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The cyclic vanadylacetate $(C_{24}H_{20}P)[V_4O_8(C_2H_3O_2)_4(NO_3)]$

Dirk Wulff-Molder and Manfred Meisel*

Anorganische und Allgemeine Chemie, Humboldt-Universität Berlin, Hessische Strasse 1–2, D-10115 Berlin, Germany
Correspondence e-mail: manfred=meisel@chemie.hu-berlin.de

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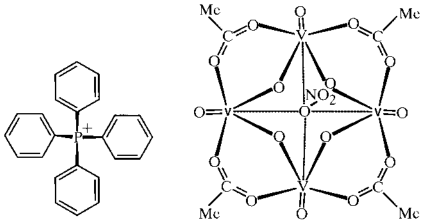
In the title complex, tetraphenylphosphonium μ_4-nitrato-κ^4O-*cyclo*-tetrakis(μ-acetato-O:O')tetra-μ-oxo-tetrakis[oxovanadium(V)], the anion lies about a twofold axis and consists of the cyclic $[V_4O_8]$ unit coordinated by four acetato ligands with interatomic V$\cdots$V distances of 3.269 (1) and 3.273 (1) Å. The double-bonded O atom [N=O 1.102 (6) and N—O 1.268 (4) Å] of the nitrato ligand links the four V atoms with V—O bond distances of 2.613 (2) and 2.813 (2) Å. The negative charge of the complex is balanced by tetraphenylphosphonium cations occupying the Na positions in the NaCl-type ionic packing of the structure.

Comment

Our attempts to synthesize $(PPh_4)[VO_2(NO_3)_2]$ resulted in the formation of the title compound, $(PPh_4)[V^V{}_4O_8(CH_3COO)_4(NO_3)]$, (I). Similar cyclic oxovanadium carboxylate complexes were described previously by Rehder (1994) and Priebsch *et al.* (1991) in $[V^V{}_3V^{IV}O_7OH({}^tBuCH_2COO)_4K][{}^tBuCH_2COO]\cdot 2{}^tBuCH_2COOH$ and by Heinrich *et al.* (1989) in the compound $(NEt_4)_2[V^V{}_3V^{IV}O_8(tca)_4(NO_3)]\cdot H_2O$ (tca^- = thiophene-2-carboxylate). Furthermore, the $[V_4O_8]$ moiety was observed as a building unit in the oxovanadium phosphonate $(NBu_4)_2[(V^V{}_4O_8)_2OV^{IV}(H_2O)_4(PhPO_3)_8Cl_2]\cdot 2Et_2O\cdot 2MeOH\cdot 4H_2O$ (Chen & Zubieta, 1994), the $[V_5O_9]$ group of compounds $(NEt_4)_2[V^VV^{IV}{}_4O_9(tca)_4Cl]\cdot MeCN$ (Heinrich *et al.*, 1989) and $(Me_2NH_2)_5(NH_4)[(V^VV^{IV}{}_4O_9)V^{IV}{}_2O_4(H_2O)_2(PhPO_3)_8(NH_4Cl)_2]\cdot 5H_2O\cdot 4DMF$ (Müller *et al.*, 1992), and the isopolyvanadates $Cs_9[H_4V^{IV}{}_{18}O_{42}X]\cdot 12H_2O$ (X = Br^- or I^-) (Müller *et al.*, 1990). The complex vanadate ion $[V^V{}_4O_8(CH_3COO)_4(NO_3)]^-$ reported here is the first example of a non-reduced cyclic vanadyl carboxylate ion. Its partly reduced counterpart $[V^V{}_3V^{IV}O_8(tca)_4(NO_3)]^{2-}$, investigated by Heinrich *et al.* (1989), indicates the capability of this type of compound to participate in reversible redox reactions.



(I)

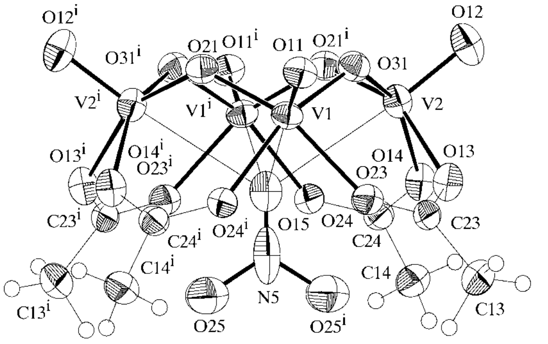


Figure 1
The structure of the cyclic anion of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. Bonds between V and O atoms are shown by heavy lines. [Symmetry code: (i) $1-x, \frac{1}{2}-y, z$.]

The structure of (I) (Fig. 1) consists of two crystallographically different phosphonium cations, P6 and P7, occupying special positions with site symmetry $\bar{4}$ (Wyckoff *b* and *a*, respectively). The cyclic anions are placed in the resulting gaps of site symmetry 2 (Wyckoff *e*), with the twofold axis of the C_{2v} symmetry of the anion coinciding with the fourfold screw axis of the crystal symmetry. Four V atoms in square pyramidal coordination are corner-connected to form a cyclic tetramer. The two lower basal O atoms of the $[OVO_4]$ pyramids belong to acetato ligands, each of them linking two metal centres. Bond distances and angles (Table 1) agree with the data of the compounds described by Heinrich *et al.* (1989), Priebsch *et al.* (1991) and Chen & Zubieta (1994) (V=O 1.54–1.65, V—O 1.77–2.07 and V$\cdots$O 2.02–2.79 Å). Mean plane calculations yield a mean distance of 0.37 (2) Å for the metal atoms above the basal plane of the square pyramids (atoms used for V1 were O21, O31, O23 and O24^i, and for V2 O21^i, O31, O13 and O14). Valence sum calculations (Brese & O'Keeffe, 1991) clearly revealed the valence of +5 for both symmetry independent V atoms.

The two different V$\cdots$O bond distances of 2.613 (2) (×2) and 2.813 (2) Å (×2) to the double-bonded O atom of the central nitrate anion [N=O 1.102 (6) and N—O 1.268 (4) Å], which reflect the local C_{2v} symmetry of the $[V_4O_8(Ac)_4(NO_3)]^-$ anion (Fig. 1), are remarkable. This low symmetry is in good agreement with the observations of Heinrich *et al.* (1989) for $[V_4O_8(tca)_4(NO_3)]^{2-}$ [V$\cdots$O 2.564 (13)–2.793 (14) Å]. Calculations of the angles between the least-squares basal planes of opposing $[OVO_4]$ pyramids yielded 60.41 (5) and 78.31 (5)° for V1/V1^i and V2/V2^i, respectively, consistent with the C_{2v} symmetry.

Experimental

Compound (I) was obtained by reacting $(Ph_4P)[VO_2Cl_2]$ with $AgNO_3$ in acetonitrile under anaerobic conditions. On slow evaporation of the filtered solution, red cube-shaped crystals up to 2 mm in diameter were obtained, which were stable in air (yield 70%, based on V). It is assumed that the acetato ligands are formed by acid hydrolysis of the acetonitrile solvent caused by traces of water.

Crystal data

$(C_{24}H_{20}P)[V_4O_8(C_2H_3O_2)_4(NO_3)]$
$M_r = 969.32$
Tetragonal, $I4_1/a$
$a = 15.856$ (2) Å
$c = 29.753$ (5) Å
$V = 7480.3$ (18) Å^3
$Z = 8$
$D_x = 1.721$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5000 reflections
$\theta = 8.1$–$20.7°$
$\mu = 1.095$ mm^{-1}
$T = 200$ (2) K
Prism, dark red
0.23 × 0.23 × 0.15 mm

Data collection

Stoe IPDS diffractometer
Oscillation scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.547$, $T_{\max} = 0.867$
32 401 measured reflections
3685 independent reflections
2503 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.071$
$\theta_{\max} = 26.06°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 36$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.112$
$S = 1.015$
3309 reflections
271 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 2.7778P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.503$ e Å^{-3}
$\Delta\rho_{\min} = -0.747$ e Å^{-3}

The difference Fourier synthesis showed the methyl groups to be disordered. Therefore, the H atoms were placed in accordance with two methyl groups in a staggered orientation. The geometrically restrained refinement was performed with isotropic displacement parameters and free C—H bond distances.

Data collection: *IPDS* (Stoe & Cie, 1996); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1994); software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1345). Services for accessing these data are described at the back of the journal.

Table 1
Selected geometric parameters (Å, °).

V1—O11	1.584 (2)	V2—O21^{i}	1.815 (2)
V1—O21	1.799 (2)	V2—O13	1.993 (2)
V1—O31	1.825 (2)	V2—O14	2.006 (2)
V1—O24^{i}	1.996 (2)	V2—O15	2.813 (2)
V1—O23	2.024 (2)	N5—O15	1.102 (6)
V1—O15	2.613 (2)	N5—O25^{i}	1.268 (4)
V2—O12	1.582 (2)	N5—O25	1.268 (4)
V2—O31	1.797 (2)		
O11—V1—O21	102.58 (10)	O21^{i}—V2—O13	154.03 (9)
O11—V1—O31	102.95 (10)	O12—V2—O14	100.27 (11)
O21—V1—O31	96.58 (9)	O31—V2—O14	153.78 (9)
O11—V1—O24^{i}	98.73 (10)	O21^{i}—V2—O14	85.80 (9)
O21—V1—O24^{i}	88.56 (9)	O13—V2—O14	79.18 (9)
O31—V1—O24^{i}	155.99 (9)	O12—V2—O15	175.74 (12)
O11—V1—O23	98.41 (10)	O31—V2—O15	73.60 (8)
O21—V1—O23	157.27 (9)	O21^{i}—V2—O15	73.23 (8)
O31—V1—O23	87.02 (9)	O13—V2—O15	83.91 (8)
O24^{i}—V1—O23	79.69 (8)	O14—V2—O15	82.92 (8)
O11—V1—O15	177.55 (10)	V1—O21—V2^{i}	129.52 (11)
O21—V1—O15	78.94 (8)	V2—O31—V1	129.27 (12)
O31—V1—O15	78.69 (8)	O15—N5—O25^{i}	122.1 (3)
O24^{i}—V1—O15	79.33 (8)	O15—N5—O25	122.1 (3)
O23—V1—O15	79.80 (8)	O25^{i}—N5—O25	115.9 (6)
O12—V2—O31	103.81 (11)	V1^{i}—O15—V1	119.04 (14)
O12—V2—O21^{i}	104.06 (11)	V1^{i}—O15—V2^{i}	74.09 (7)
O31—V2—O21^{i}	98.14 (9)	V1—O15—V2^{i}	73.98 (7)
O12—V2—O13	99.41 (11)	V2^{i}—O15—V2	114.31 (13)
O31—V2—O13	86.77 (9)		

Symmetry code: (i) $1 - x, \frac{1}{2} - y, z$.

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