

**The Crystal Structure of 2,2'-Bipyridinium(1+) (2,2'-Bipyridine)-
oxodiperoxovanadate(1-)-(3+x)-hydrogen peroxide-
(2-x)-water, (C₁₀H₉N₂)[VO(O₂)₂(C₁₀H₈N₂)]·(3+x)H₂O₂·
(2-x)H₂O, x=0.4, at -100 °C**

ROLF STOMBERG and HELGA SZENTIVANYI

Department of Inorganic Chemistry CTH/GU, Chalmers Tekniska Högskola,
S-412 96 Göteborg, Sweden.

Crystals of the title compound, the structure of which has been determined at -100 °C by single-crystal X-ray methods, are triclinic, space group *P*1 (No. 2) with $a=14.236(9)$, $b=10.848(5)$, $c=8.316(4)$ Å, $\alpha=95.22(4)$, $\beta=104.98(4)$, $\gamma=93.71(4)^\circ$, $V=1230.3(11)$ Å³ and $Z=2$. Reflexion intensities were registered with an automatic single-crystal X-ray diffractometer using MoK α radiation. Least-squares refinement of structural and thermal parameters yielded a final $R(F)$ -value of 0.052 for 3336 observed reflexions.

The crystals are composed of 2,2'-bipyridinium(1+) and (2,2'-bipyridine)oxodiperoxovanadate(1-) ions, hydrogen peroxide and water of crystallization, held together by ionic and hydrogen bond forces. 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 0.28 Å from this plane towards the vanadyl oxygen atom. The two pyridine rings of the 2,2'-bipyridine group form an angle of 7.1° with one another in the cation and of 5.4° in the ligand. The monoprotonated 2,2'-bipyridinium(1+) ion adopts the *cis* configuration.

Bond distances within the anion are: V-N_{equatorial} 2.137(4) Å, V-N_{apical} 2.284(4) Å, V=O 1.619(3) Å, V-O_{peroxo} 1.862(3)–1.942(3) Å and (O-O)_{peroxo} 1.473(4) and 1.474(4) Å. The (O-O)_{peroxo} bond distances in the hydrogen peroxide molecules are 1.458(5)–1.475(5) Å.

Vuletić *et al.* have prepared a series of oxodiperoxovanadates(V).¹ In the system V₂O₅-H₂O₂-bipy-H₂O they found one compound to which they ascribed the formula (H₂bipy)[V₂O₂(O₂)₄(bipy)₂] \cdot 6H₂O. A recent single-crystal X-ray investigation, performed by the present authors, has shown it to be (Hbipy)[H{VO(O₂)₂bipy}₂] \cdot x H₂O₂ \cdot (6- x)H₂O, $x\approx 0.5$ (I).² Within the limits of experimental error the analytical results obtained by Vuletić *et al.* are consistent with this formula; in our case some of the water of crystallization has been replaced by hydrogen peroxide. I is a rare example of a transition metal compound with two peroxometallate complexes held together by a very strong hydrogen bond (2.456(4) Å). Moreover, I contains a monoprotonated 2,2'-bipyridinium cation not often encountered.

If the reaction mixture from which I crystallizes is allowed to stand, a crystalline product with a different habit appears. The [H{VO(O₂)₂bipy}₂]⁻ complex in I might be a rather stable reaction intermediate in the formation of this new compound. It was, therefore, considered interesting to determine the formula and crystal structure of this new phase (II).

EXPERIMENTAL

Preparation. The reaction mixture for the synthesis of '(H₂bipy)[V₂O₂(O₂)₄(bipy)₂] \cdot 6H₂O'

according to Vuletić *et al.* was prepared. From this orange crystals of phase I were formed. On prolonged standing at 5 °C these were transformed to a new orange well-crystallized phase, II.

X-Ray methods. Approximate cell dimensions and the crystal symmetry were obtained from Weissenberg photographs using $\text{CuK}\alpha$ radiation. Intensity data were recorded at $-100\text{ }^\circ\text{C}$ with a SYNTEX P2₁ automatic four-circle single-crystal X-ray diffractometer using graphite-monochromatized $\text{MoK}\alpha$ radiation and a crystal with the dimensions $0.10 \times 0.20 \times 0.35\text{ mm}$. The θ - 2θ scan method was used and the 2θ scan speed was allowed to vary between 2.5 and 20 min^{-1} , depending on the intensity of the reflexion. Data were collected for $2\theta < 56^\circ$. Two reflexions, 022 and 203, measured after each forty-eighth reflexion showed no significant difference in intensity during the collection of the data. Integrated intensity values were obtained with the Lehmann-Larsen profile analysis method.³

A total of 5974 independent reflexions were measured. Of these, 3336 having $I_o > 3\sigma(I_o)$ 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

$\text{C}_{20}\text{H}_{27}\text{N}_4\text{O}_{13+x}\text{V}$, $x=0.4$ F.W. = 588.80
Space group $P\bar{1}$ (No. 2)
 $a=14.236(9)$, $b=10.848(5)$, $c=8.316(4)\text{ \AA}$,

$\alpha=95.22(4)$, $\beta=104.98(4)$, $\gamma=93.71(4)^\circ$,
 $V=1230.3(11)\text{ \AA}^3$, $Z=2$, $D_x=1.589\text{ g cm}^{-3}$,
 $\mu(\text{MoK}\alpha)=0.51\text{ mm}^{-1}$.

STRUCTURE DETERMINATION

The positions of the non-hydrogen atoms according to the formula $(\text{Hbipy})[\text{VO}(\text{O}_2)_2\text{bipy}] \cdot 3\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ were determined from a Patterson map and subsequent electron density calculations. Least-squares refinement of positional and isotropic thermal parameters for these atoms yielded an R -value of 0.097 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). The nitrogen atoms of the cation were then in *cis* position; with these in *trans* position R became 0.102. An electron density difference map showed most of the hydrogen atoms and large anisotropy of Ow1, which had a rather high B -value (5.5 \AA^2 ; $B(\text{Ow}2)=2.5\text{ \AA}^2$). Least-squares refinement of positional and anisotropic thermal parameters for the non-hydrogen atoms and positional parameters for the hydrogen atoms reduced R to 0.065. The subsequent difference map showed two rather large peaks (about 1.5 e/\AA^{-3}) around Ow1 1.4 \AA from each other. These were taken to be two oxygen atoms of a hydrogen peroxide molecule partly replacing Ow1. The electron density maps had shown the peak at Ow1 to be about 40 % larger than the other oxygen atom peaks. A hydrogen peroxide molecule (Op7/Op8) with occupation number 0.4 and a water molecule, Ow1, with occupation number 0.6 were introduced in a least-squares refinement of positional and isotropic thermal parameters for

Table 1. Atomic coordinates for $(\text{C}_{10}\text{H}_8\text{N}_2)[\text{VO}(\text{O}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)] \cdot (3+x)\text{H}_2\text{O}_2 \cdot (2-x)\text{H}_2\text{O}$, $x=0.4$ at $-100\text{ }^\circ\text{C}$. All atoms occupy the general twofold site of space group $P\bar{1}$. $Z=2$. The occupation number is 0.4 for Op7 and Op8, 0.6 for Ow1 and 1.0 for all other atoms.

$$U_{eq} = \frac{1}{3} \sum \sum U_{ij} a_i^* a_j^* a_i a_j \cos \alpha_{ij}$$

Atom	x	y	z	$U_{eq}/\text{\AA}^2$
V	0.30964(5)	0.25500(7)	0.10679(9)	0.0111(1)
O1	0.3795(2)	0.1720(3)	0.2930(4)	0.018(1)
O2	0.3227(2)	0.0896(3)	0.1444(4)	0.018(1)
O3	0.2483(2)	0.2054(3)	-0.1256(4)	0.018(1)
O4	0.2804(2)	0.3394(3)	-0.0936(4)	0.018(1)
O5	0.2164(2)	0.2863(3)	0.1756(4)	0.017(1)
Op1	0.8465(3)	0.5110(4)	0.0305(5)	0.040(1)
Op2	0.8668(3)	0.4489(3)	0.1823(4)	0.031(1)
Op3	0.5730(2)	0.1198(3)	0.3415(4)	0.027(1)
Op4	0.6033(3)	0.0797(3)	0.5100(5)	0.030(1)

Op5	0.6720(2)	0.8625(3)	0.3716(4)	0.028(1)
Op6	0.7368(2)	0.8020(3)	0.5039(4)	0.025(1)
Op7	0.0884(7)	0.5540(8)	0.2184(13)	0.034(2)
Op8	0.0525(6)	0.4366(7)	0.2665(12)	0.028(2)
Ow1	0.0636(4)	0.4947(6)	0.2477(8)	0.028(1)
Ow2	0.8112(3)	0.5692(4)	0.4614(5)	0.032(1)
N1	0.3896(2)	0.4262(3)	0.2299(4)	0.014(1)
N2	0.4600(2)	0.2592(3)	0.0562(4)	0.015(1)
N3	-0.0448(3)	-0.1269(4)	0.1469(6)	0.027(1)
N4	-0.1420(3)	0.0488(4)	0.2700(6)	0.030(1)
C1	0.3481(3)	0.5088(4)	0.3149(6)	0.018(1)
C2	0.3947(3)	0.6228(4)	0.3879(5)	0.020(1)
C3	0.4867(3)	0.6561(4)	0.3682(6)	0.020(1)
C4	0.5304(3)	0.5723(4)	0.2832(6)	0.019(1)
C5	0.4811(3)	0.4567(4)	0.2151(5)	0.014(1)
C6	0.5212(3)	0.3612(4)	0.1228(5)	0.016(1)
C7	0.6166(3)	0.3725(4)	0.1070(6)	0.021(1)
C8	0.6486(3)	0.2764(4)	0.0202(6)	0.025(1)
C9	0.5850(3)	0.1715(4)	-0.0516(6)	0.024(1)
C10	0.4915(3)	0.1664(4)	-0.0298(5)	0.018(1)
C11	-0.0058(4)	-0.2167(5)	0.0696(8)	0.039(1)
C12	0.0901(4)	-0.2052(5)	0.0776(8)	0.042(1)
C13	0.1469(4)	-0.1012(6)	0.1644(11)	0.055(2)
C14	0.1059(4)	-0.0084(5)	0.2466(8)	0.035(1)
C15	0.0076(3)	-0.0218(4)	0.2339(6)	0.019(1)
C16	-0.0444(3)	0.0717(4)	0.3103(6)	0.020(1)
C17	0.0076(3)	0.1735(4)	0.4157(6)	0.022(1)
C18	-0.0449(4)	0.2580(5)	0.4811(7)	0.034(1)
C19	-0.1461(4)	0.2370(5)	0.4420(7)	0.034(1)
C20	-0.1925(4)	0.1325(5)	0.3370(8)	0.036(1)
H(Op1)	0.861(6)	0.588(7)	0.096(10)	
H(Op2)	0.925(5)	0.461(7)	0.223(9)	
H(Op3)	0.512(5)	0.115(7)	0.323(9)	
H(Op4)	0.622(5)	0.010(7)	0.491(9)	
H(Op5)	0.701(5)	0.841(7)	0.276(9)	
H(Op6)	0.703(5)	0.803(6)	0.573(9)	
H1(Ow2)	0.801(5)	0.525(7)	0.377(9)	
H2(Ow2)	0.788(5)	0.637(7)	0.456(9)	
H(N3)	-0.114(5)	-0.141(7)	0.137(9)	
H(C1)	0.288(5)	0.483(6)	0.325(8)	
H(C2)	0.366(5)	0.680(6)	0.444(8)	
H(C3)	0.526(5)	0.736(6)	0.418(8)	
H(C4)	0.587(5)	0.592(6)	0.262(8)	
H(C7)	0.664(5)	0.449(6)	0.163(9)	
H(C8)	0.714(5)	0.281(7)	0.020(9)	
H(C9)	0.596(5)	0.111(6)	-0.108(9)	
H(C10)	0.443(5)	0.095(6)	-0.077(8)	
H(C11)	-0.052(6)	-0.302(7)	0.016(10)	
H(C12)	0.121(6)	-0.265(7)	0.016(10)	
H(C13)	0.212(6)	-0.088(8)	0.170(11)	
H(C14)	0.125(5)	0.037(7)	0.307(10)	
H(C17)	0.063(5)	0.183(6)	0.433(9)	
H(C18)	-0.013(5)	0.325(7)	0.561(10)	
H(C19)	-0.189(5)	0.288(7)	0.484(9)	
H(C20)	-0.261(5)	0.108(7)	0.305(10)	

the non-hydrogen atoms. The R -value then dropped from 0.097 to 0.078 and more reasonable B -values were obtained. Occupation numbers 0.3 and 0.5 for the hydrogen peroxide molecule and 0.7 and 0.5 for the water molecule, respectively, were also tried. These models gave slightly higher R -values and less convincing thermal parameters. In the final cycles of block-diagonal least-squares refinement the positional and anisotropic thermal parameters for the non-hydrogen atoms were refined as well as an overall scale factor and positional parameters for all hydrogen atoms except those bound to Op7, Op8 and Ow1; these could not be unambiguously identified in the difference map. The resulting R -value was 0.052. The B_{eq} 's of the carbon, nitrogen and oxygen 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:⁴ $w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1}$, with $a=20$, $c=0.015$ 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* (1974).

The highest peak in the final electron density difference synthesis was $0.50 \text{ e}/\text{\AA}^3$.

Calculations were carried out on an IBM 3033 computer, using the crystallographic programmes described in Ref. 5.

Lists of structure factors and anisotropic thermal parameters are available from R.S. on request.

RESULTS AND DISCUSSION

The positional parameters obtained for $(\text{Hbipy})[\text{VO}(\text{O}_2)_2\text{bipy}] \cdot (3+x)\text{H}_2\text{O}_2 \cdot (2-x)\text{H}_2\text{O}$, $x=0.4$, as well as U_{eq} are given in Table 1. The content of the unit cell is shown in Fig. 1, the anion in Fig. 2 and the cation in Fig. 3. Bond distances and angles are given in Table 2 and hydrogen bond distances in Table 3.

The crystals of 2,2'-bipyridinium(1+) (2,2'-bipyridine)oxodiperoxovanadate(1-)-(3+x)-hydrogen peroxide-(2-x)-water, $x=0.4$ consist of 2,2'-bipyridinium(1+) ions, (2,2'-bipyridine)-oxodiperoxovanadate(V) ions, hydrogen peroxide and water of crystallization, held together by ionic and hydrogen bond forces. One of the water molecules is partly replaced by a hydrogen peroxide molecule.

The complex is mononuclear and it thus differs from the compound $(\text{Hbipy})[\text{H}\{\text{VO}(\text{O}_2)_2\text{bipy}\}_2] \cdot x\text{H}_2\text{O}_2 \cdot (6-x)\text{H}_2\text{O}$ which crystallizes initially from the solution.² However, they both have a pentagonal bipyramidal arrangement of ligands about the vanadium atom, a configuration often met with in diperoxometallates (see Refs. and Table 3 in Ref. 6). The maximum deviation of the equatorial atoms from the pentagonal plane is 10σ (see Table 4) and might be a consequence of packing conditions and the non-rigidity of seven-coordination. The vanadium atom is displaced 0.28 \AA from the equatorial plane towards the vanadyl oxygen atom, a displacement usually encountered in this type of compound. The $\text{V}=\text{O}$, $\text{V}-\text{N}_{\text{equatorial}}$ and

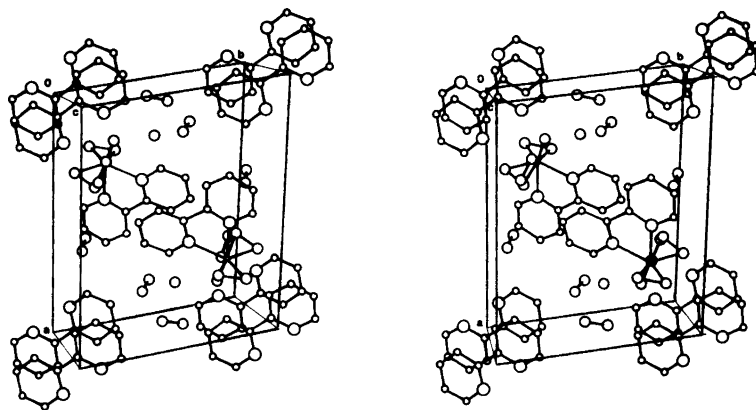


Fig. 1. Stereoscopic drawing of the unit cell.

Table 2. Bond distances and angles in $(C_{10}H_9N_2)[VO(O_2)_2(C_{10}H_8N_2)] \cdot (3+x)H_2O_2 \cdot (2-x)H_2O$, $x=0.4$ at $-100^\circ C$.

Distance/Å		Distance/Å		Distance/Å	
V-O1	1.942(3)	C2-C3	1.390(6)	Op6-H(Op6)	0.84(7)
V-O2	1.862(3)	C3-C4	1.378(6)	Ow2-H1(Ow2)	0.78(8)
V-O3	1.914(3)	C4-C5	1.392(6)	Ow2-H2(Ow2)	0.82(7)
V-O4	1.938(3)	C5-C6	1.465(6)	N3-H(N3)	0.96(7)
V-O5	1.619(3)	C6-C7	1.397(6)	C1-H(C1)	0.91(6)
V-N1	2.137(4)	C7-C8	1.382(7)	C2-H(C2)	0.92(7)
V-N2	2.284(4)	C8-C9	1.391(7)	C3-H(C3)	0.99(7)
O1-O2	1.473(4)	C9-C10	1.387(6)	C4-H(C4)	0.89(6)
O3-O4	1.474(4)	C11-C12	1.347(8)	C7-H(C7)	1.03(7)
Op1-Op2	1.458(5)	C12-C13	1.371(9)	C8-H(C8)	0.93(7)
Op3-Op4	1.470(5)	C13-C14	1.407(9)	C9-H(C9)	0.82(7)
Op5-Op6	1.475(5)	C14-C15	1.372(7)	C10-H(C10)	0.98(6)
Op7-Op8	1.468(12)	C15-C16	1.485(6)	C11-H(C11)	1.08(8)
N1-C1	1.349(6)	C16-C17	1.385(6)	C12-H(C12)	0.98(8)
N1-C5	1.363(5)	C17-C18	1.379(7)	C13-H(C13)	0.92(9)
N2-C6	1.343(5)	C18-C19	1.391(8)	C14-H(C14)	0.66(8)
N2-C10	1.349(5)	C19-C20	1.381(8)	C17-H(C17)	0.76(7)
N3-C11	1.345(7)	Op1-H(Op1)	0.93(8)	C18-H(C18)	0.94(8)
N3-C15	1.357(6)	Op2-H(Op2)	0.81(7)	C19-H(C19)	0.95(7)
N4-C16	1.343(6)	Op3-H(Op3)	0.84(7)	C20-H(C20)	0.95(8)
N4-C20	1.360(7)	Op4-H(Op4)	0.83(7)		
C1-C2	1.374(6)	Op5-H(Op5)	1.01(7)		
	Angle/°		Angle/°		
O1-V-O2	45.5(1)	C16-N4-C20	117.2(4)		
O1-V-O3	135.0(1)	N1-C1-C2	122.5(4)		
O1-V-O4	161.7(1)	C1-C2-C3	118.7(4)		
O1-V-O5	98.3(1)	C2-C3-C4	119.4(4)		
O1-V-N1	88.7(1)	C3-C4-C5	119.6(4)		
O1-V-N2	80.0(1)	C4-C5-C6	123.8(4)		
O2-V-O3	90.5(1)	N2-C6-C5	115.1(4)		
O2-V-O4	133.5(1)	N2-C6-C7	121.6(4)		
O2-V-O5	102.9(1)	C5-C6-C7	123.2(4)		
O2-V-N1	133.0(1)	C6-C7-C8	119.0(4)		
O2-V-N2	87.2(1)	C7-C8-C9	119.6(4)		
O3-V-O4	45.0(1)	C8-C9-C10	118.2(4)		
O3-V-O5	101.2(1)	N2-C10-C9	122.6(4)		
O3-V-N1	130.4(1)	N3-C11-C12	120.0(5)		
O3-V-N2	90.5(1)	C11-C12-C13	119.2(6)		
O4-V-O5	99.3(1)	C12-C13-C14	120.4(5)		
O4-V-N1	85.9(1)	C13-C14-C15	119.0(5)		
O4-V-N2	81.6(1)	N3-C15-C14	117.9(4)		
O5-V-N1	91.7(1)	N3-C15-C16	118.2(4)		
O5-V-N2	164.3(1)	C14-C15-C16	123.8(4)		
N1-V-N2	72.7(1)	N4-C16-C15	115.3(4)		
V-O1-O2	64.4(2)	N4-C16-C17	124.4(4)		
V-O2-O1	70.1(2)	C15-C16-C17	120.2(4)		
V-O3-O4	68.4(2)	C16-C17-C18	117.5(4)		
V-O4-O3	66.6(2)	C17-C18-C19	119.4(5)		
C1-N1-C5	119.0(4)	C18-C19-C20	119.5(5)		
C6-N2-C10	118.9(4)	N4-C20-C19	121.8(5)		
C11-N3-C15	123.4(4)				

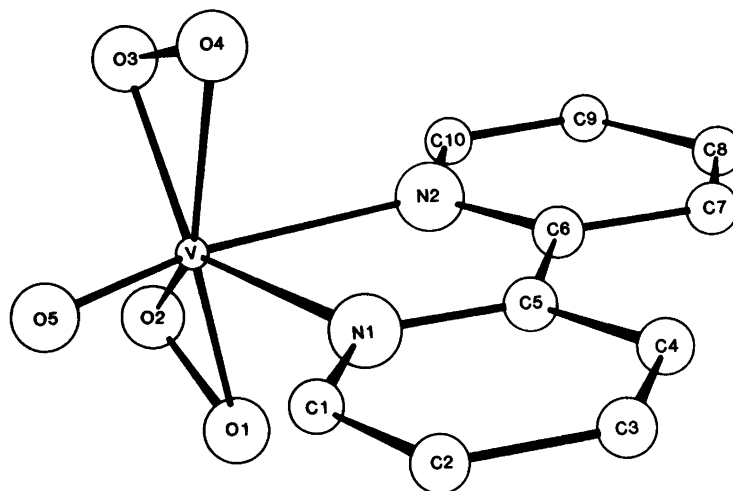


Fig. 2. The anion $[\text{VO}(\text{O}_2)_2\text{bipy}]^-$.

$\text{V}-\text{N}_{\text{apical}}$ bond distances are comparable to those observed in other peroxovanadates (see Table 3 in Ref. 6) as are the bond lengths and angles in the bipyridine ligand.^{2,6-16}

Three of four $\text{V}-\text{O}$ bonds are 0.05–0.08 Å longer than the fourth, $\text{V}-\text{O}2$. This is readily explained by the weakening of the three $\text{V}-\text{O}$ bonds as a consequence of the corresponding oxygen atoms being involved in rather strong hydrogen bonds, 2.62–2.66 Å, while O2 is not. Similar but even more pronounced elongations, 0.03–0.13 Å, of $\text{V}-\text{O}$ bonds due to hydrogen bonding were observed in $(\text{Hbipy})-[\text{H}\{\text{VO}(\text{O}_2)_2\text{bipy}\}_2 \cdot x\text{H}_2\text{O}_2 \cdot (6-x)\text{H}_2\text{O}]^2$.

The $(\text{O}-\text{O})_{\text{peroxo}}$ bond distances in the complex, 1.473–1.474 Å, are normal (see Table 3 in Ref. 6) and do not differ significantly from the $(\text{O}-\text{O})_{\text{peroxo}}$ bond distances, 1.458–1.475 Å, observed in the hydrogen peroxide molecules in this investigation.

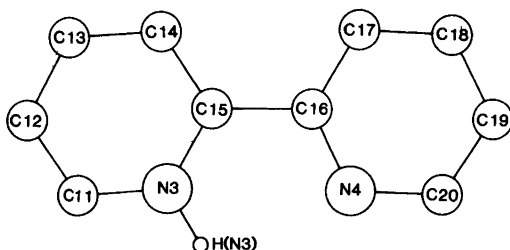


Fig. 3. The 2,2'-bipyridinium(1+) cation.

Each pyridine ring in the ligand as well as in the cation is planar within 3σ (see Table 4). The planes intersect each other at 5.4° in the ligand and at 7.1° in the cation. The two pyridine rings in the ligand thus show a more skew configura-

Table 3. Hydrogen bond distances. Ow1 and Ow2 are water oxygen atoms, Op1–Op8 hydrogen peroxide oxygen atoms and N3 and N4 2,2'-bipyridinium(1+) nitrogen atoms. The occupation number is 0.6 for Ow1, 0.4 for Op7 and Op8 and 1.0 for the other atoms.

		Distance/Å
Op1...O4	$(1-x, 1-y, \bar{z})$	2.624(5)
Op1...O5	$(1-x, 1-y, \bar{z})$	2.953(5)
Op1...Op7	$(1-x, 1-y, \bar{z})$	2.541(11)
Op1...Ow1	$(1-x, 1-y, \bar{z})$	2.917(7)
Op2...Op8	$(1+x, y, z)$	2.570(9)
Op2...Ow1	$(1+x, y, z)$	2.716(7)
Op2...Ow2	(x, y, z)	2.871(5)
Op3...O1	(x, y, z)	2.783(5)
Op4...Op5	$(x, -1+y, z)$	2.867(5)
Op5...O3	$(1-x, 1-y, \bar{z})$	2.655(5)
Op6...O1	$(1-x, 1-y, 1-z)$	2.663(5)
Op6...O5	$(1-x, 1-y, 1-z)$	2.846(5)
Op6...Ow2	(x, y, z)	2.829(5)
Op7...C12	$(x, 1+y, z)$	2.959(11)
Op8...Ow2	$(1-x, 1-y, 1-z)$	2.580(10)
Ow1...Ow2	$(1-x, 1-y, 1-z)$	2.783(7)
N3...O3	$(\bar{x}, \bar{y}, \bar{z})$	2.922(5)

Table 4. Displacements (Å) of atoms from least-squares planes in $(C_{10}H_9N_2)[VO(O_2)_2(C_{10}H_8N_2)] \cdot (3+x)H_2O_2 \cdot (2-x)H_2O$, $x=0.4$.

Defining atoms are:

Plane I O1–O4, N1 Plane III N2, C6–C10
 Plane II N1, C1–C5 Plane IV N3, C11–C15
 Plane V N4, C16–C20

Atom	Plane I	Atom	Plane II	Atom	Plane III	Atom	Plane IV	Atom	Plane V
O1	0.004(3)	N1	0.007(4)	N2	-0.005(4)	N3	-0.003(5)	N4	0.000(5)
O2	0.011(3)	C1	0.006(5)	C6	0.004(4)	C11	-0.002(6)	C16	0.004(5)
O3	-0.035(3)	C2	-0.016(5)	C7	0.002(5)	C12	-0.000(7)	C17	-0.007(5)
O4	0.036(3)	C3	0.013(5)	C8	-0.007(5)	C13	0.007(9)	C18	0.005(6)
N1	-0.016(4)	C4	0.000(5)	C9	0.006(5)	C14	-0.011(7)	C19	-0.000(6)
V	-0.284(1)	C5	-0.011(4)	C10	-0.000(4)	C15	0.009(5)	C20	-0.002(6)
N2	-1.895(4)								
O5	1.964(3)								

tion than in $[VO(O_2)(pic)(bipy)] \cdot H_2O$,⁶ $NH_4[VO(O_2)_2bipy] \cdot 4H_2O$,^{7,19} and $(Hbipy)[H\{VO(O_2)_2bipy\}_2] \cdot xH_2O_2 \cdot (6-x)H_2O$,² where the angles 2.7, 1.4 and 1.6°, respectively, were observed; this may be due to different packing conditions.

2,2'-Bipyridine itself adopts a planar *trans* configuration in a variety of solvents as shown by NMR studies.¹⁷ In strongly acidic solutions the mono- and diprotonated 2,2'-bipyridinium cations adopt skew, transoid configurations with interplanar dihedral angles of ca. 30 and 60°, respectively.¹⁸ In the present investigation the monoprotonated cation adopts the rarely observed *cis* configuration with the proton clearly associated with one of the nitrogen atoms. This seems to be due both to intrahydrogen bonding between the two nitrogen atoms and to packing conditions. As a consequence of the differences in mainly the bonding to the nitrogen atoms in the ligand and cation, respectively, the ring systems have significantly different geometries. While the two pyridine rings in the ligand are almost identical, the protonated ring differs markedly from the nonprotonated one in the cation. The most pronounced difference is that between the C–N–C angles, that of the protonated ring being 6.2(4)° larger than that of the nonprotonated one. This is accompanied by a parallel decrease of the angles at the adjacent carbon atoms; these angles are 124.4 and 121.8° in the nonprotonated ring and 117.9 and 120.0° in the protonated one, respectively.

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