

Short Communication

The Crystal Structure of Ammonium μ -Oxo-bis(oxodiperoxovanadate)(4-), $(\text{NH}_4)_4[\text{O}\{\text{VO}(\text{O}_2)_2\}_2]$. A Refinement

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In connection with our work on the formation and structure of peroxovanadates, well-formed single crystals of the title compound were obtained. Since the original structure determination was based on twinned crystals using the Weissenberg film method,¹ it was thought worthwhile to undertake a refinement using single-crystal X-ray diffractometer data.

Preparation. To 0.6 g NH_4VO_3 and 1.4 g $(\text{NH}_4)_2\text{CO}_3$ were added 20 ml H_2O and 1.2 ml 30 % H_2O_2 . Within about 2 h all solids had been dissolved. 0.3 ml 30 % H_2O_2 were added (pH became 9) and the solution was left overnight by which time crystals of $(\text{NH}_4)_4[\text{O}\{\text{VO}(\text{O}_2)_2\}_2]$ had separated. Starting with 0.45 g V_2O_5 leads to the same result.

X-Ray method. Intensity data were collected at 18 °C up to $2\theta=60^\circ$ using a SYNTEX P2₁ diffractometer (graphite-monochromatized $\text{MoK}\alpha$ radiation, crystal size $0.18\times 0.19\times 0.27$ mm, θ - 2θ scan method, 2θ scan speed 2.5-29.3 °/min. Integrated intensity values were obtained with the Lehmann-Larsen profile analysis method.² Three test reflexions (015, 123 and 261) showed no significant difference in intensity during the collection of the data ($\sigma(I)$ were 1.6, 1.6 and 3.0 %, respectively). The crystal was thus stable enough at room temperature for collection of intensity data with $\text{MoK}\alpha$ radiation. With $\text{CuK}\alpha$ radiation the stability of the crystals is considerably lower; new crystals had to be mounted for each layer line using $\text{CuK}\alpha$ radiation and the Weissenberg film method.¹

A total of 4721 independent reflexions were measured. Of these, 3106 having $I\geq 3\sigma(I)$ were regarded as being observed and were used in the subsequent calculations. The intensities were corrected for Lorentz and polarisation effects. The unit cell parameters were determined from a least-squares fit of refined diffractometer setting angles for 15 reflexions.

Crystal data

$\text{H}_{16}\text{N}_4\text{O}_{11}\text{V}_2$ F.W.=350.03
Space group $P2_1/c$ (No. 14)
 $a=6.980(2)$ Å, $b=10.107(2)$ Å, $c=16.226(7)$ Å,
 $\beta=95.40(3)^\circ$, $V=1139.7(7)$ Å³, $Z=4$,
 $D_x=2.040$ g cm⁻³, $\mu(\text{MoK}\alpha)=1.80$ mm⁻¹.

Structure refinement. Positional and isotropic thermal parameters were refined by the least-squares method starting with the parameters given by Svensson and Stomberg.¹ This led to an R -value of 0.076 for the observed reflexions ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$). With anisotropic thermal parameters the R -value was reduced to 0.050. The positions of the hydrogen atoms could not be determined unequivocally. Instead, the scattering factor for NH_4^+ , according to Davis and Whitaker,³ was used, while the atomic scattering factors for V and O were taken from Ref. 4. The weighting scheme used was $w=(30+|F_o|+0.02|F_o|^2)^{-1.5}$. The highest peak in the final electron density difference synthesis was 0.8 e/Å³. Calculations were carried out on an IBM 3033 computer, using the crystallographic programmes described in Ref. 6. Lists of structure factors and anisotropic thermal parameters are available from R.S. on request.

Results. Positional and thermal parameters are given in Table 1 and bond distances in Table 2. The unit cell is shown in Fig. 1 and the anion in Fig. 2. The results obtained by Svensson and Stomberg have been confirmed;¹ the largest and average discrepancy between corresponding positional parameters are 3σ and 1σ , respectively, while those between corresponding bond distances are 4σ and 1σ , respectively. In the dinuclear seven-coordinated pentagonal-bipyramidal complex anion the present investigation has shown that two V-O_{peroxo} bonds, V1-O3

Table 1. Atomic coordinates for $(\text{NH}_4)_4[\text{O}\{\text{VO}(\text{O}_2)_2\}_2]$ at 18 °C. All atoms occupy the general four-fold site of space group $P2_1/c$. $Z=4$. $U_{\text{eq}} = \frac{1}{3} \sum \sum U_{ij} a_i^* a_j^* \cos \alpha_{ij}$.

Atom	x	y	z	$U_{\text{eq}}/\text{Å}^2$
V1	0.26019(8)	0.30712(5)	0.03670(3)	0.0237(2)
V2	0.23401(8)	0.12567(5)	0.18515(3)	0.0254(2)
O1	0.4147(4)	0.2041(3)	-0.0289(2)	0.036(1)
O2	0.4844(4)	0.3403(3)	0.0162(2)	0.039(1)
O3	0.1825(3)	0.3593(2)	0.1420(1)	0.029(1)
O4	0.3359(4)	0.4411(2)	0.1128(2)	0.032(1)
O5	0.0914(4)	0.3667(3)	-0.0261(2)	0.042(2)
O6	0.1417(3)	0.1333(2)	0.0651(1)	0.026(1)
O7	-0.0236(4)	0.1626(3)	0.2053(2)	0.040(1)
O8	0.1148(4)	0.1798(3)	0.2789(2)	0.040(1)
O9	0.4694(3)	0.1755(2)	0.1421(2)	0.030(1)
O10	0.4669(4)	0.1997(3)	0.2309(2)	0.037(1)
O11	0.2597(5)	-0.0318(3)	0.1981(2)	0.045(2)
N1	0.2326(4)	-0.0913(3)	-0.0160(2)	0.038(2)
N2	0.2304(4)	0.7024(3)	0.1355(2)	0.029(1)
N3	0.2940(5)	0.4412(3)	0.3153(2)	0.035(1)
N4	-0.2331(5)	0.4080(4)	0.1249(2)	0.039(2)

Table 2. Bond distances (Å) in $(\text{NH}_4)_4[\text{O}\{\text{VO}(\text{O}_2)_2\}_2]$.

Distance		Distance	
V1-O1	1.896(3)	V2-O7	1.895(3)
V1-O2	1.884(3)	V2-O8	1.882(3)
V1-O3	1.914(3)	V2-O9	1.912(2)
V1-O4	1.875(3)	V2-O10	1.878(3)
V1-O5	1.601(3)	V2-O11	1.613(3)
V1-O6	2.013(2)	V2-O6	1.994(2)
V1-O9	2.522(3)	V2-O3	2.480(2)
O1-O2	1.469(4)	O7-O8	1.474(4)
O3-O4	1.465(3)	O9-O10	1.463(4)

and V2-O9, are significantly longer than the other six. This is readily explained by the weakening of these two V-O bonds as a consequence of the corresponding oxygen atoms being involved in weak V...O interactions with the opposite vanadium atom within the anion. Similar elongations, due to hydrogen bonding, have been observed in $(\text{Hbipy})[\text{H}\{\text{VO}(\text{O}_2)_2\}_2] \cdot x\text{H}_2\text{O} \cdot (6-x)\text{H}_2\text{O}$,⁷ and $(\text{Hbipy})[\text{VO}(\text{O}_2)_2\text{bipy}] \cdot (3+x)\text{H}_2\text{O} \cdot (2-x)\text{H}_2\text{O}$.⁸ Other examples of asymmetric V-O_{peroxo} bonds have been found in $\text{K}_3[\text{VO}(\text{O}_2)_2\text{ox}] \cdot \text{H}_2\text{O}$,⁹ $(\text{NH}_4)_3[\text{VF}_2\text{O}(\text{O}_2)_2]$,¹⁰ and $(\text{NH}_4)_2[\text{VFO}(\text{O}_2)_2]$ ¹¹ (Abbreviations: $\text{Hbipy} = \text{C}_{10}\text{H}_9\text{N}_2^+$, $\text{bipy} = \text{C}_{10}\text{H}_8\text{N}_2$, $\text{ox} = \text{C}_2\text{O}_4^{2-}$).

$(\text{NH}_4)_4[\text{O}\{\text{VO}(\text{O}_2)_2\}_2]$ was the first peroxovanadate to be analyzed structurally. With the present amount of structural information concerning peroxovanadates, the following conclusions can be drawn. There is a substantial change in coordination in going from $\text{K}_2[\text{VFO}(\text{O}_2)_2]$ ¹² and $\text{NH}_4[\text{VO}(\text{O}_2)_2\text{NH}_3]$ ¹³ via $(\text{NH}_4)_4[\text{O}\{\text{VO}(\text{O}_2)_2\}_2]$ and $(\text{NH}_4)_2[\text{VFO}(\text{O}_2)_2]$ ¹¹ to $(\text{NH}_4)_3[\text{VF}_2\text{O}(\text{O}_2)_2]$.¹⁰ In $\text{K}_2[\text{VFO}(\text{O}_2)_2]$ and $\text{NH}_4[\text{VO}(\text{O}_2)_2\text{NH}_3]$ vanadium is six-coordinated in the pentagonal-pyramidal way. Even in peroxovanadates with only monodentate ligands, disregarding the peroxo groups, there is, however, a tendency for vanadium to attain pentagonal-bipyramidal coordination. This is achieved by the

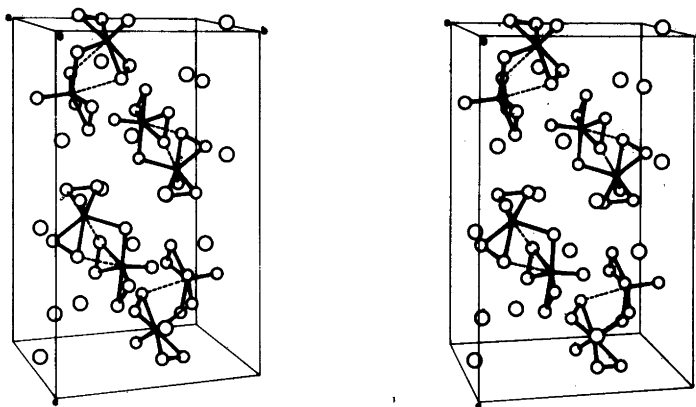


Fig. 1. Stereoscopic drawing of the unit cell of $(\text{NH}_4)_4[\text{O}\{\text{VO}(\text{O}_2)_2\}_2]$.

approach of an atom to the second apical position. In $(\text{NH}_4)_4[\text{O}\{\text{VO}(\text{O}_2)_2\}_2]$ this seventh ligating atom is an oxygen atom of a peroxy group coordinated to the other vanadium atom of the dinuclear complex at a rather large distance, 2.522(3) and 2.480(2) Å from the respective vanadium atom. In $(\text{NH}_4)_2[\text{VFO}(\text{O}_2)_2]$ the seventh ligating atom is the double-bonded oxygen atom of the neighbouring $\text{VFO}(\text{O}_2)_2^{2-}$ unit at

the comparable distance 2.505(1) Å; these units are linked together to form $\cdots\text{V}=\text{O}\cdots\text{V}=\text{O}\cdots$ chains.¹¹ $(\text{NH}_4)_3[\text{VF}_2\text{O}(\text{O}_2)_2]$ is unusual; it is the hitherto sole example of a peroxovanadate with only monodentate ligands, disregarding the peroxy groups, with an unshared atom occupying the second apical position.¹⁰ In peroxovanadates with polydentate ligands like oxalate, 2,2'-bipyridine, pyridine-2-carboxylate and pyridine-2,6-

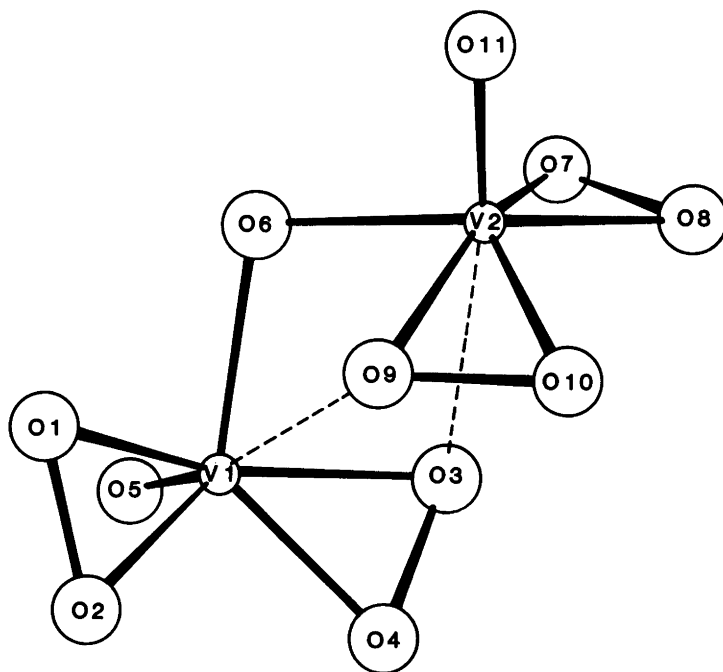


Fig. 2. The dimeric anion $[\text{O}\{\text{VO}(\text{O}_2)_2\}_2]^{4-}$.

dicarboxylate this type of coordination is familiar; in these cases the second V–L_{apical} bond lengths range between 2.211(2) and 2.290(2) Å (R.m.s. deviation is given in parenthesis).^{7-9,14-17}

The V=O bond lengths, 1.601(3) and 1.613(3) Å, are close to the average value, 1.609(7) Å, calculated from data for 11 peroxovanadates (see Table 4 in Ref. 10 and Table 3 in Ref. 17).⁷⁻¹⁷ The O–O bond lengths, 1.463(4)–1.474(4) Å, agree well with the average value, 1.464(6) Å, calculated from data for the above-mentioned 11 peroxovanadates.⁷⁻¹⁷

The maximum and r.m.s. deviations of the atoms defining the two equatorial planes in the anion, O1–O4, O6 and O6–O10, are 0.068 and 0.042 Å, respectively, but the vanadium atoms are displaced 0.453 and 0.444 Å from the respective equatorial planes towards the vanadyl oxygen atoms. Similar displacements have been observed in other oxoperoxovanadates (see Table 4 in Ref. 10 and Table 3 in Ref. 17).

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1. Svensson, I.-B. and Stomberg, R. *Acta Chem. Scand.* 25 (1971) 898.
2. Lehmann, M. S. and Larsen, F. K. *Acta Crystallogr. A* 30 (1974) 580.
3. Davies, M. F. and Whitaker, A. *Acta Crystallogr.* 21 (1966) 822.
4. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4.
5. Cruickshank, D. W. J. *Crystallographic Computing*, Munksgaard, Copenhagen 1970, p. 195.
6. Lindgren, O. *On the Oxygen Coordination of Cerium in Some Sulfates and Chromates*, Diss., Chalmers University of Technology and University of Göteborg, Göteborg 1977.
7. Szentivanyi, H. and Stomberg, R. *Acta Chem. Scand. A* 38 (1984) 101.
8. Stomberg, R. and Szentivanyi, H. *Acta Chem. Scand. A* 38 (1984) 121.
9. Begin, D., Einstein, F. W. B. and Field, J. *Inorg. Chem.* 14 (1975) 1785.
10. Stomberg, R. *Acta Chem. Scand. A* 38 (1984) 541.
11. Stomberg, R. and Olson, S. *Acta Chem. Scand. A* 38 (1984). *In press.*
12. Stomberg, R. *Acta Chem. Scand. A* 38 (1984) 223.
13. Drew, R. E. and Einstein, F. W. B. *Inorg. Chem.* 11 (1972) 1079.

14. Drew, R. E. and Einstein, F. W. B. *Inorg. Chem.* 12 (1973) 829.
15. Szentivanyi, H. and Stomberg, R. *Acta Chem. Scand. A* 37 (1983) 553.
16. Campbell, N. J., Capparelli, M. V., Griffith, W. P. and Skapski, A. C. *Inorg. Chim. Acta* 77 (1983) L215.
17. Szentivanyi, H. and Stomberg, R. *Acta Chem. Scand. A* 37 (1983) 709.

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