The Crystal Structure of Potassium Carbonato-oxodiperoxovanadate(V), K₃[VO(O₂)₂(CO₃)]

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The crystal structure of $K_3[VO(O_2)_2(CO_3)]$ has been determined and refined from single-crystal X-ray diffractometer data to a final R_F-value of 0.033 for 1521 observed reflexions. The yellow compound crystallizes in the monoclinic space group Cm (No. 8) with $a=9.822(1)$, $b=9.274(1)$, $c=5.598(1)$ Å, $\beta=130.03(1)°$ and $Z=2$.

Vanadium is pentagonal-bipyramidally coordinated and the complex anion has C_s symmetry. The two peroxo groups and one carbonato oxygen atom are almost coplanar and form the equatorial plane, while the second carbonato oxygen atom and the terminal, double-bonded oxygen atom occupy the apical positions. The vanadium atom is displaced 0.36 Å from the equatorial plane towards the double-bonded oxygen atom. The bidentate carbonato ligand is planar (crystallographic mirror plane). There is a distinct correlation between the C−O bond lengths and the extent to which the three oxygen atoms participate in other bonds.

Bond distances: $V=O_{apical}$ 1.617(3) Å, $V-O_{apical}$ 2.301(3) Å, $V-O_{equatorial}$ 2.039(3) Å, $trans$ $V-O_{peroxo}$ 1.945(2) Å, cis $V-O_{peroxo}$ 1.873(2) Å, $(O-O)_{peroxo}$ 1.467(3) Å, $C-O_{terminal}$ 1.254(4) Å, $C-O_{equatorial}$ 1.317(4) Å and $C-O_{apical}$ 1.297(4) Å.

Peroxovanadates have received an increasing attention lately, not only because of the biochemical significance of peroxometallates (see Ref. 1 and references therein) but also because of the use of vanadates as catalysts for the oxidation of olefins by hydrogen peroxide.[2-4] For the understanding of *e.g.* transition metal catalyzed oxidation reactions in which oxygen or peroxides are used as oxidizing agents, peroxometallates often being intermediates, the study of the synthesis, reactions and structures of peroxometallates is vital. Since peroxides are thermodynamically unstable it is also of importance to study the stabilizing effect of certain ligands and to correlate this with the structure.

As far as peroxovanadates are concerned the structures of some fifteen have been reported hitherto.[5-22] Among peroxovanadates with purely inorganic ligands some of those containing fluorine show remarkable stability, *e.g.* $K_2[VFO(O_2)_2]$,[16] which has a completely different structure from the corresponding ammonium salt.[19] During the preparation of $(NH_4)_2[VFO(O_2)_2]$ it was observed that crystals of this compound, while in contact with the mother liquor, transformed into $(NH_4)_3[VF_2O(O_2)_2]$;[17] the corresponding transformation has not been observed for $K_2[VFO(O_2)_2]$ or $Cs_2[VFO(O_2)_2]$.[20] Several other phases appear in the system $MVO_3-(MF,HF)-H_2O_2-H_2O$ (M=NH₄,K). From elemental analysis, infrared and Raman spectra and X-ray powder patterns two additional new types of

peroxovanadates are claimed to exist, *viz.* $M_3[HV_2O_2(O_2)_3F_4]\cdot 2H_2O$ and $(NH_4)_2[V_2O_2(O_2)_4F]\cdot nH_2O$ ($n\approx 2$).[23] Other workers have reported the synthesis of $(NH_4)_2[VO(O_2)OHF_2]$,[24] $K_4[V_2O_3(O_2)_2F_4]$,[24] $K_2[VO(O_2)_2F]$,[25] and $K_2[V_2O_3(O_2)_2F_2]$,[26] which were prepared from acidic media, and $M_2[VO(O_2)_2F]$,[27] and $M_2[V(O_2)_3F]$ (M=Na, K, NH_4),[28] from alkaline media. Fluorine obviously has a stabilizing effect which also has been observed for other peroxometallates (see, *e.g.*, Refs. 29−36 and references therein).

A polydentate ligand like the carbonate ion might be a potential stabilizing ligand. While carbonatometallates are well-known very few carbonatoperoxometallates seem to exist. Recently however, the author prepared and determined the structure of the novel peroxotungstate, $K_6[W_4O_8(O_2)_6(CO_3)]\cdot 6H_2O$, shown to be a new type of tungstate, a tetratungstate with a bridging carbonato group.[37] A carbonatoperoxovanadate with the empirical formula $K_3[VO(O_2)_2(CO_3)]$ has recently been prepared by Schwendt,[38] and the structure of this compound is reported in the present paper.

EXPERIMENTAL

Preparation. 0.23 g vanadium(V) oxide and 10 g potassium carbonate were dissolved in 50 ml 1.5 % hydrogen peroxide. The solution was left to evaporize at 5 °C. After about a week yellow plate-like crystals, intergrown in a layer manner, were obtained. (This is a modification of the method used by Schwendt, who started from potassium vanadate.[38])

X-Ray methods. X-Ray powder photographs were obtained by the Guinier-Hägg method ($CuK\alpha_1$ radiation) using $Pb(NO_3)_2$ ($a=7.8566$ Å at 21 °C) as an internal standard.

For the single-crystal work crystal fragments were cut out from the crystalline mass. Rotation and Weissenberg photographs were taken (CuK-radiation), from which systematic reflexion absences and approximate cell dimensions were obtained. Several crystals were used, most of which contained crystal satellites. One crystal fragment, shown by the appearance of the Weissenberg photographs to be a single crystal, was used for the intensity data collection. The crystals are stable for several months at 5 °C but disintegrate within about one day when exposed to CuK-radiation at room temperature. They are considerably more stable towards MoK-radiation.

Intensity data were recorded at room temperature with a SYNTEX P2$_1$ automatic four-circle single-crystal X-ray diffractometer (graphite-monochromated MoKα radiation, crystal size 0.13×0.14×0.20 mm, θ-2θ scan method, $2\theta\leqslant 90°$, scan speed 2−12 °/min, three test reflexions each forty-seventh reflexion). Integrated intensity values were obtained with the Lehmann-Larsen profile analysis method.[39] The test reflexions showed a loss in intensity of about 20 % during the collection of the data (35 h). This was corrected for. Of the 1692 independent reflexions registered, 1521 having $I\geqslant 3\sigma(I)$ were regarded as being observed and were used in the subsequent calculations. The intensities were corrected for Lorentz, polarization and absorption effects. The unit cell dimensions were determined from a least-squares fit of refined diffractometer setting angles for 15 reflexions with $2\theta>34°$.

CRYSTAL DATA

$K_3[VO(O_2)_2(CO_3)]$ F.W.=308.24

Space group *Cm* (No. 8)
$a=9.822(1)$ [9.814(2)] Å, $b=9.274(1)$ [9.260(1)] Å, $c=5.598(1)$ [5.586(1)] Å, $\beta=130.03(1)$ [130.11(1)]°, $V=390.4(1)$ [388.2(1)] Å^3, $Z=2$, $D_x=2.622$ g cm^{-3} $\mu(MoK\alpha)=2.92$ mm^{-1}. (Values within brackets are from powder data).

A list of observed lines in the powder photograph of $K_3[VO(O_2)_2(CO_3)]$, giving *hkl*, d_o and d_c, is available from the author on request.

Table 1. Atomic fractional coordinates and equivalent isotropic thermal parameters for K$_3$[VO(O$_2$)$_2$(CO$_3$)]. $B_{eq}=\frac{4}{3}\sum_i\sum_j \beta_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j$. Space group Cm. $Z=2$.

Atom	Site	x	y	z	$B_{eq}/\text{Å}^2$
V	2a	0	0	0	1.11(1)
K1	2a	0.40981(13)	0	0.9010(2)	1.81(3)
K2	4b	0.36335(9)	0.28175(6)	0.3664(2)	1.80(2)
O1	4b	−0.0245(3)	0.2073(2)	0.0143(5)	1.88(7)
O2	4b	0.1112(3)	0.1387(2)	0.3176(5)	1.74(5)
O3	2a	0.1077(4)	0	−0.1285(8)	2.00(10)
O4	2a	−0.2484(3)	0	−0.4263(6)	1.54(7)
O5	2a	−0.2448(4)	0	−0.0298(6)	1.54(7)
O6	2a	−0.5074(4)	0	−0.5192(8)	1.82(8)
C	2a	−0.3406(4)	0	−0.3305(7)	1.26(8)

Table 2. Bond distances (Å) and angles (°) in K$_3$[VO(O$_2$)$_2$(CO$_3$)].

Distance		Angle		Angle	
V−O1	1.945(2)	O1−V−O2	45.2(1)	O2−V−O5	90.7(1)
V−O2	1.873(2)	O1−V−O2′	130.6(1)	O4−V−O3	96.4(1)
V−O3	1.617(3)	O1−V−O1′	162.3(1)	O4−V−O5	60.5(1)
V−O4	2.039(3)	O1−V−O4	87.8(1)	O3−V−O5	156.9(1)
V−O5	2.301(3)	O1−V−O3	98.8(1)	V−O4−C	98.1(2)
O1−O2	1.467(3)	O1−V−O5	81.5(1)	V−O5−C	86.9(2)
C−O4	1.317(4)	O2−V−O2′	86.7(1)	O4−C−O5	114.5(3)
C−O5	1.297(4)	O2−V−O4	129.7(1)	O4−C−O6	121.7(3)
C−O6	1.254(4)	O2−V−O3	105.9(1)	O5−C−O6	123.9(3)

STRUCTURE DETERMINATION

Possible space groups, according to the systematically absent reflexions, are $C2$, Cm and $C2/m$. The C-centering and the cell content strongly indicates the presence of two mononuclear complex anions in each cell with vanadium in a two-fold special position. If the carbonato ligand acts as a bidentate non-bridging ligand and the complex has the pentagonal-bipyramidal geometry often observed, the complex cannot have a two-fold axis or a centre of symmetry, but may have a mirror plane. The only possible space group is then Cm, which was shown to be correct. Vanadium should thus occupy position 2a (x, 0, z) and since the x- and z-coordinates can be arbitrarily fixed for one atom in space group Cm, vanadium was located at (0,0,0). The other atoms were located from a series of successive electron density calculations with due regard taken to the false symmetry introduced by basing the signs of the structure factors on vanadium in the initial step.

Full-matrix least-squares refinement of positional and isotropic thermal parameters for all atoms reduced the R-value to 0.053 ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$) after absorption correction, using an empirical method for correcting diffractometer data for absorption effects due to Walker and Stuart.[40] The introduction of anisotropic thermal parameters for all atoms led to a further reduction of the R-value to 0.033. The atomic scattering factors for K, V, O and C
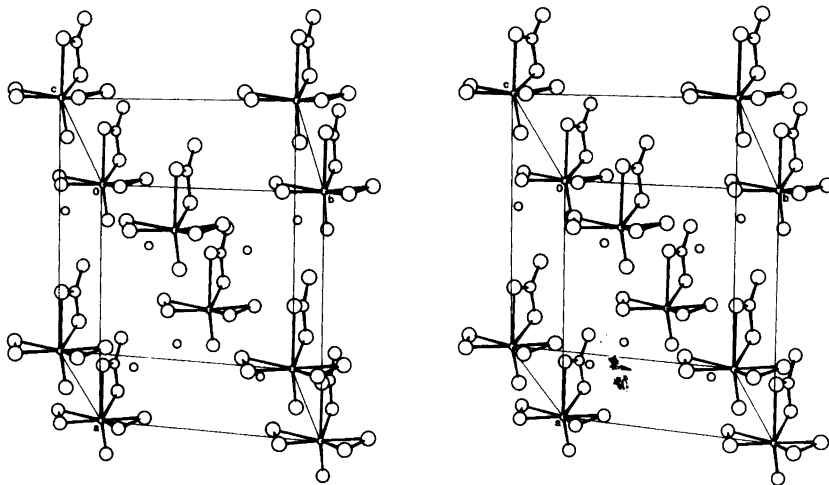
Fig. 1. Stereoscopic drawing of the unit cell of $K_3[VO(O_2)_2(CO_3)]$.

were taken from *Ref.* 41. Weights were applied according to $w=(a+|F_o|+c|F_o|^2+d|F_o|^3)^{-1}$,[42] with $a=15$, $c=0.015$ and $d=0.0004$. The highest peak in the final electron density map was 0.77 e/Å³, which appeared 1 Å from vanadium. Calculations were carried out on an IBM 3033 computer, using the crystallographic programmes described in Refs. 43 and 44. 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 1, bond distances and angles in Table 2 and cation environment in Table 3. Fig. 1 shows a stereoscopic view of the unit cell content and Fig. 2 the anion.
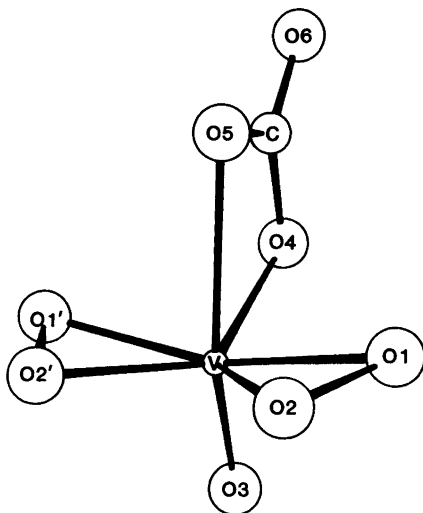

Fig. 2. The anion $[VO(O_2)_2(CO_3)]^{3-}$.

Table 3. Cation environment in $K_3[VO(O_2)_2(CO_3)]$. Distances less than 3.2 Å are included.

Distance/Å		Distance/Å	
K1···O1[ii,iii]	2.768(2)	K2···O2[i]	2.664(2)
K1···O6[iv]	2.793(3)	K2···O5[viii]	2.667(2)
K1···O3[v]	2.864(3)	K2···O2[viii]	2.721(2)
K1···O2[i,vi]	2.932(2)	K2···O6[vii]	2.794(1)
K1···O6[vii]	2.942(3)	K2···O1[viii]	2.811(2)
K1···O4[iv]	3.031(3)	K2···O4[iii]	2.878(2)
K1···O5[vii]	3.157(3)	K2···O3[iii]	3.020(3)
		K2···O1[i]	3.036(2)
		K2···O1[iii]	3.040(2)

Symmetry codes

[i]	x, y, z	[v]	$x, y, 1+z$
[ii]	$\frac{1}{2}+x, -\frac{1}{2}+y, 1+z$	[vi]	$x, -y, z$
[iii]	$\frac{1}{2}+x, \frac{1}{2}-y, 1+z$	[vii]	$1+x, y, 1+z$
[iv]	$1+x, y, 2+z$	[viii]	$\frac{1}{2}+x, 1-y, z$

The crystals of $K_3[VO(O_2)_2(CO_3)]$ consist of potassium ions and carbonatooxodiperoxovanadate(V) ions. The complex ions have C_s symmetry. Vanadium is seven-coordinated in the pentagonal-bipyramidal way first observed for $[CrO(O_2)_2(C_{12}H_8N_2)]$,[45] with a double-bonded oxygen atom, O3, and a carbonato oxygen atom, O5, at the apices. The equatorial plane is defined by the peroxo oxygen atoms O1, O2, O2′ and O1′ and the second coordinated carbonato oxygen atom O4. The maximum deviation from this plane is 0.062 Å, while the r.m.s. deviation is 0.051 Å. The non-planarity is partly due to the close contact between O2 and two potassium atoms, K2 (see Table 3). The carbonato group, the double-bonded oxygen atom O3 and vanadium are situated in a crystallographic mirror plane and the equatorial plane is perpendicular to this.

The vanadium atom is displaced 0.359 Å from the equatorial plane towards the double-bonded oxygen atom; similar observations have been made for other pentagonal-bipyramidal mononuclear oxoperoxovanadates.[7–14,17,21,22] (See also Table 4 in Ref. 17 and

Table 4. C−O bond lengths (Å) in some bidentate carbonato complexes (u=uncoordinated, c=coordinated).

Complex	C−O$_u$	C−O$_c$	Ref.
$[VO(O_2)_2(CO_3)]^{3-}$	1.254(4)	1.317(4)	this work
		1.297(4)	
$[Cr(CO_3)_4(H_2O)_2]^{4-}$	1.256(4)	1.285(4)	47
	1.266(4)	−1.299(4)	
$[(NH_3)_4Co(NH_2)(OH)Co(CO_3)_2]$	1.236(4)	1.306(4)	48
	1.237(4)	−1.324(4)	
$[Th(CO_3)_5]^{6-}$	1.236(16)	1.278(15)	49
	−1.257(16)	−1.325(15)	
$[Ce(CO_3)_5]^{6-}$	1.247(9)	1.276(8)	50
	−1.271(9)	−1.316(8)	
$[Cu(CO_3)_2]_n^{2n-}$	1.259(3)	1.303(3)	51
		1.307(3)	

Table V in Ref. 46). In pentagonal-pyrimidal six-coordinated oxoperoxovanadates the displacement is even more pronounced, *viz.* 0.44−0.53 Å.[6,16,20]

The V−O_{apical} bond *trans* to the V=O_{apical} bond is considerably weaker than the V−$O_{equatorial}$ bonds (2.301(3) Å compared to 1.873(2)−2.039(3) Å). This is a general observation made for pentagonal-bipyramidal oxoperoxometallates (see Table 6 in Ref. 5, Table 4 in Ref. 17 and Table VIII in Ref. 46), first observed by the author for $[CrO(O_2)_2(C_{12}H_8N_2)]$;[45] the effect is called the structural *trans effect*. The ultimate extreme would be pentagonal-pyrimidal six-coordination, exemplified by $NH_4[VO(O_2)_2NH_3]$,[6] $K_2[VFO(O_2)_2]$,[16] and $Cs_2[VFO(O_2)_2]$[20] while $(NH_4)_4[O\{VO(O_2)_2\}_2]$,[5,18] and $(NH_4)_2[VFO(O_2)_2]$[19] are intermediate with V−O_{apical} bond lengths of 2.50 Å. With bidentate ligands other than the peroxo group seven-coordination is usually achieved, $[VF_2O(O_2)_2]^{3-}$ being the sole example of a peroxovanadate with only monodentate ligands, disregarding the peroxo groups, with an unshared atom occupying the second apical position (*trans* to V=O) of the pentagonal-bipyramidal coordination polyhedron.

The V=O_{apical} bond length, 1.617(3) Å, does not differ significantly from the average value, 1.609(7) Å (r.m.s. deviation is given in parenthesis), calculated from data for 11 peroxovanadates (see Table 3 in Ref. 12 and Table 4 in Ref. 17).[6-8,10-14,16-18] The V−$O_{equatorial}$ bond lengths, though having typical single bond values, are considerably different. The longest, 2.039(3) Å, involves one carbonato oxygen atom. The corresponding distances in the closely related oxalatoperoxovanadates are 2.060(4),[8] 2.062(3),[11] and 2.019(3) and 2.024(3) Å,[22] respectively. The two *trans* V−O_{peroxo} bonds V−O1 and V−O1′, 1.945(2) Å, are significantly longer than the two *cis* V−O_{peroxo} bonds V−O2 and V−O2′, 1.873(2) Å. A similar asymmetry has been observed in other peroxovanadates (see Refs. 8 and 19). Possible reasons for this asymmetry have been discussed by Begin *et al.*[8]

The O−O bond length, 1.467(3) Å, agrees well with the average value, 1.464(6) Å, calculated from data for the above-mentioned 11 peroxovanadates.[6-8,10-14,16-18]

The carbonato group is planar; it is situated in a crystallographic mirror plane. There is a close correlation between the three C−O bond lengths, being significantly different, and the extent to which the oxygen atoms participate in other bonds. The bond to the terminal, uncoordinated oxygen atom O6, 1.254(4) Å, is the shortest, showing considerable double-bond character. As is evident from Table 4, this is also observed for other carbonato complexes. The C-O5 bond, 1.297(4) Å, is stronger than the C−O4 bond 1.317(4) Å, while the V−O5 bond, 2.301(3) Å, is weaker than the V−O4 bond, 2.039(3) Å. Thus, the stronger the V−O bond the weaker the corresponding C−O bond.

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