The Crystal Structures of Potassium Bis(oxalato)oxoperoxovanadate(V) Hemihydrate, $K_3[VO(O_2)(C_2O_4)_2] \cdot \frac{1}{2}H_2O$, and Potassium Bis(oxalato)dioxovanadate(V) Trihydrate, $K_3[VO_2(C_2O_4)_2] \cdot 3H_2O$

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The crystal structures of $K_3[VO(O_2)(C_2O_4)_2] \cdot \frac{1}{2}H_2O$ (**I**) and $K_3[VO_2(C_2O_4)_2] \cdot 3H_2O$ (**II**) were determined and refined by the least-squares method from single-crystal X-ray diffractometer data, collected at room temperature. Final R_F-values: 0.044 for **I** (2330 reflexions) and 0.043 for **II** (5261 reflexions). **I** crystallizes in the monoclinic space group $P2/c$ with $a = 11.724(3)$, $b = 7.508(2)$, $c = 13.199(2)$ Å, $\beta = 94.75(2)°$, $Z = 4$, and **II** in the triclinic space group $P\bar{1}$ with $a = 11.604(3)$, $b = 7.854(3)$, $c = 7.794(2)$ Å, $\alpha = 110.01(2)$, $\beta = 94.17(2)$, $\gamma = 91.34(2)°$ and $Z = 2$.

Crystals of **I** are not fully stoichiometric. They contain small amounts of bis(oxalato)dioxovanadate(V) ions and hydrogen peroxide of crystallization. The structure is disordered. Vanadium has pentagonal-bipyramidal coordination geometry. Bond distances: V=O_{apical} 1.625(6) Å, V–O_{apical} 2.142(3) Å, V–O_{peroxo} 1.871(6) and 1.882(6) Å, V–$O_{oxalato}$ 2.019(3)–2.147(3) Å, $(O–O)_{peroxo}$ 1.430(10) Å, C–$O_{terminal}$ 1.212(5)–1.233(5) Å, C–$O_{coordinated}$ 1.267(5)–1.295(5) Å and C–C 1.551(6) and 1.555(6) Å.

The results obtained for the yellow crystals of **II** are in accordance with a previous investigation of a red compound with the same composition. Bond distances: V–O 1.631(2) and 1.643(2) Å, V–O (*trans* to O_{oxo}) 2.165(2) and 2.238(2) Å, V–O (*trans* to $O_{oxalato}$) 1.993(2) and 2.014(2) Å, C–$O_{terminal}$ 1.222(2)–1.239(2) Å, C–$O_{coordinated}$ 1.264(2)–1.292(3) Å and C–C 1.552(3) and 1.554(3) Å.

Earlier attempts to prepare and analyze the structure of a potassium bis(oxalato)oxoperoxovanadate(V) were not successful.[1] Recently, however, Schwendt et al. were able to prepare $K_3[VO(O_2)(C_2O_4)_2] \cdot H_2O$.[2] Since peroxovanadates have received an increasing attention lately (see, *e.g.*, the introduction in Ref. 3 and references therein) it was thought worthwhile to examine this monoperoxovanadate(V) in the course of structural studies on peroxometallates in progress at this department. This was also considered to be advantageous in the investigation of the relation between the structure and method of thermal decomposition, performed by Schwendt *et al.*[4] The corresponding peroxo-free potassium bis(oxalato)dioxovanadate(V) was also prepared, and a structure analysis of it was performed since it differed in colour from that reported by Drew *et al.*[1] The latter might contain peroxide, not considered during the structure analysis.

Experimental

Preparation. Crystals of **I** were prepared according to Schwendt.[4] 1.38 g (10 mmol) KVO_3, 1.84 g (10 mmol) $K_2C_2O_4 \cdot H_2O$ and 1.26 g (10 mmol) $H_2C_2O_4 \cdot 2H_2O$ were dissolved in 20 ml 15 % (100 mmol) H_2O_2 at 0 °C. The solution was left to evaporate at 3 °C. Crystals were obtained within one week and were picked out before complete evaporation. Most of the product was in the form of a crystalline mass.

Crystals of **II** were prepared by dissolving 1.38 g (10 mmol) KVO_3, 1.84 g (10 mmol) $K_2C_2O_4 \cdot H_2O$ and 1.26 g (10 mmol) $H_2C_2O_4 \cdot 2H_2O$ in 20 ml water at room temperature and allowed the solution to evaporate. After a couple of days yellow crystals were obtained.

X-Ray methods. Rotation and Weissenberg photographs were taken of **I** (Cu*K*-radiation), from which systematic absences and approximate cell dimensions were obtained.

Intensity data and unit cell dimensions were obtained as described earlier.[3] The intensities were corrected for Lorentz, polarization and, for **II**, absorption effects. Crystal data and conditions for data collection are summarized in Table 1.

Structure determination

I. According to the systematically absent reflexions possible space groups are *P2/c* and *Pc*. Since $Z = 4$ and the IR-spectrum indicated mononuclear anions,[2] *P2/c* was tried first. The structure was solved by Patterson and electron density calculations. Full-matrix least-squares refinement of a scale factor and positional and anisotropic thermal parameters reduced the *R*-value to 0.054.

Table 1. Crystal data and conditions for data collection (room temperature).

	$K_3[VO_{1+x}(O_2)_{1-x}(C_2O_4)_2]-$ $\cdot(\frac{1}{2}-y)H_2O \cdot yH_2O_2, x=0.2, y=0.1$	$K_3[VO_2(C_2O_4)_2] \cdot 3H_2O$
F.W.	399.68	430.32
Crystal system	Monoclinic	Triclinic
Space group	*P2/c* (No. 13)	$P\bar{1}$ (No. 2)
a (Å)	11.724(3)	11.604(3)
b (Å)	7.508(2)	7.854(3)
c (Å)	13.199(2)	7.794(2)
α (°)	90	110.01(2)
β (°)	94.75(2)	94.17(2)
γ (°)	90	91.34(2)
V (Å^3)	1158.0(5)	664.9(3)
Z	4	2
D_x (g cm^{-3})	2.293	2.149
μ(Mo*K*α) (mm^{-1})	2.02	1.78
Crystal size (mm)	0.09×0.13×0.18	0.31×0.34×0.42
Colour	Bright dark-red	Yellow
Data collection		
Collection method	$\omega-2\theta$	$\omega-2\theta$
Scan speed (° min^{-1})	1.8–12.0	8.0–29.3
2θ range (°)	3.5–60	3.5–70
Number of independent reflexions collected	3414	5903
Number of observed independent reflexions ($I \geqq 3\sigma(I)$)	2330	5261
R_F ($=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$)	0.044	0.043
R_w	0.050	0.050
Diff. Four. max. (e Å^{-3})	0.77	0.56

Table 2. Atomic fractional coordinates and B_{eq} (B_{iso} for Op and H) for $K_3[VO_{1+x}(O_2)_{1-x}(C_2O_4)_2]\cdot(\frac{1}{2}-y)H_2O\cdot yH_2O_2$, x=0.2, y=0.1 (I). Ow denotes the oxygen atom in a water molecule and Op one in a hydrogen peroxide molecule. All atoms occupy the general four-fold site 4*g* in space group *P2/c* except Ow, which occupies the special two-fold site 2*f*. The occupation numbers are 0.60(2) for O1 and O2, 0.80(2) for O6, 0.20(2) for O1B, O2B and Op, 0.40(2) for O6B, 0.80(2) for Ow and H and 1 for all other atoms.
$B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
V	0.21474(6)	0.12822(9)	0.39431(5)	1.87(1)
K1	0.06067(9)	0.1698(1)	0.62641(7)	2.70(2)
K2	0.64155(8)	0.2843(1)	0.67894(7)	2.56(2)
K3	0.26789(9)	0.2961(2)	0.12631(8)	2.99(2)
O1	0.2489(6)	0.0311(9)	0.2689(5)	2.4(1)
O2	0.1298(6)	0.0686(8)	0.2728(4)	2.8(1)
O3	0.0578(3)	0.2245(4)	0.4160(2)	2.59(7)
O4	0.2584(3)	0.2782(5)	0.5305(2)	2.68(7)
O5	0.3874(3)	0.1459(5)	0.4005(2)	2.82(8)
O6	0.2001(6)	−0.0471(8)	0.4643(4)	3.1(1)
O7	0.2233(2)	0.3927(4)	0.3347(2)	2.30(7)
O8	0.4065(3)	0.3825(5)	0.6300(2)	2.90(8)
O9	0.5454(3)	0.2477(6)	0.4849(3)	3.45(9)
O10	0.1228(3)	0.6444(4)	0.3199(3)	2.83(8)
O11	−0.0598(3)	0.4564(5)	0.3907(3)	2.93(8)
C1	0.3642(3)	0.3040(6)	0.5539(3)	2.08(8)
C2	0.4424(3)	0.2280(6)	0.4751(3)	2.22(9)
C3	0.1333(3)	0.4871(5)	0.3421(3)	1.94(8)
C4	0.0330(3)	0.3852(6)	0.3861(3)	2.14(8)
O1 B	0.261(2)	−0.062(3)	0.468(2)	3.2(5)
O2 B	0.145(2)	−0.033(3)	0.472(2)	2.8(5)
O6 B	0.1971(9)	0.045(1)	0.2776(7)	2.3(2)
Ow	$\frac{1}{2}$	−0.018(1)	$\frac{1}{4}$	6.9(4)
Op	0.448(3)	0.024(4)	0.220(3)	5.0(6)
H	0.545(9)	0.07(1)	0.198(8)	5.00

For a few relatively weak reflexions with low θ-values F_c differed considerably from F_o. Moreover, the electron density difference map showed residual maxima ($\Delta\varrho < 1.4$ e Å^{-3}) near the peroxo oxygen atoms O1 and O2, the oxo oxygen atom O6 and the water oxygen atom Ow. These oxygen atoms also had significantly higher *B*-values, and the distance between the peroxo oxygen atoms was only 1.27 Å with the model at this stage. Refinement in space group *Pc* led to the same result. The above evidence indicates disorder and, possibly, non-stoichiometry.[6-14] The residual maxima were therefore taken to be partial oxygen atoms. Introduction of these atoms, as well as occupation numbers for them and O1, O2, O6 and Ow, in the refinement led to a further reduction of R to 0.044. Weights were applied according to $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$,[15] with $a = 60$, $c = 0.003$ and $d = 0.00002$.

Due to the observed disorder and non-stoichiometry, full data sets were collected for another two crystals, obtained in different preparations. These led to the same results within the experimental errors.

II. The close agreement between the cell data obtained in the present investigation and those obtained by Draw *et al.*,[1] indicates that the compounds might be almost identical. A structure factor calculation was, therefore, undertaken with the parameters given in Ref. 1. This led to an R-value of 0.35, due to, as became evident, a sign error in x_V in Table 1.[1] Refinement was performed as above. Absorption correction was applied according to Walker and Stuart.[16]

Table 3. Atomic fractional coordinates and B_{eq} (B_{iso} for H) for $K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$ (**II**). All atoms occupy the general, two-fold site 2*i* of space group $P\bar{1}$. Ow denotes a water oxygen atom. Labelling according to Ref. 1, if different, is given in parenthesis. $B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.

Atom	*x*	*y*	*z*	B_{eq}/Å^2
V	0.29262(3)	−0.18585(4)	0.15474(4)	1.824(7)
K1	0.47937(4)	−0.72509(7)	0.57118(7)	2.88(1)
K2	0.22804(4)	−0.73135(6)	0.15926(6)	2.42(1)
K3	0.17270(4)	0.03270(7)	0.58814(6)	2.76(1)
O12 (O1)	0.3519(1)	−0.0068(2)	0.3167(2)	2.79(4)
O3 (O4)	0.4297(1)	−0.2954(2)	0.0205(2)	2.45(4)
O4 (O5)	0.1805(1)	−0.3679(2)	−0.0873(2)	2.57(3)
O5 (O3)	0.1366(1)	−0.0857(2)	0.1927(2)	2.22(3)
O6 (O2)	0.2860(1)	−0.3413(2)	0.2515(2)	2.89(4)
O7 (O6)	0.3017(1)	−0.0600(2)	−0.0517(2)	2.51(4)
O8 (O9)	−0.0036(1)	−0.4003(2)	−0.2069(2)	3.05(4)
O9 (O7)	−0.0526(1)	−0.1287(3)	0.1107(2)	3.14(4)
O10	0.3769(2)	−0.0983(3)	−0.3173(3)	3.97(6)
O11 (O8)	0.5240(1)	−0.3410(2)	−0.2296(3)	2.91(4)
C1 (C3)	0.0756(2)	−0.3282(2)	−0.0863(2)	2.03(4)
C2 (C1)	0.0475(2)	−0.1683(3)	0.0855(2)	2.03(4)
C3 (C4)	0.3702(2)	−0.1288(3)	−0.1732(3)	2.11(4)
C4 (C2)	0.4501(2)	−0.2669(2)	−0.1285(3)	2.08(4)
Ow1	0.3196(2)	−0.6810(2)	−0.1557(3)	3.11(4)
Ow2	0.2648(2)	−0.5194(3)	0.5270(3)	3.88(5)
Ow3	−0.0024(2)	−0.7460(3)	0.5136(3)	3.85(5)
H11	0.377(4)	−0.646(7)	−0.094(7)	4.2(11)
H12	0.286(4)	−0.592(6)	−0.136(5)	2.4(8)
H21	0.224(4)	−0.486(7)	0.627(7)	4.8(11)
H22	0.265(4)	−0.414(7)	0.478(7)	4.8(12)
H31	0.004(4)	−0.717(6)	0.420(6)	3.5(9)
H32	−0.005(4)	−0.655(6)	0.605(6)	3.0(9)

The above-mentioned weighting scheme was used with $a = 15$, $c = 0.008$ and $d = 0.0004$.

The highest peaks in the final electron density difference maps appeared at about 1 Å from vanadium in both **I** and **II**.

The atomic scattering factors for K, V, O, C and H were taken from Ref. 17. Calculations were carried out on an IBM 3033 computer, using the crystallographic programmes described in Refs. 18 and 19. Lists of structure factors and anisotropic thermal parameters are available from the author on request.

Results and discussion

Atomic positional parameters and equivalent isotropic thermal parameters, B_{eq}, are given in Table 2 for **I** and in Table 3 for **II**, bond distances within the anions in Table 4, other bond distances in Table 5 and bond angles in **I** in Table 6. Fig. 1 shows a stereoscopic view of the unit cell of **I** and Fig. 2 the anion in **I** and the atomic labelling in it. The unit cell content of **II** is shown in Fig. 1 in Ref. 1. The atomic labelling in the anion in **II** is the same as in **I** (Fig. 2) except for the oxo oxygen atom which was replaced by the peroxo group O1/O2; this is denoted O12 in **II**.

Crystals of $K_3[VO_{1+x}(O_2)_{1-x}(C_2O_4)_2]\cdot(\frac{1}{2}-y)$-$H_2O\cdot yH_2O_2$, $x = 0.2$, $y = 0.1$ (**I**) consist of potassium ions, bis(oxalato)oxoperoxovanadate(V) ions, water of crystallization, and, to a small extent, bis(oxalato)dioxovanadate(V) ions and hydrogen peroxide of crystallization. Vanadium is seven-coordinated in the pentagonal-bipyramidal way, first observed for $[CrO(O_2)_2(C_{12}H_8N_2)]$,[20] with a double-bonded oxygen atom, O6, and an oxalato oxygen atom, O7, at the apices. The equatorial plane is defined by the peroxo oxygen

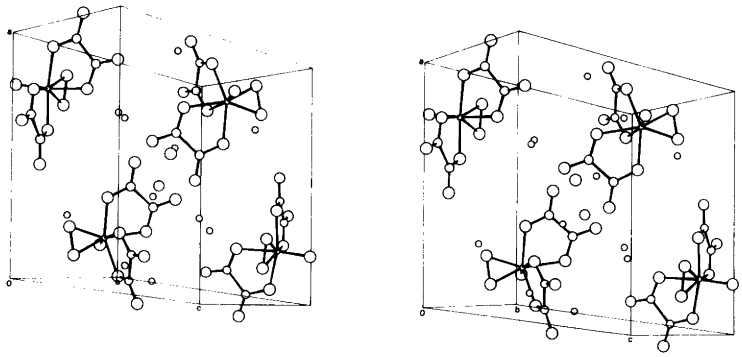

Fig. 1. Stereoscopic view of the unit cell of $K_3[VO(O_2)(C_2O_4)_2] \cdot \frac{1}{2}H_2O$. The disorder is not shown.

atoms, a second oxygen atom from the above-mentioned oxalato group and two oxygen atoms from the other oxalato group. The maximum deviation from this plane is 0.064 Å (the r.m.s. deviation is 0.049 Å), and the vanadium atom is displaced 0.247 Å from the equatorial plane towards the double-bonded oxygen atom. This coordination geometry has been met with in other oxalatooxoperoxometallates,[21-24] as well as in other pentagonal-bipyramidal mononuclear oxoperoxovanadates (see, *e.g.*, the discussion in Ref. 3 and references therein).

The brightly coloured yellow crystals of $K_3[VO_2(C_2O_4)_2] \cdot 3H_2O$ (**II**) consisted of potassium ions, bis(oxalato)dioxovanadate(V) ions with distorted octahedral geometry, and water of crystallization. The present investigation has shown that the structure of **II** is identical with that of the bright red compound in Ref. 1. (The average discrepancy between bond distances is 1.4 σ and the maximum deviation in positional parameters is less than 5 σ). The difference in colour is probably due to traces of peroxide in the red compound, since this was obtained in the presence of hydrogen peroxide in an attempt to prepare **I**.[1] A similar difference in colour has been observed for $K_2VO_2F_3$.[25]

The present investigation has shown that if hydrogen peroxide is added to a solution from which crystals of $K_3[VO_2(C_2O_4)_2] \cdot 3H_2O$ are suitably obtainable upon evaporation, the corresponding monoperoxo complex is formed. In this case one of the two oxo oxygen atoms in the bis(oxalato)dioxovanadate(V) ion has been replaced by a peroxo group. This substitution may be incomplete and in the present case 20 % of the anions are unsubstituted. Incomplete substitution of oxo oxygen atoms by peroxo groups have been observed in other peroxometallates, too, especially bulky ones with few oxygen positions to be replaced.[13,14,26] Some of the water molecules have also been replaced by hydrogen peroxide molecules. This is not uncommon among peroxovanadates.[9,10] The extreme case is $K_3[VO(O_2)_2(C_2O_4)] \cdot H_2O_2$,[23] in which all water molecules in $K_3[VO(O_2)_2(C_2O_4)] \cdot H_2O$[22] have been replaced.

The crystals of **I** are disordered. 20 % of the anions have a different orientation from the rest, and this is obtained by turning the anion about the vanadium atom so that the oxo oxygen atom O6 and the peroxo group O1/O2 on one hand and the oxalato groups on the other change places. Only O1, O2 and O6 could be resolved in the two orientations, all other atoms being indistinguishably superimposed in pairs. From the standpoint of packing conditions of bulky anions this difference is rather small inasmuch as the centre of the peroxo group O1/O2 in one orientation almost coincides (within 0.13 Å) with that of

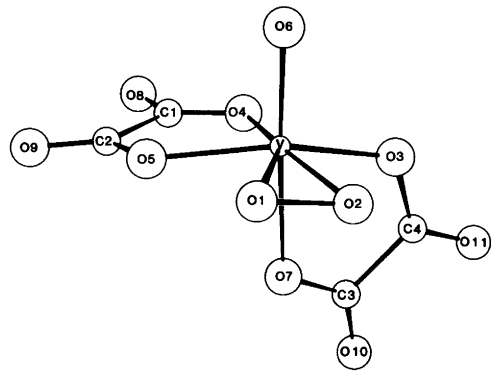

Fig. 2. The anion $[VO(O_2)(C_2O_4)_2]^{3-}$.

Table 4. Bond distances (Å) within the anions in **I** and **II**.

	I	II		I	II
V–O1	1.882(6)		C1–O8	1.233(5)	1.239(2)
V–O2	1.871(6)		C1–C2	1.551(6)	1.552(3)
V–O12		1.631(2)	C2–O5	1.289(5)	1.289(2)
V–O3	2.019(3)	2.014(2)	C2–O9	1.212(5)	1.222(3)
V–O4	2.147(3)	2.238(2)	C3–O7	1.281(5)	1.265(2)
V–O5	2.024(3)	1.993(2)	C3–O10	1.221(5)	1.233(3)
V–O6	1.625(6)	1.643(2)	C3–C4	1.555(6)	1.554(3)
V–O7	2.142(3)	2.165(2)	C4–O3	1.295(5)	1.292(3)
O1–O2	1.430(10)		C4–O11	1.218(5)	1.226(3)
C1–O4	1.267(5)	1.264(2)			

the oxo oxygen atom O6 in the other. The presence of the hydrogen peroxide molecules may influence the disorder. If the anions have their main orientation the consequence would be a rather short distance, 2.48(3) Å, between Op and O1. When the anions have the other orientation the shortest distance, between Op and O5, is 2.70(3) Å, and this is a normal hydrogen bond distance. In the presence of the peroxo-free anion there is enough space for the hydrogen peroxide molecule.

The anions in **I** and **II** show great similarities. A striking feature is the structural *trans* effect, first observed among peroxometallates for $[CrO(O_2)_2(C_5H_5N)]$.[27,28] The effect is a substantial weakening of a bond *trans* to an oxo oxygen atom. In the extreme case, uncommon among peroxometallates, an atom *trans* to the oxo oxygen atom is completely missing, examples being the above-mentioned peroxochromate.[27,28]

$M_2[VFO(O_2)_2]$ (M=K, Cs)[11,12] and $NH_4[VO(O_2)_2(NH_3)]$.[29] $(NH_4)_2[VFO(O_2)_2]$ present an intermediate example; the V–O bond *trans* to V=O is 2.505(1) Å.[30] The anions in **I** and **II** belong to the group of examples in which the bond elongation goes no further than about 0.2 Å. When a peroxo group replaces one of the oxo oxygen atoms in **II** an increased strength of the bond *trans* to the peroxo group is observed.

Disregarding the peroxo group in **I** and the corresponding oxo oxygen atom in **II** and the effect of these atoms on the V–O bonds *trans* to them, the bond lengths in **I** and **II** show great similarities (Table 4) as well as with those in the anion in $(NH_4)_3[VO_2(C_2O_4)_2]$.[31] The effect of the weakening of a bond from vanadium to an oxalato oxygen atom is accompanied by an increased

Table 5. Other bond distances (Å) in **I** and **II**.

I		II	
Ow–H	1.12(10)	Ow1–H11	0.78(5)
Op–Op	1.39(6)	Ow1–H12	0.78(4)
V–O1B	1.78(2)	Ow2–H21	0.90(5)
V–O2B	1.83(2)	Ow2–H22	1.02(5)
V–O6B	1.66(1)	Ow3–H31	0.84(5)
O1B–O2B	1.38(3)	Ow3–H32	0.82(4)

Table 6. Bond angles (°) in **I**.

O1–V–O2	44.8(3)	O6–V–O7	166.0(2)
O1–V–O3	121.7(2)	V–O1–O2	67.2(3)
O1–V–O4	152.4(2)	V–O2–O1	68.0(4)
O1–V–O5	77.0(2)	V–O3–C4	118.3(3)
O1–V–O6	103.1(3)	V–O4–C1	116.4(3)
O1–V–O7	90.9(2)	V–O5–C2	119.8(3)
O2–V–O3	77.3(2)	V–O7–C3	114.9(2)
O2–V–O4	156.4(2)	O3–C4–O11	124.9(4)
O2–V–O5	120.7(2)	O3–C4–C3	114.5(3)
O2–V–O6	102.7(3)	O4–C1–O8	126.2(4)
O2–V–O7	86.8(2)	O4–C1–C2	113.7(3)
O3–V–O4	81.4(1)	O5–C2–O9	124.8(4)
O3–V–O5	153.0(1)	O5–C2–C1	113.7(3)
O3–V–O6	94.0(2)	O7–C3–O10	125.7(4)
O3–V–O7	77.9(1)	O7–C3–C4	114.2(3)
O4–V–O5	76.3(1)	O8–C1–C2	120.1(4)
O4–V–O6	88.7(2)	O9–C2–C1	121.5(4)
O4–V–O7	78.8(1)	O10–C3–C4	120.1(4)
O5–V–O6	100.6(3)	O11–C4–C3	120.6(4)
O5–V–O7	82.9(1)	H–Ow–H	106(11)

Table 7. C–O and C–C bond lengths (Å) in some complex oxalates and, for comparison, in an uncoordinated oxalate ion. Abbreviations: ox = oxalate, en = ethylenediamine, mal = malonate, c = coordinated, u = uncoordinated.

Compound	C–O_c (long M–O)	C–O_c (normal M–O)	C–O_u	C–C	Ref.
$K_3[VO_{1+x}(O_2)^{1-x}(ox)_2]\cdot(\frac{1}{2}-y)H_2O\cdot yH_2O_2$	1.267 (5)		1.233 (5)	1.551 (6)	This work
	1.281 (5)		1.221 (5)	1.555 (6)	
		1.289 (5)	1.212 (5)		
		1.295 (5)	1.218 (5)		
$K_3[VO_2(ox)_2]\cdot 3H_2O$	1.264 (2)		1.239 (2)	1.552 (3)	This work
	1.265 (2)		1.233 (3)	1.554 (3)	
		1.289 (2)	1.222 (3)		
		1.292 (3)	1.226 (3)		
$K_3[VO_2(ox)_2]\cdot 3H_2O$	1.257 (3)		1.240 (3)	1.550 (3)	1
	1.263 (3)		1.224 (4)	1.551 (4)	
		1.287 (3)	1.220 (3)		
		1.290 (4)	1.221 (3)		
$(NH_4)_3[VO_2(ox)_2]\cdot 2H_2O$	1.263 (3)		1.239 (3)	1.531 (4)	31
	1.262 (4)		1.241 (4)	1.544 (4)	
		1.280 (4)	1.234 (4)		
		1.291 (3)	1.221 (3)		
$K_3[VO(O_2)_2(ox)]\cdot H_2O$	1.258 (7)		1.241 (7)	1.550 (8)	22
		1.282 (7)	1.219 (7)		
$K_2[MoO(O_2)_2(ox)]$	1.266 (20)		1.213 (23)	1.561 (25)	21
		1.287 (23)	1.207 (25)		
$K_2[WO(O_2)_2(ox)]$	1.281 (11)		1.217 (13)	1.540 (13)	24
		1.295 (11)	1.207 (12)		
$Na_3[VFO(ox)_2]\cdot 6H_2O$	1.280 (5)		1.239 (5)	1.556 (7)	33
		1.293 (5)	1.235 (5)	1.541 (6)	
		1.287 (6)	1.235 (6)		
		1.291 (6)	1.230 (6)		
$(NH_4)_2[VO(ox)_2(H_2O)]\cdot H_2O$	1.259 (4)		1.237 (5)	1.542 (6)	34
		1.283 (4)	1.226 (5)	1.549 (6)	
		1.284 (6)	1.217 (6)		
		1.275 (5)	1.217 (6)		
$[Co(ox)(en)_2][Co(CN)_2(mal)(NH_3)_2]\cdot 3H_2O$		1.276 (5)	1.222 (6)	1.556 (6)	35
		1.282 (5)	1.239 (6)		
Na_2ox			1.253 (3)	1.568 (4)	36
			1.265 (3)		

strength of the corresponding C–O bond. Among the peroxometallates this effect was first observed for $K_2[MoO(O_2)_2(C_2O_4)]$.[21] The bonds between the carbon atoms and the uncoordinated oxygen atoms are even stronger. This is a general effect observed in other oxalato complexes as well as the correlation between the C–O_c and C–$O_u$bond lengths; the longer the C–O_c bond length the shorter is the C–O_u length (see Table 7 and, *e.g.*, the compilation of C–O and C–C bond lengths in simple oxalates in Refs. 21 and 32).

The V=O bond lengths are close to the average value, 1.609(7) Å (r.m.s. deviation is given in parenthesis), calculated from data for 11 peroxovanadates(V) (see Table 3 in Ref. 37 and Table 4 in Ref. 38). These values show that the V=O bond is best described as a double bond. The V–O_{peroxo} bond lengths are close to those reported for *cis* V–O_{peroxo} bond lengths in diperoxovanadates, *e.g.* 1.874(2) and 1.880(2) Å in $(NH_4)_2[VFO(O_2)_2]$,[30] and 1.890(2) and 1.887(2) Å in $(NH_4)_3[VF_2O(O_2)_2]$,[38] and to 1.887(5) and

1.862(5) Å observed in the monoperoxovanadate $[VO(O_2)(C_5H_4NCOO)(C_{10}H_8N_2)] \cdot H_2O$.[37] See also Table 3 in Ref. 37 and Table 4 in Ref. 4. The peroxo group is thus symmetrically coordinated; in several other peroxovanadates a small asymmetry has been found. The $V–O_{peroxo}$ bonds and two of the $V–O_{oxalato}$ bonds have bond orders close to unity, while the remaining V–O bonds are considerably weaker (*vide supra*). The $(O–O)_{peroxo}$ bond is rather short but not significantly different from those reported for other monoperoxovanadates. For example, it is 1.424(7) Å in $[VO(O_2)(C_5H_4NCOO)(C_{10}H_8N_2)] \cdot H_2O$,[37] 1.441(3) Å in $NH_4[VO(O_2)(H_2O)\{C_5H_3N(COO)_2\}] \cdot xH_2O$,[39] and 1.435(3) Å in $[VO(O_2)(C_5H_4NCOO)(H_2O)_2]$.[40] Due to the disorder in **I** the bond distances observed with the anion in the less populated position are rather uncertain but do not differ significantly from other observations.

The planar CO_2 groups in the two oxalato groups are twisted in both **I** and **II**. In **I** the twist angles about the C–C bonds are 2.4 and 5.8° and in **II** 3.6 and 7.9°, respectively. This non-planarity of the oxalato groups as well as the above-mentioned slight non-planarity in the bis(oxalato)oxoperoxovanadate ion, consistent with the non-rigidity of seven-coordination, seem to be due to packing conditions.

There is plenty of room for the water molecule, reflected by the rather high thermal motion of Ow and the possibility to replace it by the larger hydrogen peroxide molecule. It is hydrogen bonded only to O5 (2.764(5) Å; the angle Ow–H...O5 is almost linear, being 161(9)°), like the hydrogen peroxide molecule (Op...O5 is 2.70(3) Å). The potassium ions K1 and K3 have six nearest neighbours and K2 seven at distances less than 3.0 Å in both **I** and **II**. Their coordination polyhedra are highly irregular.

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