

Piperazinium aquabis(oxalato)oxovanadate(IV) sesquihydrate

Ling Lin,^a Shufang Wu,^a
Changcang Huang,^{b*} Hanhui
Zhang,^a Xihe Huang^a and
Zhaoxun Lian^a

^aDepartment of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, People's Republic of China, and ^bDepartment of Chemistry and Key Laboratory for Chemistry of Solid Materials, Fuzhou University, Fuzhou, Fujian 350002, People's Republic of China

Correspondence e-mail: cchuang@fzu.edu.cn

Received 2 April 2004

Accepted 14 April 2004

Online 24 April 2004

A mononuclear V^{IV} complex, (C₄H₁₂N₂)[VO(C₂O₄)₂(H₂O)]·1.5H₂O, with bis(oxalate) ligands, has been synthesized under hydrothermal conditions. The structure contains aquabis(oxalato)oxovanadium(IV) complex anions, [VO(C₂O₄)₂(H₂O)]²⁻, and diprotonated piperazine cations, [C₄N₂H₁₂]²⁺. The ions are connected through hydrogen bonds to form a three-dimensional network with micropores, where uncoordinated water molecules are located with the some degree of disorder. The V center has distorted octahedral geometry with one terminal O atom, four O atoms from two oxalate groups and one water O atom. The two oxalate groups are *cis* arranged. The V–O bond lengths are in the range 1.599 (2)–2.216 (2) Å.

Key indicators

Single-crystal X-ray study

T = 298 K

Mean σ (C–C) = 0.004 Å

H-atom completeness 83%

Disorder in solvent or counterion

R factor = 0.035

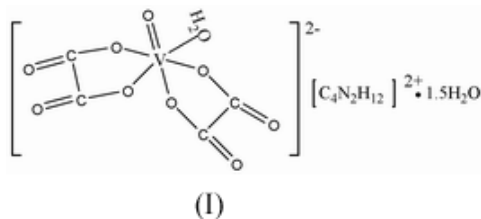
wR factor = 0.105

Data-to-parameter ratio = 14.5

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Comment

Tetravalent vanadium exists usually as VO²⁺. Some oxovanadium(IV) complexes have been developed for their specific applications in catalysis (Mishra & Kumar, 2002; Maurya *et al.*, 2003). Since the oxalate group can function as a bisbidentate ligand, coordination to two metal ions affords a wide variety of polynuclear complexes, several oxovanadium complexes with oxalate ligands have been synthesized and structurally characterized (Oughtred *et al.*, 1976; Zhou *et al.*, 1983; Cortes *et al.*, 1994; Salta *et al.*, 1996; Zheng *et al.*, 1998; Belaj *et al.*, 2000). In these oxovanadium complexes, the V atoms have distorted octahedral coordination geometry, and most of them have negatively charged complex ions and monovalent counterions.



In this paper, we report the crystal structure of the title compound, (I), a new oxovanadium–oxalate complex with the divalent organic piperazinium cation. The structure of (I) is shown in Fig. 1. Selected geometric parameters of the anion are given in Table 1. The V atom is octahedrally coordinated by one terminal O atom, four O atoms from two *cis* oxalate groups and one water O atom which is *cis* to the oxo group. The coordination octahedron is heavily distorted, with V–O bond lengths ranging from 1.599 (2) to 2.216 (2) Å, and O–V–O bond angles ranging from 75.24 (6) to 103.18 (8)° between *cis* O atoms and from 159.85 (8) to 169.55 (8)° between *trans* O atoms. The V1=O1 double-bond length of

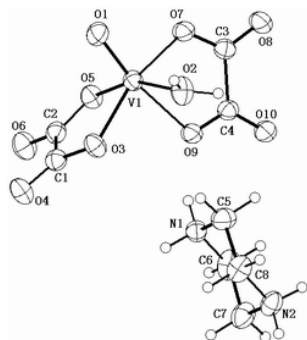


Figure 1
A view of the complex anion and the cation in (I), with displacement ellipsoids drawn at the 50% probability level. The disordered uncoordinated water molecules are not shown for clarity.

1.599 (2) Å is the shortest, and the V1—O3, V1—O5 and V1—O7 bond lengths are almost equal (Table 1), while V1—O9 [2.216 (2) Å] is much longer than the others due to the *trans* influence. The O1—V1—O(*cis*) angles are distinctly larger and the O9—V1—O(*cis*) angles smaller than 90° because of repulsion between the π electrons of the V1=O1 bond and the σ bonding pairs. All the atoms from each oxalate and the central V atom are arranged in quite planar configurations, with mean deviations of 0.067 (9) and 0.035 (8) Å, respectively, and with a dihedral angle between the two planes of 85.9 (4)°. Both oxalate ligands are less twisted than those in [VO(C₂O₄)(H₂O)₃] \cdot 3H₂O (Belaj *et al.*, 2000) and (NH₄)₂[VO(C₂O₄)₂H₂O] \cdot H₂O (Oughtred *et al.*, 1976). In the title compound, the torsion angles of the oxalate ligands are 6.32 (8) and 5.10 (8)° around C1—C2 and C3—C4, respectively, and those in [VO(C₂O₄)(H₂O)₃] \cdot 3H₂O and (NH₄)₂[VO(C₂O₄)₂H₂O] \cdot H₂O are more than 10°. The elongated C—C bond lengths [1.551 (4) and 1.546 (3) Å] in the oxalates are in agreement with the values found in other oxalate complexes. The piperazinium cation is in a chair configuration. The complex anions and piperazinium cations are held together by hydrogen bonds (Table 2) as well as by electrostatic interactions. The piperazinium cations are connected to the complex anions *via* donation from N—H groups to the O-atom acceptors of the oxalate groups. The coordinated water molecules and the oxalate groups of neighboring anions also form hydrogen bonds. This hydrogen-bonding system links the cations and the anions into a three-dimensional network with micropores (Fig. 2). The uncoordinated water molecules are located inside the pores with some degree of disorder. There are weak hydrogen bonds between the uncoordinated water molecules and the anions and cations (Table 2).

Experimental

The title compound was prepared from VOSO₄, oxalic acid and piperazine under hydrothermal conditions. All chemicals were of reagent grade and were used as commercially obtained. A mixture of VOSO₄, oxalic acid and piperazine in H₂O (7 ml) in a molar ratio of 1:2:2:550 was heated in a sealed Teflon-lined steel autoclave at 393 K for 3 d. The autoclave was cooled to ambient temperature spontaneously. Green single crystals were obtained in about 60% yield.

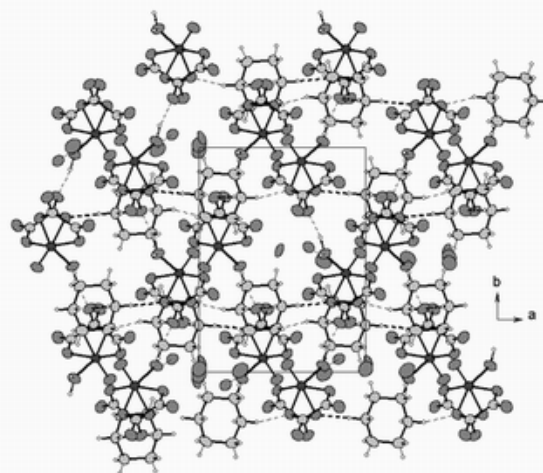


Figure 2
The crystal packing of (I). Hydrogen bonds are shown as dashed lines.

The product was collected by filtration, washed with distilled water and dried in air at ambient temperature.

Crystal data

(C₄H₁₂N₂)[VO(C₂O₄)₂·(H₂O)] \cdot 1.5H₂O
 M_r = 376.18
 Monoclinic, $P2_1/n$
 a = 9.9464 (9) Å
 b = 12.5099 (12) Å
 c = 12.5779 (9) Å
 β = 110.585 (3)°
 V = 1465.1 (2) Å³
 Z = 4

D_x = 1.705 Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 9344 reflections
 θ = 12–18°
 μ = 0.74 mm⁻¹
 T = 298 (2) K
 Block, green
 0.35 \times 0.32 \times 0.30 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
 ω -2 θ scans
 13 526 measured reflections
 3285 independent reflections
 2183 reflections with $I > 2\sigma(I)$

R_{int} = 0.043
 θ_{max} = 27.5°
 h = -12 \rightarrow 12
 k = -16 \rightarrow 16
 l = -16 \rightarrow 15

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.035
 $wR(F^2)$ = 0.106
 S = 0.92
 3285 reflections
 226 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.056P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max}$ = 0.001
 $\Delta\rho_{max}$ = 0.50 e Å⁻³
 $\Delta\rho_{min}$ = -0.25 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

V1—O1	1.5990 (18)	O4—C1	1.216 (3)
V1—O3	1.9898 (16)	O5—C2	1.283 (3)
V1—O5	2.0192 (17)	O6—C2	1.222 (3)
V1—O7	2.0211 (16)	O7—C3	1.277 (3)
V1—O2	2.0221 (18)	O8—C3	1.226 (3)
V1—O9	2.2162 (17)	O9—C4	1.260 (3)
O3—C1	1.294 (3)		
O1—V1—O3	103.18 (8)	O5—V1—O2	159.85 (8)
O1—V1—O5	100.24 (9)	O7—V1—O2	93.14 (7)
O3—V1—O5	80.39 (7)	O1—V1—O9	169.55 (8)
O1—V1—O7	94.41 (8)	O3—V1—O9	87.23 (7)
O3—V1—O7	162.15 (7)	O5—V1—O9	82.14 (7)
O5—V1—O7	93.66 (7)	O7—V1—O9	75.24 (6)
O1—V1—O2	98.12 (9)	O2—V1—O9	81.30 (7)
O3—V1—O2	87.42 (7)		

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1A \cdots O10^i$	0.90	1.94	2.826 (3)	169
$N1-H1B \cdots O9$	0.90	1.90	2.783 (3)	165
$N2-H2A \cdots O6^{ii}$	0.90	1.96	2.848 (3)	168
$N2-H2B \cdots O5^{iii}$	0.90	1.92	2.774 (3)	158
$O2-H101 \cdots O10^{iv}$	0.91	1.780	2.681 (3)	163
$O2-H102 \cdots OW1$	0.88	1.78	2.647 (3)	166
$O2-H102 \cdots OW2$	0.88	1.89	2.726 (7)	157

Symmetry codes: (i) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$; (iii) $1 + x, y, z$; (iv) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

The piperazinium H atoms were positioned geometrically ($C-H = 0.93$ Å and $N-H = 0.90$ Å) and refined using a riding model, with $U_{iso} = 1.2U_{eq}$ of the parent atom. The H atoms of the coordinated water were fixed at positions found from difference Fourier maps, with $U_{iso}(H) = 1.2U_{eq}(O)$. The H atoms of uncoordinated water molecules could not be located due to disorder.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1993); software used to prepare material for publication: *SHELXL97/2* (Sheldrick, 1997).

We gratefully acknowledge Mr Guang-can Xiao and Mrs Hua Yin for data collection. The work was financially supported by the Student Research Training Program (SRTP) and the Foundation of Science and Technology of Fuzhou University (XKJ-QD-00-06).

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