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$(Et_4N)_4[V_4O_{12}]\cdot 2H_2O$

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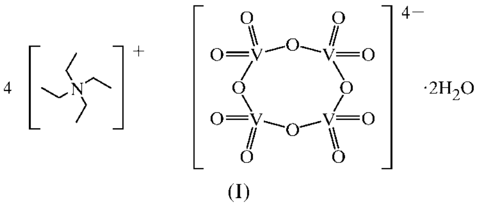
The title compound, tetrakis(tetraethylammonium) *cyclo*-tetra-μ-oxo-tetrakis[dioxovanadium(V)] dihydrate, $(C_8H_{20}N)_4[V_4O_{12}]\cdot 2H_2O$, was obtained by reacting V_2O_5 with $(C_2H_5)_4NOH$. It consists of a discrete centrosymmetric molecular anion, $[V_4O_{12}]^{4-}$, where four tetrahedral VO_4 units share two vertices with each other to form a ring. A water molecule is attached on each side of the ring through hydrogen bonds.

Comment

Tetraalkylammonium salts of metavanadate, $(R_4N)[VO_3]$, have been widely used as starting materials for the syntheses of polyvanadates in aprotic solvents since their first preparation (Abe *et al.*, 1994; Abe, Akashi *et al.*, 1996; Abe, Isobe *et al.*, 1996; Akashi *et al.*, 1991; Attanasio *et al.*, 1993; Day *et al.*, 1990; Hayashi *et al.*, 2000, 2001; Kawanami *et al.*, 2000; Nakano *et al.*, 2001). However, $(R_4N)[VO_3]$ itself has not been fully characterized to date. It is assumed to be a tetrameric compound with a ring structure, $(R_4N)_4[V_4O_{12}]$, because it readily gives organometallic compounds that have a V_4O_{12} ring, but this assumption has never been confirmed by an X-ray structure analysis. Trimeric $(R_4N)_3[V_3O_9]$ has recently been isolated from an aged DMF solution, a solvent seldom used in the syntheses of polyvanadates (Hamilton *et al.*, 2002). We have isolated the title metavanadate salt as the tetraethylammonium salt, (I), from an acetonitrile solution and found that the anion does have the expected V_4O_{12} ring structure (Fig. 1).



(I)

The V—O distances in (I) [1.643 (2)–1.822 (2) Å] are all normal for a vanadate and compare well with those observed for other compounds that contain a V_4O_{12} ring. The ring in (I) assumes a twisted-boat–chair conformation, similar to that observed for $[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]^{2-}$ (Akashi *et al.*, 1991), $[Zn(2,2'\text{-bipy})_3]_2[V_4O_{12}]\cdot 11H_2O$ (2,2′-bipy is 2,2′-bipyridine; Zhang *et al.*, 1997) and $[Ni(2,2'\text{-bipy})_3]_2[V_4O_{12}]\cdot 11H_2O$ (Yang *et al.*, 1998), and not the twisted-chair conformation observed for $\{[(\eta\text{-}C_8H_{12})Ir]_2(V_4O_{12})\}^{2-}$ (Day *et al.*, 1990).

As can be seen in Fig. 1, two water molecules are attached to the $[V_4O_{12}]^{4-}$ anion of (I) through hydrogen bonds, one to each face. Each water molecule bridges two terminal V=O O atoms. The $[(V_4O_{12})(H_2O)_2]^{4-}$ anion is surrounded by $C_8H_{20}N^+$ cations, and no other interactions are observed between the anions and/or water molecules (Fig. 2).

The structure of the $[(V_4O_{12})(H_2O)_2]^{4-}$ anion as a whole very closely resembles that of $[\{(\eta^3\text{-}C_4H_7)_2Rh\}_2(V_4O_{12})]^{2-}$, a vanadate-supported organorhodium complex. It is interesting to note that the V1=O2 [1.659 (2) Å] and V2=O4 [1.665 (2) Å] distances in (I) are virtually the same as those between the V and O atoms that bridge the V and Rh atoms in $\{[(\eta^3\text{-}C_4H_7)_2Rh]_2[V_4O_{12}]\}^{2-}$ [1.652 (5) and 1.670 (5) Å].

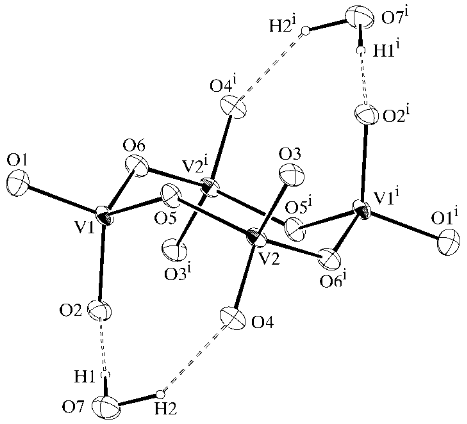


Figure 1
A view of the $[(V_4O_{12})(H_2O)_2]^{4-}$ anion of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $-x, -y, -z$].

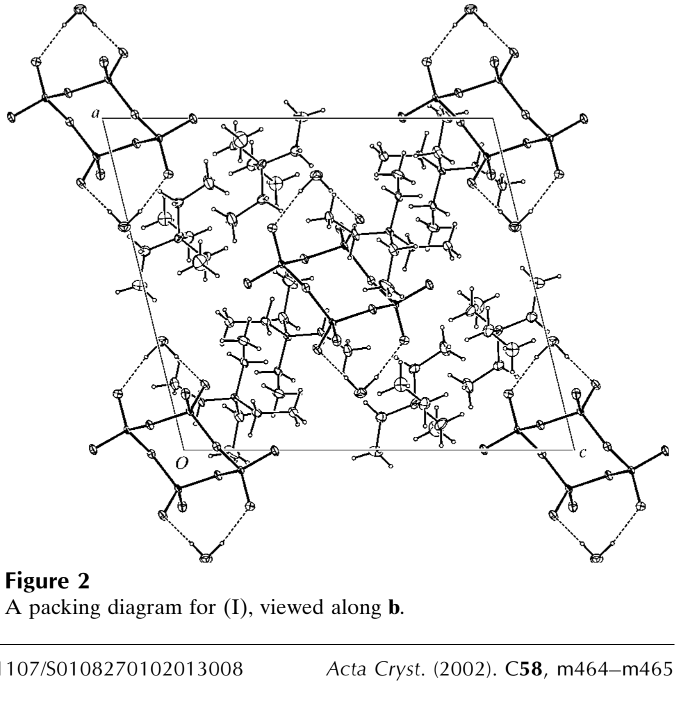


Figure 2
A packing diagram for (I), viewed along **b**.

The $[(V_4O_{12})(H_2O)_2]^{4-}$ anion observed here can be viewed as a vanadate-supported water complex. In fact, the same adsorption geometry is proposed for water molecules adsorbed on V_2O_5 (Ranea *et al.*, 2000). A similar vanadate-supported water complex can be found in $[Zn(2,2'\text{-bipy})_3]_2[V_4O_{12}]\cdot 11H_2O$, although the $[V_4O_{12}]^{4-}$ anion in that compound is also hydrogen-bonded to many other water molecules.

The water molecules in (I) are bound relatively tightly onto the surface of the $[V_4O_{12}]^{4-}$ anion. The compound does not lose these water molecules even if it is dried under vacuum over P_2O_5 for more than 12 h. The TG–DTA (thermogravimetry–differential thermal analysis) of (I) gives a well defined peak at around 373 K that accounts for a 3.8% weight loss. This is consistent with the dissociation of two water molecules. The dissociation enthalpy was determined to be 103 kJ mol^{-1}, which allows us to estimate the binding energy of a water molecule on the $[V_4O_{12}]^{4-}$ surface to be ~51 kJ mol^{-1}.

Experimental

The crude product of (I) was prepared by dissolving V_2O_5 (2.0 g, 0.011 mmol) in a 10% aqueous solution of Et_4NOH (35 ml, 0.022 mmol), stirring the solution for 18 h, evaporating it to dryness under vacuum, dissolving the resulting solid in warm acetonitrile (100 ml), filtering off a small amount of insoluble material, adding diethyl ether (800 ml) to the filtrate, collecting by filtration the white precipitate which formed, and drying it under vacuum for 8 h (yield 73%, 3.8 g, 4.0 mmol). Crystals of (I) suitable for X-ray diffraction were obtained by dissolving the crude product (0.10 g) in warm acetonitrile (7 ml), adding *m*-xylene (5 ml) with stirring, and allowing the mixture to stand at ambient temperature overnight. The crystals gave a satisfactory elemental analysis; calculated (found) for $C_{32}H_{84}N_4O_{14}V_4$: C 40.59 (40.33), H 8.79 (8.89), N 5.78 (5.88), V 21.6 (21.4)%.

Crystal data

$(C_8H_{20}N)_4[V_4O_{12}]\cdot 2H_2O$
$M_r = 952.79$
Monoclinic, $P2_1/n$
$a = 14.0187\ (3)$ Å
$b = 10.5729\ (2)$ Å
$c = 16.0212\ (4)$ Å
$\beta = 103.836\ (1)^\circ$
$V = 2305.7\ (1)$ Å^3
$Z = 2$
$D_x = 1.372$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4000 reflections
$\theta = 1.0$–30.5°
$\mu = 0.85$ mm^{-1}
$T = 90\ (2)$ K
Plate, colourless
$0.40 \times 0.30 \times 0.02$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.631$, $T_{max} = 0.983$
22 145 measured reflections
7001 independent reflections
3962 reflections with $I > 2\sigma(I)$
$R_{int} = 0.114$
$\theta_{max} = 30.5^\circ$
$h = -16 \rightarrow 20$
$k = -14 \rightarrow 15$
$l = -21 \rightarrow 22$

Refinement

Refinement on F^2
$R(F) = 0.058$
$wR(F^2) = 0.141$
$S = 0.92$
7001 reflections
244 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0673P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -0.87$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O7—H1···O2	0.94	1.85	2.792 (3)	178
O7—H2···O4	1.04	1.91	2.853 (3)	149

The water H atoms were located from difference Fourier syntheses and no refinements were applied. The H atoms in the tetraethylammonium cations were refined using a riding model, with C—H distances in the range 0.98–0.99 Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1072). Services for accessing these data are described at the back of the journal.

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