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The Crystal Structure of Ammonium Difluorooxodiperoxovanadate(V), $(NH_4)_3[VF_2O(O_2)_2]$

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A new peroxovanadate, ammonium difluorooxodiperoxovanadate(V), $(NH_4)_3[VF_2O(O_2)_2]$, has been synthetized and its structure determined at room temperature by single-crystal X-ray methods. The compound crystallizes as pale-yellow prismatic crystals belonging to space group $P2_12_12_1$ (No. 19) with a=6.866(2) Å, b=8.365(1) Å, c=13.264(2) Å, V=761.7(2) Å^3 and Z=4. The structure was solved by Patterson and Fourier methods and least-squares refinement gave a final $R(F)$-value of 0.027 for 1611 observed independent reflexions.

The ligands form a pentagonal bipyramid around vanadium, the configuration being similar to that of $[CrO(O_2)_2phen]$. The two peroxo groups and one fluorine atom form the pentagonal plane while the other fluorine atom and the double-bonded oxygen atom occupy the apical positions. The vanadium atom is displaced 0.309 Å from the equatorial plane towards the apical oxygen atom. The peroxo groups are slightly asymmetrically coordinated, the two *trans* $V-O_{peroxo}$ bond distances, 1.921(2) and 1.927(2) Å, being significantly longer than the two *cis* $V-O_{peroxo}$ bond distances, 1.890(2) and 1.887(2) Å. Other bond distances are: V=O 1.609(2) Å, $V-F_{equatorial}$ 1.958(1) Å, $V-F_{apical}$ 2.306(1) Å, $(O-O)_{peroxo}$ 1.462(2) and 1.466(2) Å and N–H 0.80(4)–0.97(4) Å.

Despite the importance of peroxovanadates, *e.g.* in catalytic processes (see Refs. in Ref. 1), hitherto the structures of only four peroxovanadates with purely inorganic ligands, namely $(NH_4)_4[O\{VO(O_2)_2\}_2]$,[2a,b] $NH_4[VO(O_2)_2(NH_3)]$,[3] $(NH_4)_3[V(O_2)_4]$[4] and $K_2[VFO(O_2)_2]$[1] have been determined by single-crystal X-ray methods. Recent interest in fluoroperoxovanadates ($K_2[VFO(O_2)_2]$ was reported for the first time in 1980),[5] has prompted us to elucidate their structures, the first analysis dealing with $K_2[VFO(O_2)_2]$.[1] In the system $NH_4^+-V_2O_5-F^-$ $-H_2O_2$ band-shaped crystals of $(NH_4)_2[VFO(O_2)_2]$ are readily formed. On prolonged standing in contact with the mother liquor, these crystals are transformed to other vanadates, mostly without peroxide, due to decomposition. In some cases a few pale-yellow well-formed prismatic crystals appeared and the band-shaped crystals turned into polycrystalline aggregates of this compound, shown by the present structure investigation to be $(NH_4)_3[VF_2O(O_2)_2]$, a completely new compound.

EXPERIMENTAL

X-Ray methods. Intensity data were recorded at 18 °C using a SYNTEX $P2_1$ automatic four-circle single-crystal X-ray diffractometer, graphite-monochromatized Mo$K\alpha$ radiation and a crystal with the dimensions 0.17×0.19×0.24 mm. The $\omega-2\theta$ scan method was used and the 2θ scan speed was allowed to vary between 2.3 and 29.3° min^{-1}. Data were collected for $2\theta \leq 70°$. A profile analysis based on the Lehmann-Larsen method[6] was applied to the 96-step profile collected for each reflexion. Two test reflexions were measured after each forty-eighth reflexion; they showed no significant difference in intensity during the collection of the data.

A total of 1965 independent reflexions were measured. Of these, 1611 having $I \geq 3\sigma(I)$ were used in the subsequent calculations. Corrections were made for Lorentz and polarization effects but not for absorption.

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The unit cell parameters were determined from a least-squares fit of refined diffractometer setting angles for 15 reflexions.

CRYSTAL DATA

$(NH_4)_3[VF_2O(O_2)_2]$ F.W.=223.05
Space group $P2_12_12_1$ (No. 19)
a=6.866(2) Å, b=8.365(1) Å, c=13.264(2) Å, V=761.7(2) Å^3, Z=4, D_c=1.945 g cm^{-3}, μ(Mo$K\alpha$)=1.41 mm^{-1}.

STRUCTURE DETERMINATION

The structure was solved by Patterson and electron density calculations. Full-matrix least-squares refinement of positional and isotropic thermal parameters for the non-hydrogen atoms reduced the R-value to 0.045 ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$). From a subsequent electron density difference map all the hydrogen atoms were located (peak heights 0.43–0.64 e Å^{-3}). Introduction of the positional parameters for the hydrogen atoms and anisotropic thermal parameters for the non-hydrogen atoms reduced the R-value to 0.027 in the final cycles of refinement. The isotropic thermal parameters for the nitrogen atoms were used as the B_{iso}'s for the corresponding hydrogen atoms and were not refined. The weighting scheme used was $w=(a+|F_o|+c|F_o|^2+d|F_o|^3)^{-1}$ with a=50, c=0.005 and d=0.003.[7] The scattering factors for V, F, O and N were taken from Ref. 8 as were the dispersion corrections. An electron density difference synthesis calculated after the final cycle of refinement showed no peak higher than 0.30 e Å^{-3}.

Calculations were carried out on an IBM 3033 computer using the crystallographic programmes described in Ref. 9. Lists of structure factors and anisotropic thermal parameters are available from the author on request.

RESULTS AND DISCUSSION

Positional parameters and U_{eq} are given in Table 1, bond distances and angles in Table 2 and hydrogen bond distances in Table 3. Fig. 1 shows a stereoscopic picture of the unit cell content and Fig. 2 the anion.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters for $(NH_4)_3[VF_2O(O_2)_2]$. $U_{eq}=\frac{1}{3}(U_{11}+U_{22}+U_{33})$.

Atom	x	y	z	U_{eq}/Å^2
V	0.16656(4)	0.00292(4)	0.10045(2)	0.0140(1)
F1	0.3180(2)	−0.1726(1)	0.0422(1)	0.0226(8)
F2	0.4134(2)	−0.0202(2)	0.2175(1)	0.0244(9)
O1	0.0502(3)	−0.1457(2)	0.1930(1)	0.0246(9)
O2	0.0091(3)	0.0221(2)	0.2167(1)	0.0255(10)
O3	0.2270(3)	0.2224(2)	0.1108(1)	0.0227(9)
O4	0.3582(3)	0.1417(2)	0.0404(1)	0.0218(10)
O5	0.0053(2)	0.0045(3)	0.0124(1)	0.0281(9)
N1	0.3353(4)	0.2412(2)	0.3355(2)	0.0229(11)
N2	0.1202(3)	0.5467(2)	0.0834(2)	0.0234(10)
N3	0.3025(3)	−0.2563(3)	0.3588(2)	0.0252(13)
H1	0.213(7)	0.281(5)	0.330(4)	0.023
H2	0.354(7)	0.156(5)	0.301(3)	0.023
H3	0.342(7)	0.203(5)	0.397(3)	0.023
H4	0.410(7)	0.321(6)	0.320(3)	0.023
H5	0.013(7)	0.568(5)	0.042(4)	0.024
H6	0.070(6)	0.547(5)	0.152(3)	0.024
H7	0.150(7)	0.456(5)	0.072(3)	0.024
H8	0.218(7)	0.608(5)	0.070(3)	0.024
H9	0.245(7)	−0.209(5)	0.417(3)	0.026
H10	0.331(7)	−0.187(5)	0.314(3)	0.026
H11	0.424(7)	−0.294(5)	0.382(4)	0.026
H12	0.224(7)	−0.328(6)	0.340(3)	0.026

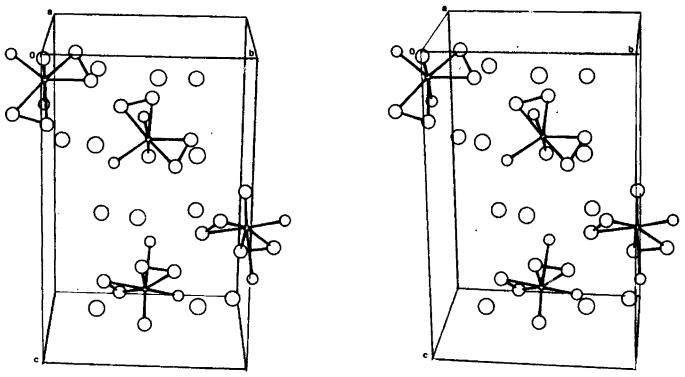

Fig. 1. Stereoscopic drawing of the unit cell of $(NH_4)_3[VF_2O(O_2)_2]$. The hydrogen atoms are not shown.

The crystals of $(NH_4)_3[VF_2O(O_2)_2]$ consist of ammonium ions and difluorooxodiperoxovanadate(V) ions, held together by ionic and hydrogen bond forces. The anion seems to be the first example of a seven-coordinated mononuclear diperoxovanadate with purely inorganic ligands.

In $[VF_2O(O_2)_2]^{3-}$ the configuration of ligands around vanadium is pentagonal bipyramidal, *i.e.* that usually encountered in seven-coordinated peroxometallates (see Table V in Ref. 10, which summarizes the coordination geometries of 66 transition metal peroxo complexes). The equatorial plane is defined by the atoms O1–O4 and F1; the maximum deviation from this plane is 0.032 Å, while the r.m.s. deviation is 0.024 Å. The largest deviation of the atoms V, F1, F2 and O5 from the plane defined by these atoms and the midpoint between O2 and O3 is 0.012 Å. This plane forms an angle of 90.1° with the equatorial plane; the point symmetry is, therefore, approximately C_s.

The vanadium atom is displaced 0.309 Å from the equatorial plane towards the apical, double-bonded oxygen atom (O5). In other pentagonal-bipyramidal mononuclear oxoperoxovanadates observed displacements range between 0.25 and

Table 2. Bond distances (Å) and angles (°) in $(NH_4)_3[VF_2O(O_2)_2]$.

V–F1	1.958(1)	F1–V–F2	79.2(1)
V–F2	2.306(1)	F1–V–O1	89.3(1)
V–O1	1.921(2)	F1–V–O2	133.6(1)
V–O2	1.890(2)	F1–V–O3	129.9(1)
V–O3	1.887(2)	F1–V–O4	85.8(1)
V–O4	1.927(2)	F1–V–O5	94.9(1)
V–O5	1.609(2)	F2–V–O1	79.7(1)
O1–O2	1.466(2)	F2–V–O2	83.0(1)
O3–O4	1.462(2)	F2–V–O3	82.6(1)
N1–H1	0.90(5)	F2–V–O4	80.0(1)
N1–H2	0.85(4)	F2–V–O5	174.1(1)
N1–H3	0.88(4)	O1–V–O2	45.2(1)
N1–H4	0.86(5)	O1–V–O3	132.4(1)
N2–H5	0.94(5)	O1–V–O4	159.7(1)
N2–H6	0.97(4)	O1–V–O5	100.5(1)
N2–H7	0.80(4)	O2–V–O3	89.1(1)
N2–H8	0.86(4)	O2–V–O4	132.6(1)
N3–H9	0.95(4)	O2–V–O5	101.4(1)
N3–H10	0.85(4)	O3–V–O4	45.0(1)
N3–H11	0.94(5)	O3–V–O5	101.3(1)
N3–H12	0.84(5)	O4–V–O5	99.5(1)

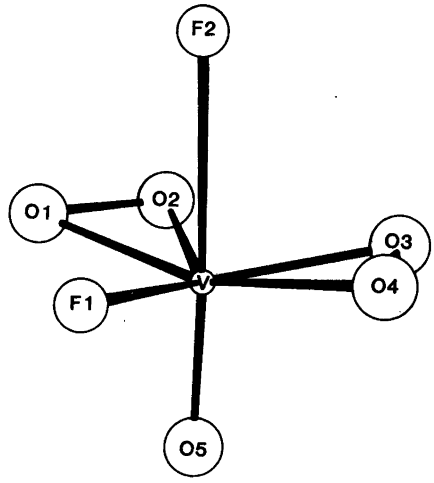

Fig. 2. The anion $[VF_2O(O_2)_2]^{3-}$.

Table 3. Hydrogen bond distances (Å) in $(NH_4)_3[VF_2O(O_2)_2]$.[a]

N1···F2^{i}	2.731(3)
N1···F2	2.743(2)
N1···O1^{ii}	2.836(3)
N1···F1^{i}	2.970(3)
N1···F1^{iii}	2.992(3)
N2···F1^{iv}	2.766(2)
N2···O2^{ii}	2.803(3)
N2···O3	2.834(2)
N2···F1^{v}	2.862(3)
N2···O4^{v}	2.902(3)
N2···O5^{vi}	2.965(3)
N2···O1^{iv}	2.993(3)
N3···O4^{vii}	2.818(3)
N3···O4^{iii}	2.818(3)
N3···F2	2.827(3)
N3···O1	2.949(3)
N3···O2^{viii}	3.003(3)

[a] Symmetry superscripts: ^{i} $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; ^{ii} $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; ^{iii} $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$; ^{iv} $x, 1+y, z$; ^{v} $-\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$; ^{vi} $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$; ^{vii} $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; ^{viii} $\bar{x}, -\frac{1}{2}+y, \frac{1}{2}-z$.

0.32 Å (see Table 4 and, *e.g.*, Table V in Ref. 10) and are therefore fairly constant. In pentagonal-pyramidal six-coordinated oxoperoxovanadates the displacement is more pronounced, *i.e.* 0.44–0.47 Å (see Table 4 and, *e.g.*, Table V in Ref. 10). In the latter case the equatorial atoms do not experience repulsive forces from the second apical position, thus explaining the larger displacement. The apical atoms F2 and O5 are fairly equally remote from the equatorial plane (1.995 and 1.915 Å, respectively); this is a general observation in this type of compound. With two identical $M-X_{apical}$ bonds there is hardly any displacement of the central atom in seven-coordinated peroxo complexes (see Table V in Ref. 10).

In the $[VFO(O_2)_2]^{2-}$ ion in $K_2[VFO(O_2)_2]$ vanadium is pentagonal pyramidally coordinated; there is no atom *trans* to the double-bonded oxygen atom at a distance less than 3.1 Å.[1] The situation is quite different in $(NH_4)_2[VFO(O_2)_2]$.[1,11] The anions form chains, $[VFO(O_2)_2]_n^{2n-}$, in which the double-bonded oxygen atom forms the link to the vanadium atom in the neighbouring unit *via* a long bond and occupies the apical *trans* position in that unit. The V···O distance is 2.505(1) Å and the O=V···O

Table 4. Certain bond distances (Å) and distances (Å) from the equatorial plane P in purely inorganic oxodiperoxovanadates. L_{ap}=apical atom other than the vanadyl oxygen atom. L_{eq}=equatorial atom other than O_{peroxo}.

Compound	V=O$_{ap}$	V−O$_{peroxo}$	V···L$_{ap}$	V···L$_{eq}$	(O−O)$_{peroxo}$	V···P	O$_{ap}$···P	L$_{ap}$···P	Ref.
$(NH_4)_3[VF_2O(O_2)_2]$	1.609(2)	1.887(2)	2.306(1)	1.958(1)	1.462(2)	0.309	1.915	1.995	This paper
		−1.927(2)			−1.466(2)				
$NH_4[VO(O_2)_2(NH_3)]$	1.606(3)	1.882(3)	2.926(3)	2.110(4)	1.472(4)	0.461	2.057	2.463	3
		−1.883(3)							
$K_2[VFO(O_2)_2]$[a]	1.605(7)	1.858(7)	>3.1	1.900(5)	1.468(7)	0.457	2.074	—	1
	−1.620(5)	−1.930(5)		−1.906(3)	−1.505(6)	−0.471	−2.076	—	1
$(NH_4)_4[O\{VO(O_2)_2\}_2]$	1.601(3)	1.875(3)	2.480(2)	1.994(2)	1.463(4)	0.444	2.053	2.015	2a,b[b]
	−1.613(3)	−1.914(3)	−2.522(2)	−2.013(2)	−1.474(4)	−0.453	−2.056	−2.026	
$(NH_4)_2[VFO(O_2)_2]$	1.613(1)	1.874(2)	2.505(1)	1.929(1)	1.460(2)	0.364	1.975	2.139	11
		−1.905(1)			−1.462(2)				

[a] Disordered; due to the disorder the true errors are probably larger than the e.s.d.'s. [b] The values given are those obtained from a refinement of the structure (Ref. 2a) using single-crystal diffractometer data (Ref. 2b).

angle 174.8(1)°. Each unit can be described as a pentagonal pyramid. Vanadium can thus be considered to be pentagonal bipyramidally coordinated. The distance between the vanadium atom and the pentagonal plane is 0.364 Å.

It is a general observation made for pentagonal-bipyramidal oxoperoxometallates that the $M-L_{apical}$ bond (*trans* to the M=O bond) is longer than the $M-L_{equatorial}$ bonds (see Table 4 and, *e.g.*, Table 6 in Ref. 2a and Table VIII in Ref. 10). This is also true for the $[VF_2O(O_2)_2]^{3-}$ ion in which the $V-F_{apical}$ bond is 2.306(1) Å and $V-F_{equatorial}$ is 1.958(1) Å. $[VF_2O(O_2)_2]^{3-}$ seems, however, to be the first example of a mononuclear seven-coordinated oxoperoxovanadate with only monodentate ligands, disregarding the peroxo groups.

In many cases $V-O_{peroxo}$ bonds are symmetric. In $(NH_4)_3[VF_2O(O_2)_2]$ the V–O1 and V–O4 bond lengths (*trans*), 1.921(2) and 1.927(2) Å, are significantly longer than the V–O2 and V–O3 bond lengths (*cis*), 1.890(2) and 1.887(2) Å. The $V-O_{peroxo}$ bonds are thus asymmetric in the $[VF_2O(O_2)_2]^{3-}$ ion. Other examples of this kind of asymmetry have been observed in $(NH_4)_4[O\{VO(O_2)_2\}_2]$,[2b] $K_3[VO(O_2)_2ox]\cdot H_2O$,[12] $(Hbipy)[H\{VO(O_2)_2bipy\}_2]\cdot xH_2O_2\cdot(6-x)H_2O$,[13] and $(Hbipy)[VO(O_2)_2bipy]\cdot(3+x)H_2O_2\cdot(2-x)H_2O$;[14] $ox=C_2O_4^{2-}$, $Hbipy=C_{10}H_9N_2^+$, $bipy=C_{10}H_8N_2$.

The V=O, O–O and N–H bond lengths are normal as can be seen in Tables 2 and 4, and from Table 3 it can be concluded that the structure is stabilized by substantial hydrogen bonding.

There seems to be a profound difference between the potassium and ammonium fluorooxoperoxovanadates. The monofluorooxodiperoxovanadates are not isomorphous and, while the potassium salt can be kept in contact with its mother liquor for months without change, the ammonium salt can undergo conversion to the difluorooxodiperoxovanadate within a few days. The possibility of hydrogen bonding in the ammonium compound may play an important role in stabilizing the difluoro complex.

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