et al.* (1985) reported an exopolyhedral heterocyclic platinaundecaborane [μ-2,7-($SCSNEt_2$)-7-(PMe_2Ph)-*nido*-7-$PtB_{10}H_{11}$] *via* a ligand-exchange-type process from the reaction of [7,7-$(PMe_2Ph)_2$-*nido*-7-$PtB_{10}H_{12}$] with [$AuBr_2(SCSNEt_2)$]. The reactions of CS_2 with metallated boron-containing cluster compounds result in a series of exopolyhedral cyclic compounds containing five-membered *M*—S—C—S—B rings; metals include Rh (Ferguson *et al.*, 1990), Re and Os (Coldicott, 1994), and Ir (Coldicott, 1994; Coldicott *et al.*, 1996). We have developed a further type of exopolyhedral cyclization process resulting in a five-membered *M*—S—C—O—B ring on the eleven-vertex metallaborane; this occurs *via* a direct process from the reaction of $MCl_2(PPh_3)_2$ (M = Ni, Pt) or $MCl_2(PPh_3)_3$ (M = Ru) and $(NEt_4)_2B_{10}H_{10}$ with PhCOSH in dichloromethane solution (Dou, Hu, Yao *et al.*, 1997; Dou, Hu, Sun *et al.*, 1997; Hu *et al.*, 1997, 1998; Yao *et al.*, 1998). We report here another example of thiobenzoate linkage, a platinaundecaborane, (I), [$(PPh_3)(PhCOS)PtB_{10}H_9(PPh_3)$].$1.5CHCl_3$.



(I)

The cluster has a *nido*-eleven-vertex $\{PtB_{10}\}$ polyhedral skeleton and has a five-membered Pt—S—C—O—B ring of exopolyhedral cyclization *via* one thiobenzoate. Its structure is shown in Fig. 1. The Pt atom is bound to the S atom of thiobenzoate, the P atom of the PPh_3 ligand and four B atoms of the $\{PtB_{10}\}$ cage. The Pt—P and Pt—S bond lengths are similar to those in previous reports (Beckett *et al.*, 1985; Hu *et al.*, 1998). The Pt—B bond lengths [2.187 (12)–2.256 (10) Å] are significantly shorter than the corresponding distances in non-cyclized platinaundecaboranes [2.214 (5)–2.301 (6) (Boocock *et al.*, 1981) and 2.206 (12)–2.342 (13) Å (Crook *et al.*, 1984)]. This could be due to the formation of the five-membered Pt—S—C—O—B ring. This ring is only approximately planar (r.m.s. deviation 0.0577 Å). Cyclization occurs on the B11 atom of the open PtB_4 face, which is similar to our previous report (Hu *et al.*, 1998), but on the B2 atom in the work of Beckett *et al.* (1985). In the cluster, a PPh_3 ligand connects with the

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