

Studies on Peroxovanadates

I. The Crystal Structure of Ammonium μ -Oxo-bis(oxodiperoxovanadate(V)), $(\text{NH}_4)_4[\text{O}(\text{VO}(\text{O}_2)_2)_2]$

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The crystal structure of ammonium μ -oxo-bis(oxodiperoxovanadate(V)), $(\text{NH}_4)_4[\text{V}_2\text{O}_{11}]$, has been determined from visually estimated X-ray data by Patterson and Fourier methods and refined by the least-squares technique to a final R -value of 0.108 for 708 observed reflexions.

The crystals are monoclinic, space group $P2_1/c$, and the unit cell, which contains four formula units, has the dimensions $a = 6.962$ (1) Å, $b = 10.118$ (2) Å, $c = 16.212$ (4) Å, $\beta = 95.43$ (2)° and $V = 1136.9$ Å³.

The crystals contain μ -oxo-bis(oxodiperoxovanadate(V)) ions, $[\text{V}_2\text{O}_{11}]^{4-}$, and ammonium ions, the two vanadium atoms of the dinuclear anion being linked together by a single non-linear oxygen bridge.

Each vanadium atom is coordinated by four oxygen atoms of two peroxo groups and the bridging oxygen atom, the five atoms forming a pentagonal plane. 2.04 Å above this plane and 1.61 Å from the vanadium atom, on the average, there is an oxide oxygen atom, and 2.03 Å below the equatorial plane and 2.50 Å from the vanadium atom, an oxygen atom of a peroxo group, bonded to the other vanadium atom within the same complex ion. The configuration of ligands about the vanadium atoms can thus be described as pentagonal bipyramidal.

Average bond distances are: $\text{V}-\text{O}_{\text{bridge}}$ 2.01 Å, $\text{V}-\text{O}_{\text{peroxo}}$ 1.87 Å, $\text{V}-\text{O}_{\text{oxo}}$ 1.61 Å, and $(\text{O}-\text{O})_{\text{peroxo}}$ 1.44 Å.

A large number of transition metal peroxo compounds are known, the peroxomolybdates and peroxovanadates belonging to the more complex systems. Notwithstanding the considerable amount of work on the peroxovanadates, little is known with certainty about the composition of the crystalline phases, separating out from aqueous solutions. The conflicting literature on this subject is fully brought out in the review article by Connor and Ebsworth.¹ It was not until the X-ray method was adopted in conjunction with the preparative work that the formation and structures of the peroxochromates and peroxomolybdates could be elucidated unambiguously.^{2,3} The same method has now been used to study the peroxovanadates.

From investigations on the peroxomolybdates it could be concluded that in aqueous solution

(a) the number of peroxo groups per molybdenum atom attains the maximum value of four in alkaline solution,

(b) increasing acidity, within certain limits, increases the degree of polynuclearity, and

(c) increasing hydrogen peroxide concentration decreases the degree of polymerization.^{3,4}

The same conclusions would seem to be valid for the peroxovanadates.¹

The dinuclear complex, $[\text{V}_2\text{O}_{11}]^{4-}$, which occurs in the ammonium salt $(\text{NH}_4)_4[\text{V}_2\text{O}_{11}]$, first reported by Melikov and Pissarevski,⁴ is especially interesting. It differs in stoichiometry from the corresponding molybdenum and tungsten analogues, $[\text{Mo}_2\text{O}_{11}(\text{H}_2\text{O})_2]^{2-}$ and $[\text{W}_2\text{O}_{11}(\text{H}_2\text{O})_2]^{2-}$.⁵⁻⁷ In these anions each metal atom is coordinated to a water molecule which completes the pentagonal bipyramidal arrangement of ligands about the metal atom. The anhydrous tetraperoxodivanadate ion cannot, therefore, be isomorphous with the tetraperoxodimolybdate and tetraperoxoditungstate ions, but might well exhibit six-coordination of pentagonal pyramidal type observed in $[\text{CrO}(\text{O}_2)_2\text{py}]$.^{8,9}

EXPERIMENTAL

Preparation. The crystals, which were prepared according to Melikov and Pissarevski,⁴ were twinned (see below).

Analysis. The vanadium content was determined gravimetrically as silver vanadate¹⁰ and the peroxide content by titration with a permanganate solution. (Found: V 29.1; O_2^{2-} 37.3. Calc. for $(\text{NH}_4)_4[\text{V}_2\text{O}_{11}]$: V 29.1; O_2^{2-} 36.6.) When the compound was heated at 240°C for 48 h, a weight loss of 48.3% was obtained, the residue being identified as V_2O_5 by means of powder photographs. The theoretical loss in weight is 48.0%.

X-Ray methods. Accurate cell dimensions were obtained from X-ray powder photographs obtained by the Guinier-Hägg method using $\text{CuK}\alpha_1$ radiation and $\text{Pb}(\text{NO}_3)_2$ ($a = 7.8566 \text{ \AA}$ at 21°C) as an internal standard.

For the single crystal work, multiple film (5 films) equi-inclination Weissenberg photographs were taken with rotation about [100] (layer lines 0–6) and [001] (layer line 0) using $\text{CuK}\alpha$ radiation. Due to the low stability of the compound, new crystals had to be mounted for each layer line. 708 independent reflections were registered.

Due to twinning, two reflections were registered for every hkl with $h \neq 0$ (the crystallographic bc -planes of the twinned individuals coincide and the angle between the a^* -axis of one twin and the a^* -axis of the other is $2 \cdot (\beta - 90^\circ)$). The intensities were corrected for Lorentz and polarization effects, but no correction was applied for absorption owing to the small size of the crystals and their almost square cross-section ($\mu R \approx 0.4$).

Computing methods. The computational work was performed at Göteborg Universities' Computing Centre, using IBM 360/50 and 65 computers and a set of programmes in use at this Department.^{11,12}

The atomic scattering factors used in the calculation of the structure factors were taken from Cromer and Waber.¹³

UNIT CELL AND SPACE GROUP

The unit cell dimensions were obtained from the measured $\sin^2\theta$ values by a least-squares procedure using 58 observed lines. The cell dimensions thus determined were $a = 6.962(1) \text{ \AA}$, $b = 10.118(2) \text{ \AA}$, $c = 16.212(4) \text{ \AA}$, $\beta =$

Table 1. Observed lines in the powder diagram (Guinier focusing camera) of $(\text{NH}_4)_4[\text{V}_2\text{O}_{11}]$.

$h k l$	$10^3 \sin^2 \theta_{\text{obs}}$	$10^3 \sin^2 \theta_{\text{calc}}$	I_{obs}	d_{obs}
0 1 1	809	807	w	8.564
0 0 2	913	911	w	8.061
1 0 0	1231	1235	w	6.943
0 1 2	1485	1491	st	6.320
1 1 0	1807	1814	st	5.730
1 1 $\bar{1}$	1941	1942	m	5.529
1 0 $\bar{2}$		1945		
1 1 1	2139	2143	w	5.267
0 2 0	2316	2318	st	5.061
1 0 2	2339	2347	st	5.036
0 2 1	2538	2546	m	4.835
0 1 $\bar{3}$	2629	2629	m	4.750
0 2 2	3221	3229	m	4.292
1 2 0	3554	3553	w	4.086
1 1 $\bar{3}$		3563		
0 0 4	3631	3644	w	4.042
1 2 $\bar{1}$	3671	3680	w	4.020
1 1 3	4164	4166	m	3.775
0 2 3	4369	4368	m	3.685
1 2 2	4660	4665	m	3.569
2 0 0	4935	4940	st	3.467
1 1 $\bar{4}$	5042	5057	w	3.430
1 2 $\bar{3}$	5305	5302	st	3.344
0 3 1	5446	5443	w	3.301
1 2 3	5898	5904	st	3.172
2 1 1	5951	5948	st	3.157
0 3 2	6130	6126	m	3.111
0 1 5	6263	6274	st	3.078
1 2 4	6810	6796	w	2.952
2 1 $\bar{3}$	6972	6967	vw	2.917
1 3 2	7158	7161	m	2.879
2 2 0	7262	7258	m	2.858
0 3 3		7265		
1 3 2	7580	7562	w	2.798
0 2 5	8016	8012	vw	2.720
0 0 6	8201	8200	m	2.690
2 1 4	8359	8360	w	2.664
2 2 2	8590	8571	w	2.628
1 3 3	8805	8802	w	2.596
0 4 0	9264	9272	m	2.531
0 4 1	9501	9499	m	2.499
1 2 5	9726	9749	vw	2.470
2 2 3	9931	9910	w	2.444
2 3 $\bar{1}$	10180	10182	w	2.414
1 4 1	10832	10835	vw	2.340
3 0 0	11087	11115	w	2.313
1 4 2	11197	11217	vw	2.302
2 2 4	11716	11706	vw	2.250
2 0 6	11917	11935	w	2.231
2 1 6	12474	12514	vw	2.181
3 0 2	12603	12628	vw	2.170
3 1 $\bar{3}$	12841	12840	vw	2.150

Table 1. Continued.

0 3 6	13403	13415	vw	2.104
3 2 2	13729	13741	vw	2.079
2 2 5}	13962	{13956	vw	2.061
3 2 1}		{13962		
2 4 0	14223	14212	vw	2.042
1 4 4	14548	14553	m	2.019
3 1 3	14668	14648	w	2.011
2 3 5	14899	14845	w	1.996
1 4 5	15706	15699	w	1.944
1 5 1	15861	15849	w	1.934

95.43(2)°, and $V = 1136.9 \text{ \AA}^3$. Observed and calculated values of $\sin^2\theta$ are listed in Table 1. The systematically absent reflections were:

$$h0l \text{ with } l = 2n + 1$$

$$0k0 \text{ with } k = 2n + 1$$

which is in accordance with the monoclinic space group $P2_1/c$ (No. 14).

The density of the crystals determined by weighing a sample in air and in benzene is 2.04 g/cm^3 . The density calculated for a unit cell containing four formula units is 2.05 g/cm^3 .

Table 2. Atomic coordinates, expressed in fractions of the cell edges, and isotropic thermal parameters for $(\text{NH}_4)_4[\text{V}_2\text{O}_{11}]$. Space group $P2_1/c$, $Z = 4$. All atoms occupy general positions (4e). The temperature factor is $\exp(-B \sin^2\theta/\lambda^2)$. The numbers in parantheses are the standard deviations of the last significant figures.

Atom	x	y	z	$B (\text{\AA}^2)$
V(1)	0.2611 (6)	0.3066 (4)	0.0367 (3)	2.48 (8)
V(2)	0.2348 (6)	0.1253 (4)	0.1851 (3)	2.68 (8)
O(1)	0.4144 (25)	0.2065 (18)	-0.0285 (11)	3.77 (37)
O(2)	0.4830 (27)	0.3405 (18)	-0.0142 (11)	4.01 (40)
O(3)	0.1805 (22)	0.3582 (15)	0.1417 (9)	2.61 (32)
O(4)	0.3337 (25)	0.4391 (18)	0.1143 (11)	3.63 (37)
O(5)	0.0913 (25)	0.3640 (18)	-0.0242 (11)	3.55 (37)
O(6)	0.1390 (23)	0.1349 (16)	0.0644 (10)	2.88 (33)
O(7)	-0.0185 (24)	0.1575 (17)	0.2063 (11)	3.48 (37)
O(8)	0.1181 (25)	0.1774 (18)	0.2778 (11)	3.57 (37)
O(9)	0.4626 (26)	0.1698 (17)	0.1433 (11)	3.78 (39)
O(10)	0.4691 (25)	0.1984 (18)	0.2302 (10)	3.61 (37)
O(11)	0.2628 (29)	-0.0348 (21)	0.1978 (13)	5.05 (45)
N(1)	0.2328 (28)	-0.0886 (20)	-0.0154 (11)	2.63 (41)
N(2)	0.2283 (29)	0.7011 (20)	0.1371 (12)	2.68 (40)
N(3)	0.2892 (31)	0.4420 (22)	0.3167 (13)	3.21 (44)
N(4)	-0.2348 (30)	0.4073 (21)	0.1245 (13)	3.07 (43)

Table 3. Observed and calculated structure factors for $(\text{NH}_4)_4[\text{V}_4\text{O}_{11}]$. The columns are successively l , $|F_o|$, and $|F_c|$.

0	0	0	8	10	-11	5	14	-13	16	0	-8	1	4	L	14	56	55	12	0	8		
4	63	70	9	34	30	6	21	23	17	23	-24	-14	U	-2	16	22	-21	13	0	13		
6	121	123	10	37	30	7	17	14	7	17	14	-13	31	-36	0	0	0	14	0	-4		
8	22	-21	11	0	-6	6	11	11				-12	23	-3				15	0	9		
10	0	2	12	0	-2	0	12	L	-16	19	-23	-11	0	16	-17	0	-13	2	4	L		
12	59	-61	13	29	28	0	22	-20	-15	0	2	-10	0	19	-16	0	7	-15	2	4	L	
14	28	-32	14	23	23	0	33	-20	-14	0	1	-9	30	-15	-15	18	-18	-15	2	0	-7	
16	0	3	15	14	1C	1	0	3	-13	0	-3	-8	0	19	-14	0	-6	-14	0	-7		
18	25	-26	16	0	3	2	0	3	-12	24	-33	-7	31	-36	-13	0	15	-13	0	-9		
20	10	-12	17	0	3	3	0	-10	-11	0	-14	-4	0	0	-12	51	-62	-12	16	21		
			18	0	1	4	0	-1	-10	20	-25	-5	26	26	-11	45	-54	-11	0	-1		
0	1	L	0	6	L	5	19	-17	-9	76	75	-4	0	15	-10	0	-13	-10	25	81		
2	137	125	0	72	69	7	14	-15	-6	0	-8	-6	20	22	-3	0	0	-9	41	-49		
3	80	-86	0	55	-52	0	0	0	-7	38	40	-2	0	0	0	11	-8	58	-59	-8	19	-20
4	15	-20	1	0	3	0	0	0	-6	0	-9	-1	39	37	-7	38	34	-7	40	-43		
5	117	104	2	0	3	0	0	0	-5	0	19	0	4	0	-6	49	-65	-6	25	28		
6	39	43	3	30	-30	-16	0	0	-4	36	35	1	52	53	-5	81	-64	-5	76	-73		
7	62	-67	4	31	32	-14	0	-24	-3	27	27	2	46	-49	-4	78	-67	-4	19	-17		
8	21	24	5	46	-41	-12	0	9	-2	109	81	3	24	-24	-3	24	-24	-3	39	8		
9	31	-38	6	0	9	-10	0	-7	-1	10	-17	4	0	-13	-2	24	-28	-2	56	-50		
10	0	-6	7	100	-98	-8	0	3	0	24	-22	5	47	44	-1	21	24	-1	32	-31		
11	53	53	8	0	-7	4	0	-8	4	0	0	-5	0	0	-4	0	-4	0	0	34		
12	0	4	9	22	18	-4	25	-26	2	63	57	7	40	-56	1	30	-31	1	0	-8		
13	0	-5	10	13	-19	-2	119	113	3	72	-73	8	45	-43	2	48	65	2	0	-15		
14	22	-25	11	31	-35	2	193	-176	4	100	83	9	30	-31	3	14	-8	3	31	32		
15	14	14	12	17	-16	4	21	23	5	36	-41	10	0	-4	4	57	60	4	25	-24		
16	16	-14	13	29	-27	6	68	-63	6	28	-28	11	0	5	5	116	-104	5	67	62		
17	0	11	14	0	0	8	98	-84	5	0	5	12	0	5	6	89	82	6	20	19		
18	0	-4	15	27	26	10	30	26	8	45	45	13	40	5	7	0	10	7	43	42		
19	0	-7	16	14	-14	12	25	-23	0	50	-55	14	0	5	8	98	88	8	26	-28		
20	18	-18	17	0	5	14	0	15	11	39	-40	-13	0	-11	10	0	12	10	0	-8		
0	2	L	0	7	L	1	3	L	12	0	-7	-13	0	17	11	68	-68	11	28	26		
0	124	-113	1	21	21	-17	0	18	13	23	22	-12	27	29	12	43	-43	12	0	-1		
L	97	95	2	13	-15	-14	0	18	14	0	5	-11	0	20	13	0	2	13	0	3		
2	56	-56	3	30	-34	-16	0	18	15	23	-23	-10	0	17	14	0	-13	16	24	-22		
3	78	-78	4	51	-48	-8	0	18	16	26	-23	-9	0	1	15	0	-2	15	0	2		
4	46	-46	5	0	-4	-14	21	33	0	0	-1	-8	0	0	-20	16	-15	16	19	18		
5	22	15	6	0	-1	-13	0	-8	1	4	L	-7	29	34								
6	0	-5	7	28	-22	-6	0	20	-14	0	5	-6	20	17	0	5						
7	44	-49	8	19	17	-11	0	10	-15	0	22	-9	0	0	-16	0	-17	-15	0	-12		
8	14	-15	9	17	-19	-10	0	2	-4	0	14	-4	0	-14	-16	0	-17	-14	0	-4		
9	47	-52	10	26	24	-5	-57	-57	-3	19	21	-3	19	21	-15	0	31	-13	24	-24		
10	51	50	11	0	0	-8	77	74	-1	0	-1	-58	-58	-16	0	-12	-12	19	21	-6		
11	0	-3	12	0	-13	-7	0	3	-11	0	16	0	0	0	-13	0	-10	-11	0	-6		
12	24	24	13	25	-26	-6	0	-12	-10	40	40	0	0	-17	-12	18	-24	-10	20	-20		
13	0	12	14	0	-6	-5	23	-18	-9	31	37	2	34	-33	-11	0	-11	-9	0	14		
14	0	5	15	0	3	-4	45	-39	-8	0	10	3	29	-35	-10	26	-41	-8	0	20		
15	0	8	16	0	3	-3	40	-40	-7	0	-5	3	0	-17	-9	81	85	-7	0	-2		
16	24	24	17	0	7	-2	31	-35	-6	0	-10	4	21	21	-8	20	-20	-6	38	40		
17	24	26	0	8	L	-1	55	53	-5	57	-55	-5	0	-4	-7	0	5	-5	78	76		
18	10	10	1	0	-24	0	136	-169	-4	36	31	6	0	0	-6	14	24	-4	21	-30		
19	10	14	1	0	0	1	40	-24	-3	18	-24	7	63	-65	-5	92	77	-3	0	5		
0	3	L	2	30	-29	2	28	-32	-2	36	-36	8	28	-27	-4	43	-30	-2	40	37		
1	62	56	3	14	13	3	78	66	-1	14	-20	0	3	33	-15	3	35	1	54	85		
2	91	75	5	18	18	5	0	6	1	48	-41	11	0	-15	-11	42	38	1	83	85		
3	84	87	6	14	14	6	57	-58	2	39	43	12	0	7	0	39	-46	2	22	-23		
4	14	-25	7	12	12	7	38	-43	34	-34	34	13	0	-13	3	39	-40	3	0	13		
5	15	15	8	30	-27	8	49	44	4	65	-65	14	0	7	2	71	73	4	15	20		
6	43	-43	9	0	8	9	83	58	5	0	-1	15	13	15	4	17	17	5	48	42		
7	34	43	10	21	20	10	40	35	6	18	18											
8	0	-6	11	14	10	11	15	19	7	36	31	1	8	L	5	0	-1	7	0	-11		
9	0	-10	12	0	23	12	0	6	6	20	19	-12	0	4	6	25	-24	8	21	-21		
10	11	-16	13	0	0	13	0	-14	9	18	14	-11	0	6	7	30	32	9	21	-30		
11	43	-44	14	0	5	14	49	48	10	53	-47	-10	38	-42	8	0	2	10	0	16		
12	0	11	15	0	1	15	19	19	11	33	33	-9	0	24	9	46	-45	11	0	-16		
13	0	-9	16	0	0	16	0	-1	12	27	18	-4	0	-17	10	33	-32	12	24	-25		
14	14	-14	0	9	L	17	0	-8	13	17	19	-7	0	0	11	33	-33	13	25	-26		
15	17	-19	1	15	14	0	0	-13	14	0	-13	-6	0	0	8	12	0	14	0	-8		
16	0	8	2	0	0	15	20	22	15	20	22	-5	0	4	13	25	30	15	22	-21		
17	24	-22	3	3	3	-17	22	-29	-3	22	-29	-4	46	-53	14	0	-17					
18	15	19	4	37	-37	-16	0	0	-15	24	26	-3	31	-38	15	26	-22					
0	4	L	5	17	14	-15	25	-28	-14	0	4	-1	0	7				-14	2	4	L	
0	162	-138	7	0	-4	-13	0	8	-13	0	-12	0	24	30				-13	0	20		
1	124	-107	8	18	-18	-12	0	4	-12	0	-8	1	0	0	-16	2	-3	-12	7	22		
2	0	11	9	0	0	-11	26	-35	-11	0	-7	2	0	-2	-15	22	13	-10	0	16		
3	99	58	10	35	-30	-10	25	-32	-10	0	4	3	0	-10	-14	0	2	-9	27	-29		
4	0	7	11	0	9	-8	0	8	-9	18	-24	4	48	54	-13	0	1	-8	18	22		
5	73	67	12	0	7	-8	39	-43	-8	0	-15	5	0	-13	-14	0	-6	-7	29	36		
6	51	-53	13	0	-6	-7	56	55	-6	22	27	7	0	9	-10	18	18	-6	0	-8		
7	65	65	14	0	9	-5	51	41	-5	18	-26	8	0	19	-9	50	60	-7	4	11		
8	21	25	15	0	10	-4	0	-12	-4	0	14	9	27	21	-8	19	22	-3	0	-12		
9	36	38	16	0	13	-3	125	120	-3	32	-32	10	37	33	-7	32	-31	-2	0	-10		
10	0	5	1	16	14	-2	0	-8	-2	20	-20	11	0	-6	-6	24	22	-1	65	53		
12	0	-5	2	20	19	-1	68	55	-1	62	-54				-5	62	-59	0	27	26		
13	15	20	3	0	8	0	24	23	0	83	84	-18	18	25	-3	0	5	2	0	10		
14	0	2	4	17	15	1	0	5	1	24	25	-18	18	25	-3							

Table 3. Continued.

-10	25	-22	5	24	-19	-14	0	-2	6	27	21	4	32	-31	4	5	L	-5	0	1	
-9	0	-1	6	0	4	-13	32	-28	7	0	0	6	64	55	-6	40	-36	-4	47	42	
-8	23	-29	7	0	7	-12	32	26	8	0	4	8	23	-27	-5	53	-47	-3	32	-33	
-7	0	7	8	59	-53	-11	34	-31	5	32	30	-4	69	61	-4	69	61	-2	27	22	
-6	0	-1	9	43	-39	-10	21	-30	10	23	24	-10	21	27	-3	26	-24	-1	0	-12	
-5	0	-6	10	17	-17	-9	0	-4	11	0	2	-10	31	27	-2	0	-14	0	18	-13	
-4	69	-65	11	0	0	-8	0	-6	12	0	7	-9	0	27	-1	44	-42	1	38	-30	
-3	0	-10	12	26	-24	-7	0	8	13	27	26	-8	25	20	0	44	-33	2	27	25	
-2	40	38	13	0	6	-4	48	43	-11	24	-17	-4	0	-17	4	22	-18	6	0	-3	
-1	49	-43	14	41	-36	-5	26	25	3	7	L	-6	87	83	2	47	42	4	24	-19	
0	23	18	15	0	-13	-4	58	-59	-12	0	-6	-5	57	57	3	29	-22	5	0	1	
1	38	-35	0	39	44	-3	36	29	-11	24	-17	-4	0	-17	4	22	-18	6	0	-3	
2	19	-18	3	2	L	-2	33	29	-10	18	-11	-3	45	-59	-2	16	19	0	4	6	L
3	0	0	16	0	0	-1	51	49	-9	25	25	-2	16	19	0	0	14	7	0	5	
4	60	54	15	31	22	0	51	48	-8	0	13	-1	14	-22	0	0	14	9	0	10	
5	36	-31	-14	0	7	1	44	41	-7	18	-19	0	17	25	1	43	37	10	23	-23	
6	0	16	-13	26	-24	2	0	-1	-6	0	4	1	23	29	2	25	23	5	5	L	
7	0	-1	-12	19	17	3	32	30	-5	0	4	1	14	-22	0	0	14	9	0	10	
8	0	14	-11	44	39	4	43	39	-4	0	16	3	50	-54	5	0	L	-3	0	8	
9	0	17	-10	41	36	5	19	-19	-3	16	14	4	0	9	-10	0	4	-4	0	0	
10	0	15	-9	0	4	6	0	-7	-2	37	56	5	45	38	-6	21	15	-2	25	-14	
11	0	8	-8	67	63	7	0	-1	-1	0	-17	6	59	-58	-6	64	62	-1	0	-15	
12	0	-5	-7	34	-29	8	0	-2	0	0	-4	7	0	-9	-4	49	-56	0	32	25	
13	0	5	-6	40	37	-9	41	-43	1	35	35	8	20	-27	-2	32	-43	2	0	9	
14	0	2	-5	0	8	10	18	17	3	0	-5	-10	26	28	4	0	3	3	35	31	
15	0	2	-4	28	31	11	18	-17	4	0	9	-8	0	9	6	32	-25	4	0	-8	
16	0	7	-3	99	-105	12	0	-18	-4	20	9	3	35	-29	5	L	-5	0	5	0	
17	0	13	-2	17	13	13	16	-21	5	0	3	-9	35	-29	5	0	5	0	5	0	
18	0	-9	-1	42	-50	14	0	4	6	20	-18	-8	0	-22	-8	0	-22	6	23	22	
19	0	0	9	0	44	15	24	-24	7	32	32	-7	32	32	-7	5	1	28	25	14	
20	0	9	1	25	23	-15	15	-11	8	0	8	-6	29	-23	-0	18	-18	8	0	-3	
21	0	-6	2	76	-56	-6	21	-6	9	0	6	-5	46	-36	-5	17	-19	9	0	8	
22	0	-8	6	41	-35	0	5	-5	10	10	-18	-4	59	-41	-4	59	-41	10	13	14	
23	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
24	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
25	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
26	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
27	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
28	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
29	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
30	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
31	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
32	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
33	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
34	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
35	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
36	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
37	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
38	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
39	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
40	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
41	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
42	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
43	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
44	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
45	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
46	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
47	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
48	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
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50	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
51	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
52	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
53	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
54	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
55	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
56	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
57	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
58	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
59	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
60	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
61	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
62	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
63	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
64	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
65	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
66	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
67	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
68	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
69	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
70	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
71	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
72	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
73	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
74	0	13	4	59	-51	-14	0	7	11	0	-2	-3	41	-46	-3	0	5	0	0	0	
75	0	0	5	59	54	-13	0	-5	12	16	-18	-2	0	-13	-2	0	-8	5	6	L	
76	0	-12	6	41	-35	0	5	-5	-1	0	1	-1	51	65	-1	33	45	-10	13	-6	
77	0	13	4																		

refined by a least-squares procedure. Positional parameters, isotropic temperature coefficients and a scale factor for each zone were refined. The weighting factor, w , was calculated according to Cruickshank,¹⁴ $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$, with $a = 30$, $c = 0.05$, and $d = 0$. Reflections too weak to be observed were given zero weight. The final R value was 0.108.

The atomic parameters, together with their standard deviations, are given in Table 2, and observed and calculated structure factors in Table 3.

The contributions from the hydrogen atoms to the structure factors were not taken into account.

The result of the refinement was confirmed by a three-dimensional difference electron density calculation, in which the largest discrepancy corresponded to a peak of $1 \text{ e}/\text{\AA}^3$ which is less than one tenth of the height of a nitrogen peak in the F_o synthesis. The difference map showed no anisotropy effects.

DESCRIPTION AND DISCUSSION

The crystals of $(\text{NH}_4)_4[\text{V}_2\text{O}_{11}]$ contain dinuclear complex ions and ammonium ions. The unit cell content projected on (010) is shown in Fig. 1. The mean configuration about the vanadium atoms is pentagonal bipyramidal

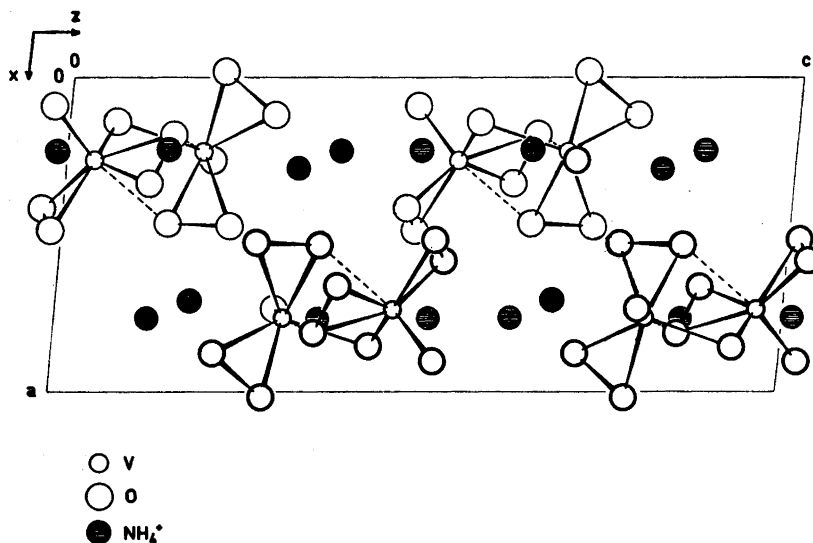


Fig. 1. The crystal structure of $(\text{NH}_4)_4[\text{V}_2\text{O}_{11}]$ viewed along the b -direction.

(*cf.* Fig. 2), the four oxygen atoms of two peroxy groups and a bridging oxygen atom forming a pentagonal plane, while a double-bonded oxygen atom and an oxygen atom belonging to a peroxy group, coordinated to the other vanadium atom within the anion, occupy the apical positions. Bond distances and angles are given in Table 4, and packing distances in Table 5.

Table 4. Bond distances and angles in $(\text{NH}_4)_4[\text{V}_2\text{O}_{11}]$.

	Distance (Å)		Distance (Å)
V(1)–O(1)	1.870 (18)	V(2)–O(7)	1.857 (18)
–O(2)	1.851 (19)	–O(8)	1.851 (18)
–O(3)	1.915 (15)	–O(9)	1.839 (18)
–O(4)	1.875 (18)	–O(10)	1.876 (18)
–O(5)	1.578 (18)	–O(11)	1.642 (21)
–O(6)	2.004 (17)	–O(6)	2.009 (16)
–O(9)	2.531 (18)	–O(3)	2.478 (16)
O(1)–O(2)	1.449 (26)	O(7)–O(8)	1.442 (24)
O(3)–O(4)	1.447 (24)	O(9)–O(10)	1.436 (24)
V(1)···V(2)	3.044 (6)		
	Angle (°)		Angle (°)
O(1)–V(1)–O(2)	45.8 (8)	O(7)–V(2)–O(8)	45.8 (8)
–O(3)	151.8 (8)	–O(9)	153.2 (8)
–O(4)	129.4 (8)	–O(10)	131.6 (8)
–O(5)	106.2 (8)	–O(11)	104.7 (9)
–O(6)	86.2 (7)	–O(6)	86.4 (7)
–O(9)	77.3 (7)	–O(3)	76.3 (6)
O(1)–O(2)–V(1)	67.8 (10)	O(7)–O(8)–V(2)	67.3 (10)
O(2)–V(1)–O(3)	132.3 (8)	O(8)–V(2)–O(9)	133.6 (8)
–O(4)	89.1 (8)	–O(10)	90.2 (8)
–O(5)	105.1 (9)	–O(11)	103.6 (9)
–O(6)	130.6 (8)	–O(6)	130.2 (7)
–O(9)	88.5 (7)	–O(3)	83.8 (7)
O(2)–O(1)–V(1)	66.4 (10)	O(8)–O(7)–V(2)	66.9 (10)
O(3)–V(1)–O(4)	44.9 (7)	O(9)–V(2)–O(10)	45.5 (8)
–O(5)	101.0 (8)	–O(11)	101.1 (9)
–O(6)	82.6 (7)	–O(6)	81.2 (7)
–O(9)	74.5 (6)	–O(3)	77.1 (7)
O(3)–O(4)–V(1)	69.0 (9)	O(9)–O(10)–V(2)	65.9 (10)
O(4)–V(1)–O(5)	107.2 (9)	O(10)–V(2)–O(11)	104.6 (9)
–O(6)	124.2 (7)	–O(6)	123.9 (7)
–O(9)	80.6 (7)	–O(3)	80.8 (7)
O(4)–O(3)–V(1)	66.1 (9)	O(10)–O(9)–V(2)	68.6 (10)
O(5)–V(1)–O(6)	98.6 (8)	O(11)–V(2)–O(6)	101.2 (9)
–O(9)	164.2 (8)	–O(3)	170.7 (8)
O(6)–V(1)–O(9)	66.0 (6)	O(6)–V(2)–O(3)	69.5 (6)
V(1)–O(6)–V(2)	98.7 (7)		

The two vanadium atoms of the dinuclear anion are linked together by an oxygen bridge, the V–O–V angle being 98.7°. In the corresponding tetraperoxodimallates $\text{K}_2\text{Mo}_2\text{O}_{11}\cdot 4\text{H}_2\text{O}$ and $\text{K}_2\text{W}_2\text{O}_{11}\cdot 4\text{H}_2\text{O}$, the Mo–O–Mo and W–O–W angles are 136.1° and 139°, respectively.^{5,7} The large difference between the angles is a consequence of the absence of a coordinated water molecule in the vanadium complex in contrast to the molybdenum and tungsten analogues. In the latter complexes, the pentagonal bipyramidal arrangement of ligands about the metal atom is completed by a long metal-water bond (2.33–2.47 Å). The corresponding apical position in the vanadium complex is occupied by an oxygen atom at about 2.50 Å, belonging to the peroxy group, coordinated to the other vanadium atom within the same anion. Thus, the tetraperoxodivanadate anion can be described as being composed of two pentagonal bipyramids sharing faces, while the tetraperoxodimolybdate and the

Table 5. Packing distances less than 3.5 Å in $(\text{NH}_4)_4[\text{V}_2\text{O}_{11}]$. The first atom symbols refer to the coordinates given in Table 2. After the second atom symbols, the unit cell translations in the a , b , and c directions are given within brackets. The number immediately following the brackets denotes the symmetry operation performed on the original coordinates of the atom according to Table 2, as given in the *International Tables for X-Ray Crystallography*, Vol. I.

O1-N1	(0 0 0)1	3.26 Å	O6-N1	(0 0 0)2	2.68 Å
-N1	(1 0 0)2	2.76	O7-N1	(0 0 0)2	3.38
-N2	(1 1 0)2	3.32	-N2	(0-1 0)3	3.08
-N3	(0 0 -1)4	2.98	-N3	(0-1 0)3	2.88
O2-O2	(1 1 0)2	3.27	-N4	(0 0 0)1	3.17
-O4	(1 1 0)2	3.10	O8-N2	(0-1 0)3	2.90
-N1	(1 0 0)2	3.23	-N3	(0 0 0)1	2.97
-N2	(1 1 0)2	2.99	-N4	(0-1 0)3	3.22
-N4	(1 0 0)1	2.92	O9-N1	(-10 0)2	3.21
-N4	(0 1 0)2	3.48	-N3	(1-1 0)3	2.92
O3-N2	(0 0 0)1	3.49	-N4	(1 0 0)1	3.23
-N3	(0 0 0)1	2.99	O10-O11	(1 0 0)3	3.42
-N4	(0 0 0)1	2.92	-N2	(1-1 0)3	2.86
O4-N2	(0 0 0)1	2.78	-N3	(0 0 0)1	3.15
-N3	(0 0 0)1	3.32	-N3	(1-1 0)3	3.22
-N4	(1 0 0)1	3.01	O11-N1	(0 0 0)1	3.49
O5-O5	(0 1 0)2	3.16	-N2	(0-1 0)1	2.85
-O8	(0 0 -1)4	3.26	-N3	(1-1 0)3	3.16
-N2	(0 1 0)2	2.82	-N4	(0-1 0)3	2.96
-N4	(0 0 0)1	3.49	N1-N2	(0-1 0)1	3.26
-N4	(0 1 0)2	3.05	-N3	(0 0 -1)4	3.16
O6-N1	(0 0 0)1	2.72			

tetraperoxoditungstate are built up of pentagonal bipyramids sharing corners. The achievement of the closer contact between the pyramids in the vanadium complex necessitates the bending together of the two vanadate groups of the complex. This also supports the conclusion drawn that the vanadium atoms are best described as being seven-coordinated in contrast to the six-coordination exhibited in $[\text{CrO}(\text{O}_2)_2\text{py}]$, in which there is no atom in the seventh position of the pentagonal bipyramid^{8,9} corresponding to the dotted line in Fig. 2a. The involvement of O(3) and O(9) in the weak interaction with V(2) and V(1), respectively, has a noticeable effect on the $\text{O}_{\text{bridge}}-\text{V}-\text{O}_{\text{peroxo}}$ angle, the $\text{O}(6)-\text{V}(1)-\text{O}(3)$ and $\text{O}(6)-\text{V}(2)-\text{O}(9)$ angles being significantly less than the corresponding $\text{O}(6)-\text{V}(1)-\text{O}(1)$ and $\text{O}(6)-\text{V}(2)-\text{O}(7)$ angles.

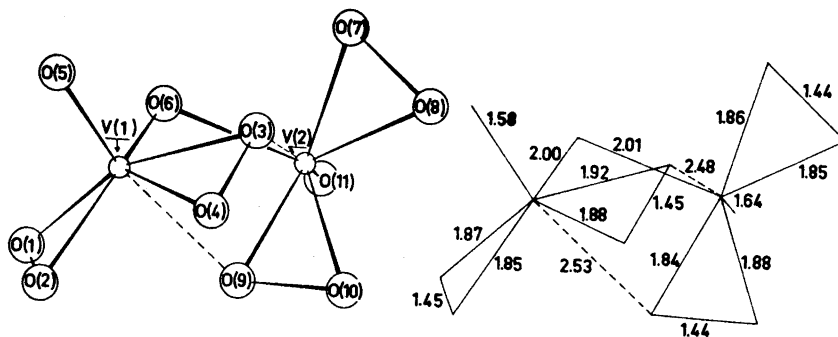


Fig. 2. a. The $[\text{O}(\text{VO}(\text{O}_2)_2)_2]^{4-}$ ion.

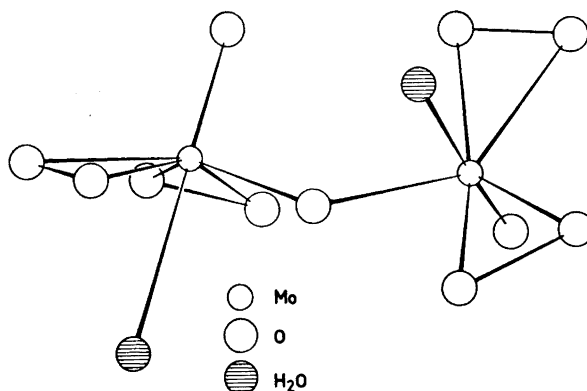


Fig. 2. b. The $[\text{O}(\text{MoO}(\text{O}_2)_2(\text{H}_2\text{O}))_2]^{2-}$ ion.

Equations, in cartesian coordinates, of the least-squares planes through the pentagonal groups associated with V(1) and V(2), respectively, are:

$$\mathbf{A} \quad -0.0965 X + 0.9842 Y - 0.1486 Z - 1.0955 = 0$$

$$\mathbf{B} \quad -0.6437 X + 0.4150 Y - 0.6430 Z + 0.0701 = 0$$

The distances of selected atoms from the planes **A** and **B** are:

A - O(1)	0.05 Å	B - O(6)	0.01 Å
O(2)	0.07	O(7)	0.02
O(3)	0.03	O(8)	0.03
O(4)	0.06	O(9)	0.04
O(6)	0.01	O(10)	0.05
V(1)	0.44	V(2)	0.42
O(5)	2.02	O(11)	2.06
O(9)	2.03	O(3)	2.03

Thus, within each pentagonal group, the atoms are almost coplanar.

The planes **A** and **B** make an angle of 55.5° with one another. The corresponding values in $\text{K}_2\text{Mo}_2\text{O}_{11} \cdot 4\text{H}_2\text{O}$ and $\text{K}_2\text{W}_2\text{O}_{11} \cdot 4\text{H}_2\text{O}$ are 66.9° and 62.1° , respectively. The best lines drawn through O(5), V(1) and O(9), and O(11), V(2) and O(3), are almost perpendicular to the planes **A** and **B**, the angles being 89.3° and 89.9° , respectively.

In seven-coordinated transition metal peroxo complexes, in which the two metal-apical atom bonds have different bond orders, it has been observed that the metal atom is displaced from the equatorial pentagonal plane in the direction of the ligand atom coordinated with the highest bond order (see Table 6). This is also true for $(\text{NH}_4)_4[\text{V}_2\text{O}_{11}]$. It can, moreover, be seen from Table 6, that the longer the $\text{M}-\text{X}_{\text{apical}}$ bond, the larger is the displacement of the metal atom from the equatorial plane, and the shorter is the diametrically opposite $\text{M}-\text{Y}_{\text{apical}}$ bond.

Table 6. Displacements of the metal atom M from the equatorial pentagonal plane in some transition metal peroxo compounds. X and Y denote the diametrically opposite apical atoms.

Compound	M-equatorial plane (Å)	M-X (Å)	M-Y (Å)	Ref.
[Cr(O ₂) ₂ (NH ₃) ₃]	0.00	2.08	2.11	15
K ₃ [Cr(O ₂) ₂ (CN) ₃]	0.02	2.09	2.11	16
[Cr(O ₂) ₂ (H ₂ O)en](H ₂ O)	0.04	2.03	2.05	17
[CrO(O ₂) ₂ phen]	0.27	1.56	2.26	18
[CrO(O ₂) ₂ dipy]	0.31	1.57	2.23	19
[CrO(O ₂) ₂ py]	0.51	1.58	—	8
K ₂ [MoO(O ₂) ₂ F ₂](H ₂ O)	0.18	1.64	2.02	20
(NH ₄) ₃ F[MoO(O ₂) ₂ F ₄]	0.23	1.67	2.03	21
K ₂ [MoO(O ₂) ₂ (C ₂ O ₄)]	0.35	1.68	2.26	22
K ₄ [O(MoO(O ₂) ₂ (H ₂ O)) ₂](H ₂ O) ₂	0.38	1.66	2.45	6
K ₂ [O(WO(O ₂) ₂ (H ₂ O)) ₂](H ₂ O) ₂	0.35	1.68	2.36	7
(NH ₄) ₄ [O(VO(O ₂) ₂) ₂]	0.43	1.61	2.50	This paper

The average V—O_{peroxo} distance of 1.87 Å is in good agreement with the mean V—O_{peroxo} distance 1.89 Å, observed for (NH₄)₃[V(O₂)₄].²³ It also compares well with Cr—O_{peroxo} distances as a consequence of the similar magnitude of the vanadium and chromium atoms.² As expected, Mo—O_{peroxo} distances are about 0.10 Å longer.^{5,6,20-22,24,25} The V—O_{peroxo} bond distances also fall within the range 1.65–2.08 Å, observed for the V—O_{equatorial} bond lengths in vanadates and polyvanadates²⁶⁻³⁸ (see Table VI in Ref. 34, and Table 9 in Ref. 38).

The V—O_{oxo} distances are 1.58 Å and 1.64 Å. These short bond lengths indicate a bond order of approximately two. For the square pyramidal configurations of oxygen atoms about V(V) the V—O_{apical} bond lengths range between 1.49 Å and 1.68 Å (see Ref. 34). It is interesting to note that in these complexes a sixth oxygen atom, completing a distorted octahedron, is found at distances between 2.22 Å and 3.41 Å. Furthermore, the shorter one V—O_{apical} bond length, the longer is the other. This agrees well with the observations made for (NH₄)₄[V₂O₁₁], the longer interaction distances being 2.53 Å and 2.48 Å.

The average O—O_{peroxo} distance, 1.44 Å, is shorter than the value of 1.49 Å, observed in simple peroxides (see reference list in Ref. 2), but it is

Table 7. (O—O)_{peroxo} distances observed in some transition metal peroxo complexes.

Compound	(O—O) _{peroxo} (Å)	Ref.
Peroxo chromates	1.40–1.47	2, 19
Peroxo molybdates	1.36–1.55	6, 20–22, 24, 25, 31, 42
Peroxo tungstates	1.50	7
Peroxo vanadates	1.31–1.45	23, this paper
Peroxo niobates	1.40–1.48	43–45

comparable to those found in transition metal peroxo complexes, in which a bond-shortening appears to prevail, as can be seen from Table 7.

The coordination about vanadium has been described as pentagonal bipyramidal. It may, however, also be described as trigonal bipyramidal in terms of the π bonding picture,^{2,46} where the peroxo group is treated as a unit.

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