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# The Crystal Structure of Ammonium (2,2′-Bipyridine)oxodiperoxovanadate(V) Tetrahydrate, $NH_4[VO(O_2)_2(C_{10}H_8N_2)] \cdot 4H_2O$, at −100 °C

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The crystal structure of ammonium (2,2′-bipyridine)oxodiperoxovanadate(V) tetrahydrate, $NH_4[VO(O_2)_2(C_{10}H_8N_2)] \cdot 4H_2O$, has been determined at −100 °C by single-crystal X-ray methods. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a=7.089(2)$ Å, $b=18.087(7)$ Å, $c=12.798(3)$ Å, $\beta=90.57(2)°$, $V=1640.8(9)$ Å$^3$ and $Z=4$. Refinement by the least-squares method gave a final $R$-value of 0.050 for 2221 observed independent reflexions.

The structure is comprised of ammonium ions, (2,2′-bipyridine)oxodiperoxovanadate(V) ions and water of crystallization, held together by ionic and hydrogen bond forces. Vanadium is seven-coordinated. The geometry of the anion is a distorted pentagonal bipyramid with the vanadyl oxygen atom and one nitrogen atom from 2,2′-bipyridine at the apices and the peroxo groups and the other nitrogen atom forming the pentagonal plane. The vanadium atom is displaced 0.32 Å from this plane towards the vanadyl oxygen atom. Interatomic distances within the anion are: $V-N_{equatorial}$ 2.149(4) Å, $V-N_{apical}$ 2.288(3) Å, $V=O$ 1.619(3) Å, $V-O_{peroxo}$ 1.880(3)−1.911(3) Å and $(O-O)_{peroxo}$ 1.465(4) and 1.471(4) Å.

As part of a project on transition metal peroxo complexes at this department, attention has been focused on the structures of mixed-ligand vanadium(V) peroxo complexes. Of this type, only the structures of $NH_4[VO(O_2)_2(NH_3)]$,[1] $NH_4[VO(O_2)_2(H_2O)\{C_5H_3N(COO)_2\}] \cdot xH_2O$,[2] and $K_3[VO(O_2)_2(C_2O_4)] \cdot H_2O$,[3] all being monomeric, have been published to date. Beiles *et al.* report a compound, which they denote $(NH_4)_2(bipy)_2 \cdot H_2V_2O_{11} \cdot H_2O_2 \cdot 3H_2O$,[4] and Sala-Pala *et al.* another with the formula $NH_4[V(O_2)_3bipy] \cdot 3H_2O$.[5] According to Vuletić *et al.*, these two compounds seem to resemble $NH_4[VO(O_2)_2bipy] \cdot 4H_2O$, which they have prepared.[6] It was, therefore, thought worthwhile to determine their crystal structures in order to elucidate the nature of these three compounds.

## EXPERIMENTAL

*Preparation*. Crystals were prepared according to Beiles *et al.*,[4] Sala-Pala *et al.*,[5] as well as Vuletić *et al.*,[6] those obtained by the first method were recrystallized from a 15 % aqueous solution of hydrogen peroxide.

*X-Ray methods.* X-Ray powder photographs were obtained by the Guinier-Hägg method and single crystal photographs by the multiple film, equi-inclination Weissenberg technique, using Cu*Kα* radiation at room temperature. These photographs indicated that the compounds obtained in the three different preparations are identical, shown in the present investigation to be $NH_4[VO(O_2)_2bipy] \cdot 4H_2O$.

The single crystal photographs were taken with rotation about [100] (layer lines 0−6) and [010] (layer line 0). Because of the low stability of the compound, new crystals had to be mounted for each layer line. A total of 1177 independent reflexions were registered. The intensities were corrected for Lorentz and polarization effects.

For the refinement of the crystal structure, intensity data were recorded with a SYNTEX P2$_1$ automatic four-circle single-crystal X-ray dif-

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fractometer, using graphite-monochromatized Mo$K\alpha$ radiation and a crystal with the dimensions 0.19×0.19×0.28 mm. The temperature was maintained at −100 °C with the SYNTEX LT1 low-temperature device. The $\omega$–$2\theta$ scan method was used and the $2\theta$ scan speed was allowed to vary between 2 and 15° min$^{-1}$, depending on the intensity of the measured reflexion. Data were collected for $2\theta \leq 55°$. A profile analysis based on the Lehmann-Larsen method[7] was applied to the 96-step profile collected for each reflexion. A reflexion measured after each twenty-fourth reflexion showed no significant difference in intensity during the collection of the data.

A total of 3792 independent reflexions were measured. Of these, 2221 having $I_o \geq 3\sigma(I_o)$ were regarded as being observed and were used in the subsequent calculations. The intensities were corrected for Lorentz and polarization effects but not for absorption.

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

## CRYSTAL DATA

Ammonium (2,2′-bipyridine)oxodiperoxovanadate(V) tetrahydrate, $NH_4[VO(O_2)_2(C_{10}H_8N_2)] \cdot 4H_2O$. F.W.=377.22. Space group: $P2_1/n$ (No. 14; non-standard setting). General positions: $\pm(x,y,z)$, $\pm(\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z)$.

| | At −100 °C | At 18 °C (Ref. 19) |
|---|---|---|
| $a$ (Å) | 7.089(2) | 7.114(1) |
| $b$ (Å) | 18.087(7) | 18.142(2) |
| $c$ (Å) | 12.798(3) | 12.845(1) |
| $\beta$ (°) | 90.57(2) | 90.52(1) |
| $V$ (Å$^3$) | 1640.8(9) | 1657.8 |

$Z=4$, $D_x=1.52$ g cm$^{-3}$, $\mu(\text{Mo}K\alpha)=0.69$ mm$^{-1}$, $\mu(\text{Cu}K\alpha)=5.8$ mm$^{-1}$.

## STRUCTURE DETERMINATION

Single crystal photographs showed, with a few minor deviations, that $I(hkl)$ and $I(hk\bar{l})$ are almost equal. On all films, reflexions of the type $h0l$ with $h+l=2n+1$ and $0k0$ with $k=2n+1$ were missing. With the exception of nine weak reflexions, $hk0$-reflexions with $k=2n+1$ were also missing. The effect of the angle $\beta$ deviating slightly from 90° could clearly be observed on upper-level photographs. Thus, though undoubtedly monoclinic, the crystals exhibit almost orthorhombic symmetry (approximately space group $Pmnb$ or $P2_1nb$). While waiting for an automatic single-crystal diffractometer to be installed at the department, a preliminary structure analysis was performed, taking advantage of the pseudo orthorhombic symmetry.

Since the true space group, $P2_1/n$, is centrosymmetric, $Pmnb$ was first tested. The positions of all non-hydrogen atoms were determined from a Patterson map and subsequent electron density calculations. Least-squares refinement of positional and anisotropic thermal parameters yielded an $R$-value of 0.13 ($R=\Sigma| |F_o| - F_c| |/\Sigma|F_o|$), a reasonable value considering that film data and unstable crystals had been used. No attempt was made to refine the structure in space group $P2_1/n$ using film data.

Refinement of the structural parameters, based on diffractometer data, was performed later. Because of the instability of the crystals at room temperature, data were collected at −100 °C. Least-squares refinement of an overall scale factor and positional and isotropic thermal parameters for all the non-hydrogen atoms yielded an $R$-value of 0.10. Refinement of positional and anisotropic thermal parameters for the non-hydrogen atoms and positional parameters for the non-water hydrogen atoms reduced $R$ to 0.050. The $B_{iso}$'s of the carbon and ammonium nitrogen atoms were used as the $B_{iso}$'s for the corresponding hydrogen atoms, and were not refined. The weighting scheme used was that of Cruickshank:[8] $w=(a+|F_o|+c|F_o|^2+d|F_o|^3)^{-1}$, with $a=10.0$, $c=0.020$ and $d=0.0$. The scattering factors for V, O, N, C and H were taken from the *International Tables for X-Ray Crystallography, Vol. IV.*

The highest peak in the final electron density difference synthesis, 0.86 e Å$^{-3}$, appeared 1.05 Å from vanadium.

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 R.S. upon request.

## RESULTS AND DISCUSSION

According to the literature three peroxovanadates have been found in the system $NH_4^+ - VO_3^-$

*Table 1.* Atomic coordinates and thermal parameters (Å$^2$) for $NH_4[VO(O_2)_2(C_{10}H_8N_2)] \cdot 4H_2O$ at −100 °C. Space group $P2_1/n$.
$U_{eq}=\frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j\cos\alpha_{ij}$

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| V | 0.24868(10) | 0.55911(4) | 0.26888(5) | 0.0244(2) |
| O1 | 0.5147(4) | 0.5608(2) | 0.2460(2) | 0.0373(7) |
| O2 | 0.4392(4) | 0.6308(2) | 0.2851(2) | 0.0364(7) |
| O3 | −0.0159(4) | 0.5649(2) | 0.2408(3) | 0.0378(7) |
| O4 | 0.0662(4) | 0.6339(2) | 0.2813(2) | 0.0368(7) |
| O5 | 0.2429(5) | 0.5183(2) | 0.3813(2) | 0.0416(8) |
| Ow1 | 0.4431(5) | 0.3540(3) | 0.5088(3) | 0.0689(12) |
| Ow2 | 0.7568(5) | 0.8406(2) | 0.1138(2) | 0.0427(8) |
| Ow3 | 0.7541(5) | 0.2152(2) | 0.2790(3) | 0.0603(10) |
| Ow4 | 0.0584(5) | 0.3533(2) | 0.5147(3) | 0.0540(10) |
| N1 | 0.2447(5) | 0.4558(2) | 0.1860(3) | 0.0312(8) |
| N2 | 0.2543(5) | 0.5862(2) | 0.0943(2) | 0.0284(8) |
| N3 | 0.7406(5) | −0.0029(2) | 0.1067(3) | 0.0340(8) |
| C1 | 0.2400(8) | 0.3910(3) | 0.2378(4) | 0.0424(11) |
| C2 | 0.2356(9) | 0.3235(3) | 0.1866(5) | 0.0534(14) |
| C3 | 0.2342(8) | 0.3230(3) | 0.0778(4) | 0.0506(13) |
| C4 | 0.2376(7) | 0.3888(3) | 0.0244(4) | 0.0401(11) |
| C5 | 0.2438(6) | 0.4550(2) | 0.0798(3) | 0.0280(9) |
| C6 | 0.2509(6) | 0.5277(2) | 0.0287(3) | 0.0273(9) |
| C7 | 0.2557(6) | 0.5371(3) | −0.0799(3) | 0.0342(10) |
| C8 | 0.2629(7) | 0.6082(3) | −0.1200(3) | 0.0398(11) |
| C9 | 0.2652(7) | 0.6675(3) | −0.0529(4) | 0.0423(11) |
| C10 | 0.2607(7) | 0.6543(3) | 0.0534(4) | 0.0385(11) |
| H(C1) | 0.232(9) | 0.395(4) | 0.326(5) | |
| H(C2) | 0.240(9) | 0.281(4) | 0.236(6) | |
| H(C3) | 0.246(9) | 0.274(4) | 0.032(6) | |
| H(C4) | 0.235(9) | 0.383(4) | −0.047(6) | |
| H(C7) | 0.251(8) | 0.494(4) | −0.122(5) | |
| H(C8) | 0.258(9) | 0.616(4) | −0.195(6) | |
| H(C9) | 0.265(10) | 0.713(4) | −0.065(6) | |
| H(C10) | 0.275(9) | 0.690(4) | 0.098(5) | |
| H1(N3) | 0.756(7) | −0.052(3) | 0.117(4) | |
| H2(N3) | 0.750(7) | 0.004(3) | 0.039(4) | |
| H3(N3) | 0.639(8) | 0.014(3) | 0.143(4) | |
| H4(N3) | 0.864(8) | 0.016(3) | 0.135(4) | |

$-H_2O_2$–bipy$-H_2O$.[4–6] The aim of the present investigation was to deduce their structures. The crystalline products obtained from the three different synthetic procedures were shown, however, to be identical. Sala-Pala *et al.* found, from Weissenberg photographs, that their crystalline product, which they formulate $NH_4[V(O_2)_3bipy] \cdot 3H_2O$, is orthorhombic with $a$=12.83(5) Å, $b$=18.13(3) Å, $c$=7.11(2) Å, $D_m$=1.49 g cm$^{-3}$, $Z$=4, and $D_c$=1.51 g cm$^{-3}$.[5] Within 1$\sigma$ these data are the same as those found in this work for $NH_4[VO(O_2)_2bipy] \cdot 4H_2O$, which was found to be monoclinic (see crystal data). That Sala-Pala *et al.* found their substance to be orthorhombic is understandable, since normal care taken in the interpretation of the Weissenberg films might easily lead to that conclusion (this is more fully explained under the heading Structure Determination). There is a plausible explanation to the question why the formulæ deduced by Beiles *et al.* and by Sala-Pala *et al.* probably are wrong. In determining the peroxide content they have used iodometry and might have overlooked the fact that also vanadium(V) oxidizes iodide ions.

The positional parameters obtained for

*Table 2.* Bond distances (Å) and angles (°) in $NH_4[VO(O_2)_2(C_{10}H_8N_2)] \cdot 4H_2O$. Values in square brackets refer to film data.

| | Distance | | | Angle |
|---|---|---|---|---|
| V–O1 | 1.911(3) | [1.90(1)] | O1–V–O2 | 45.4(1) |
| V–O2 | 1.883(3) | [1.86(1)] | O1–V–O3 | 159.9(1) |
| V–O3 | 1.909(3) | [1.90(1)] | O1–V–O4 | 133.0(1) |
| V–O4 | 1.880(3) | [1.86(1)] | O1–V–O5 | 100.2(2) |
| V–O5 | 1.619(3) | [1.61(1)] | O1–V–N1 | 86.9(1) |
| V–N1 | 2.149(4) | [2.15(1)] | O1–V–N2 | 79.6(1) |
| V–N2 | 2.288(3) | [2.28(1)] | O2–V–O3 | 133.3(1) |
| O1–O2 | 1.465(4) | [1.47(1)] | O2–V–O4 | 89.3(1) |
| O3–O4 | 1.471(4) | [1.47(1)] | O2–V–O5 | 104.0(2) |
| N1–C1 | 1.347(6) | [1.32(2)] | O2–V–N1 | 131.2(1) |
| N1–C5 | 1.359(5) | [1.32(2)] | O2–V–N2 | 86.6(1) |
| C1–C2 | 1.386(7) | [1.42(3)] | O3–V–O4 | 45.7(1) |
| C2–C3 | 1.392(8) | [1.40(4)] | O3–V–O5 | 99.1(2) |
| C3–C4 | 1.373(7) | [1.32(3)] | O3–V–N1 | 86.9(1) |
| C4–C5 | 1.392(6) | [1.44(2)] | O3–V–N2 | 80.3(1) |
| C5–C6 | 1.470(6) | [1.46(2)] | O4–V–O5 | 103.3(2) |
| C6–C7 | 1.401(6) | [1.39(2)] | O4–V–N1 | 131.5(1) |
| C7–C8 | 1.385(7) | [1.38(3)] | O4–V–N2 | 87.0(1) |
| C8–C9 | 1.374(7) | [1.38(3)] | O5–V–N1 | 92.4(2) |
| C9–C10 | 1.381(7) | [1.35(2)] | O5–V–N2 | 165.2(1) |
| N2–C10 | 1.338(6) | [1.36(2)] | N1–V–N2 | 72.8(1) |
| N2–C6 | 1.351(5) | [1.33(2)] | V–O1–O2 | 66.2(2) |
| C1–H(C1) | 1.14(7) | | V–O2–O1 | 68.2(3) |
| C2–H(C2) | 1.00(8) | | V–O3–O4 | 66.1(2) |
| C3–H(C3) | 1.07(7) | | V–O4–O3 | 68.2(2) |
| C4–H(C4) | 0.93(8) | | C1–N1–C5 | 118.9(4) |
| C7–H(C7) | 0.95(6) | | C6–N2–C10 | 118.6(4) |
| C8–H(C8) | 0.97(7) | | N1–C1–C2 | 122.2(4) |
| C9–H(C9) | 0.85(7) | | C1–C2–C3 | 118.6(5) |
| C10–H(C10) | 0.86(6) | | C2–C3–C4 | 119.4(5) |
| N3–H1(N3) | 0.90(5) | | C3–C4–C5 | 119.5(4) |
| N3–H2(N3) | 0.88(5) | | N1–C5–C4 | 121.3(4) |
| N3–H3(N3) | 0.91(5) | | N1–C5–C6 | 115.8(3) |
| N3–H4(N3) | 1.01(5) | | C4–C5–C6 | 123.0(4) |
| | | | N2–C6–C5 | 115.2(3) |
| | | | N2–C6–C7 | 121.3(4) |
| | | | C5–C6–C7 | 123.5(4) |
| | | | C6–C7–C8 | 118.9(4) |
| | | | C7–C8–C9 | 119.5(4) |
| | | | C8–C9–C10 | 118.7(5) |
| | | | N2–C10–C9 | 123.0(4) |

$NH_4[VO(O_2)_2bipy] \cdot 4H_2O$ in the last refinement cycle, as well as $U_{eq}$ are given in Table 1. The content of the unit cell is shown in Fig. 1 and the anion in Fig. 2. Bond distances and angles are given in Table 2 and hydrogen bond distances in Table 3.

Table 1 shows that the largest deviation from *Pmnb*-symmetry, exhibited by C3, is 0.112(6) Å. Bond distances obtained by refining the parameters in space group *Pmnb* using film data do not differ significantly from those obtained by refining the parameters in space group $P2_1/n$ using diffractometer data (see Table 2).

The crystals of ammonium (2,2′-bipyridine)-oxodiperoxovanadate(V) tetrahydrate consist of ammonium ions, (2,2′-bipyridine)oxodiperox-

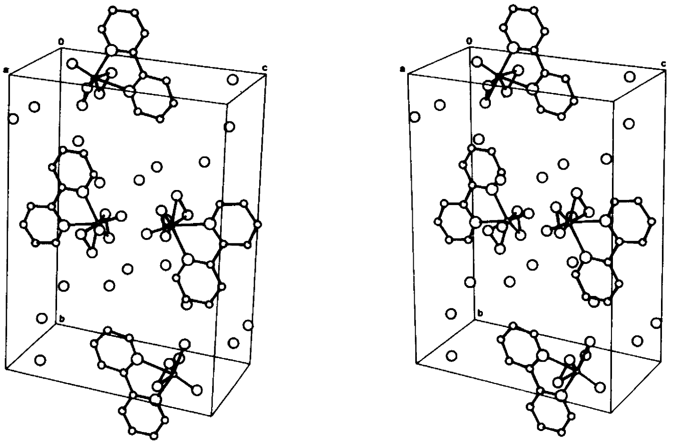

*Fig. 1.* Stereoscopic drawing of the unit cell of $NH_4[VO(O_2)_2bipy] \cdot 4H_2O$.

ovanadate(V) ions and water of crystallization, held together by ionic and hydrogen bond forces.

$[VO(O_2)_2(bipy)]^-$ has a pentagonal bipyramidal arrangement of ligands, as shown in Fig. 2, a configuration observed in several transition metal peroxo complexes (see, *e.g.*, Refs. 2,3,10–16). The distances from the equatorial plane (plane I), defined by O1, O2, O3, O4 and N1, to these atoms and to V, O5 and N2 are given in Table 4. Within the limits of experimental error the defining atoms all lie in this plane. The atoms V, O5, N1 and N2 and the midpoints between O1 and O3 and O2 and O4 also lie in a plane (plane II). Planes I and II form an angle of 89.6° with one another.

*Table 3.* Hydrogen bond distances (Å). Ow1–Ow4 are water oxygen atoms and N3 is the ammonium nitrogen atom.

| | | Distance |
|---|---|---|
| N3···O1 | $(\frac{3}{2}-x,-\frac{1}{2}+y,\frac{1}{2}-z)$ | 2.797(5) |
| N3···O3 | $(\frac{1}{2}-x,-\frac{1}{2}+y,\frac{1}{2}-z)$ | 2.813(5) |
| N3···O5 | $(\frac{1}{2}+x,\frac{1}{2}-y,-\frac{1}{2}+z)$ | 2.897(4) |
| N3···Ow2 | $(x,-1+y,z)$ | 2.835(5) |
| Ow1···O2 | $(1-x,1-y,1-z)$ | 2.772(5) |
| Ow1···Ow2 | $(\frac{3}{2}-x,-\frac{1}{2}+y,\frac{1}{2}-z)$ | 2.667(5) |
| Ow1···Ow4 | $(x,y,z)$ | 2.729(5) |
| Ow2···Ow3 | $(\frac{3}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$ | 2.653(5) |
| Ow2···Ow4 | $(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$ | 2.771(5) |
| Ow3···O2 | $(\frac{3}{2}-x,-\frac{1}{2}+y,\frac{1}{2}-z)$ | 2.786(5) |
| Ow3···O4 | $(\frac{1}{2}-x,-\frac{1}{2}+y,\frac{1}{2}-z)$ | 2.806(5) |
| Ow4···O4 | $(-x,1-y,1-z)$ | 2.774(5) |

The vanadium atom is displaced 0.318 Å from the pentagonal plane towards the vanadyl oxygen atom. Such a displacement is usually observed for transition metal peroxo compounds (see, *e.g.*, Table 6 in Ref. 11). When the apical atoms are different, or one is missing, this displacement is in the range 0.2–0.5 Å, the latter value being observed for pentagonal pyramidal complexes like $[CrO(O_2)_2py]$ and $[VO(O_2)_2(NH_3)]^-$, while 0.3 Å is commonly encountered in pentagonal bipyramidal compounds.

The $V-O_{peroxo}$ bond lengths, 1.880–1.911 Å, lie in the range of $V-O_{peroxo}$ distances previously reported[1–3,11] and are normal vanadium-oxygen single bond distances.

The distances between the oxygen atoms in the peroxo groups, 1.465 and 1.471 Å, compare well with other observations (see, *e.g.*, Refs. 1–3 and Table 7 in Ref. 11).

The V=O bond length, 1.619 Å, is in good agreement with the corresponding values reported for vanadium peroxo compounds.[1–3,11]

Each pyridine ring in the bipyridine ligand is planar and the planes intersect each other at 1.4°. The deviations of the atoms from the respective plane, as well as from the plane $x=\frac{1}{4}$, are given in Table 4. Bond distances and angles within the bipyridine group are in good agreement with data peviously reported.[14,17] The difference between $V-N_{equatorial}$ and $V-N_{apical}$ distances, 2.149 and

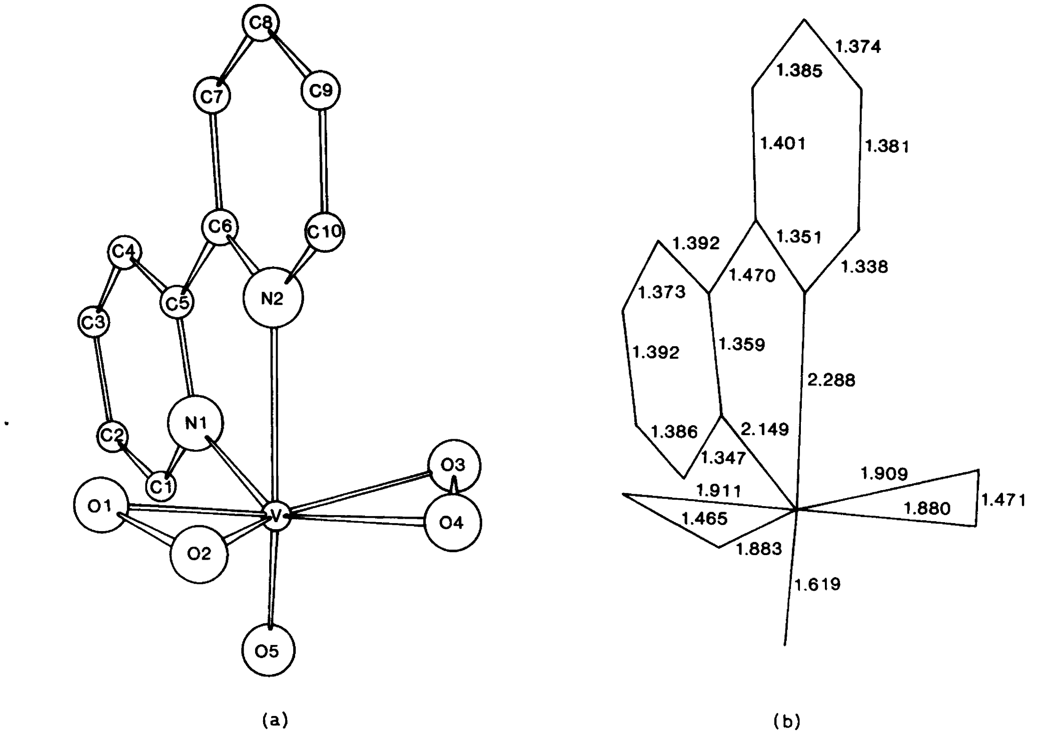

*Fig. 2.* The anion $[VO(O_2)_2bipy]^-$.

*Table 4.* Displacements (Å) of atoms from least-squares planes in $NH_4[VO(O_2)_2(C_{10}H_8N_2)] \cdot 4H_2O$.

Defining atoms are:

| | |
|---|---|
| Plane I | O1, O2, O3, O4, N1 |
| Plane II | V, O5, N1, N2, the midpoints between O1 and O3 (O1/O3) and O2 and O4 (O2/O4) |
| Plane III | N1, C1–C5 |
| Plane IV | N2, C6–C10 |
| Plane V | $x=\frac{1}{4}$ |

| Atom | Plane I | Atom | Plane II | Atom | Plane III | Atom | Plane IV | Atom | Plane V |
|---|---|---|---|---|---|---|---|---|---|
| O1 | 0.011(3) | V | −0.001(1) | N1 | −0.001(4) | N2 | −0.003(4) | N1 | 0.037(4) |
| O2 | −0.007(3) | O5 | 0.002(4) | C1 | 0.004(5) | C6 | 0.003(4) | C1 | 0.071(5) |
| O3 | 0.010(3) | N1 | −0.002(4) | C2 | −0.003(6) | C7 | −0.001(5) | C2 | 0.102(6) |
| O4 | −0.006(3) | N2 | 0.002(4) | C3 | −0.001(6) | C8 | −0.001(5) | C3 | 0.112(6) |
| N1 | −0.008(4) | O1/O3 | 0.000(3) | C4 | 0.004(5) | C9 | 0.001(5) | C4 | 0.088(5) |
| V | −0.318(1) | O2/O4 | −0.002(3) | C5 | −0.003(4) | C10 | 0.001(5) | C5 | 0.044(4) |
| N2 | −1.928(4) | O1 | −1.881(3) | | | | | C6 | −0.006(4) |
| O5 | 1.943(4) | O2 | −1.324(3) | | | | | C7 | −0.041(5) |
| | | O3 | 1.881(3) | | | | | C8 | −0.091(5) |
| | | O4 | 1.321(3) | | | | | C9 | −0.108(5) |
| | | | | | | | | C10 | −0.076(5) |
| | | | | | | | | N2 | −0.030(4) |

2.288 Å, is also in good agreement with earlier results.[14,17,18]

The ammonium ion is hydrogen bonded to the two peroxo oxygen atoms O1 and O3, the vanadyl oxygen atom, O5, and one of the water molecules, with bond distances ranging from 2.80 to 2.90 Å. The X···H−N angles are almost linear (144−168°).

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