

The Crystal Structure of (2,2'-Bipyridine)oxoperoxo(pyridine-2-carboxylato)vanadium(V) Hydrate, $[\text{VO}(\text{O}_2)(\text{C}_5\text{H}_4\text{NCOO})(\text{C}_{10}\text{H}_8\text{N}_2)] \cdot \text{H}_2\text{O}$, at -100°C

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The crystal structure of (2,2'-bipyridine)oxoperoxo(pyridine-2-carboxylato)vanadium(V) hydrate, $[\text{VO}(\text{O}_2)(\text{C}_5\text{H}_4\text{NCOO})(\text{C}_{10}\text{H}_8\text{N}_2)] \cdot \text{H}_2\text{O}$, has been determined at -100°C by single-crystal X-ray methods. The compound crystallizes in the monoclinic space group $P2_1/a$ with $a=14.276(6)$ Å, $b=10.697(4)$ Å, $c=11.949(4)$ Å, $\beta=66.51(3)^\circ$, and $Z=4$. Refinement by the least-squares method gave a final R -value of 0.043 for the 1198 observed, independent reflexions.

Vanadium is surrounded by a pentagonal bipyramidal arrangement of ligands, the peroxo group, the nitrogen atom and one carboxylate oxygen atom from pyridine-2-carboxylate and one nitrogen atom from 2,2'-bipyridine forming the pentagonal plane, while the vanadyl oxygen atom and the other nitrogen atom from 2,2'-bipyridine occupy the apical positions. The vanadium atom is displaced 0.27 Å from the pentagonal plane towards the vanadyl oxygen atom. Interatomic distances within the molecule are: $\text{V}-\text{O}_{\text{peroxo}}$ 1.862(5) and 1.887(5) Å, $(\text{O}-\text{O})_{\text{peroxo}}$ 1.424(7) Å, $\text{V}=\text{O}$ 1.604(5) Å, $\text{V}-\text{O}_{\text{equatorial}}$ 2.039(5) Å, $\text{V}-\text{N}_{\text{equatorial}}$ (mean) 2.127(6) Å and $\text{V}-\text{N}_{\text{apical}}$ 2.270(6) Å.

The known oxoperoxovanadates(V) can, according to Schwendt *et al.*,¹ be classified as $\text{M}_n^I[\text{VO}(\text{O}_2)_2\text{L}]$, $\text{M}_n^I[\text{VO}(\text{O}_2)_2(\text{LL}')]$, $\text{M}_n^I[\text{VO}(\text{O}_2)(\text{LL}')_2]$ and $\text{M}_n^I[\text{VO}(\text{O}_2)(\text{L})(\text{LL}'\text{L}')]_2$, where L, LL', and LL'L' are mono-, bi- and tridentate ligands, respectively. In connection with our syntheses² of $(\text{C}_{10}\text{H}_{10}\text{N}_2)[\text{VO}(\text{O}_2)_2(\text{C}_{10}\text{H}_8\text{N}_2)]_2 \cdot 6\text{H}_2\text{O}$ according to Vuletić *et al.*,³ a crystalline phase, which proved to be $[\text{VO}(\text{O}_2)-$

$(\text{C}_5\text{H}_4\text{NCOO})(\text{C}_{10}\text{H}_8\text{N}_2)] \cdot \text{H}_2\text{O}$, was once obtained. Since no pyridine-2-carboxylic acid was added to the reaction mixture, 2,2'-bipyridine, which is quite a stable molecule, had obviously been oxidized to pyridine-2-carboxylic acid by hydrogen peroxide, vanadium(V) probably acting as a catalyst. The compound is obtainable in a more straightforward way as described in the Preparation section. This new compound, abbreviated $[\text{VO}(\text{O}_2)(\text{pic})(\text{bipy})] \cdot \text{H}_2\text{O}$, can be regarded as a special case of $\text{M}_n^I[\text{VO}(\text{O}_2)(\text{LL}')_2]$ with $n=0$ and two different bidentate ligands. Its crystal structure is reported in this paper.

EXPERIMENTAL

Preparation 0.62 g (0.0050 mol) pyridine-2-carboxylic acid was dissolved in 10 ml 2–3 % hydrogen peroxide. 0.48 g (0.0025 mol) vanadium pentoxide was added in small portions while the reaction mixture was kept at about 5°C . To the dark red solution 0.78 g (0.0050 mol) 2,2'-bipyridine, dissolved in 10 ml ethanol, was added. The resulting solution was allowed to crystallize in a refrigerator. Dark red crystals were developed within half an hour.

Data collection. X-Ray reflexion intensities from a crystal of the dimensions $0.09 \times 0.09 \times 0.18$ mm were measured at -100°C with a SYNTeX $P2_1$ automatic four-circle single-crystal X-ray diffractometer using graphite-monochromatized $\text{MoK}\alpha$ radiation. The temperature was kept at -100°C with a SYNTeX LT1 low-temperature device. The θ – 2θ scan method was used and the 2θ scan speed was allowed to vary between 2 and

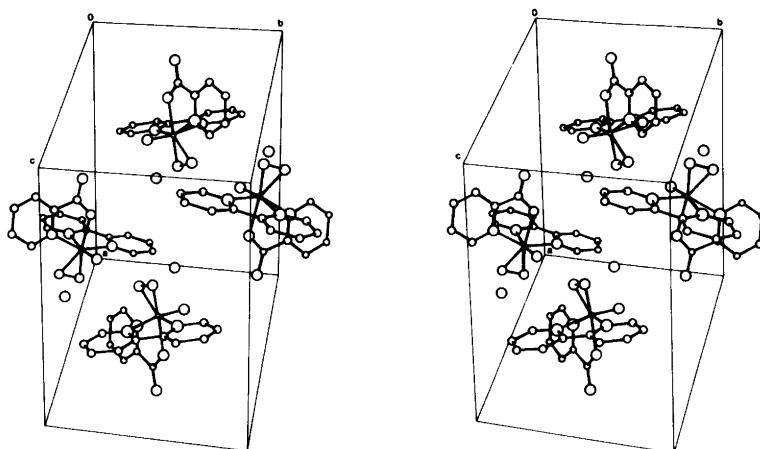


Fig. 1. Stereoscopic drawing of the unit cell of $[\text{VO}(\text{O}_2)(\text{pic})(\text{bipy})] \cdot \text{H}_2\text{O}$.

12°min^{-1} depending on the intensity of the measured reflexion. Data were collected for $2\theta \leq 55^\circ$. A profile analysis based on the Lehmann-Larsen method⁴ 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 data collection.

Of the 2197 independent reflexions, 1198 with $I_o > 3\sigma(I_o)$ 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 by a least-squares fit of refined diffractometer setting angles for eight reflexions.

CRYSTAL DATA

$\text{C}_{16}\text{H}_{14}\text{N}_3\text{O}_6\text{V}$; F.W. = 395.25

Space group $P2_1/a$ (No. 14; non-standard setting) $a = 14.276(6) \text{ \AA}$, $b = 10.697(4) \text{ \AA}$, $c = 11.949(4) \text{ \AA}$, $\beta = 66.51(3)^\circ$, $Z = 4$, $D_c = 1.57 \text{ g cm}^{-3}$, $\mu(\text{MoK}\alpha) = 0.67 \text{ mm}^{-1}$.

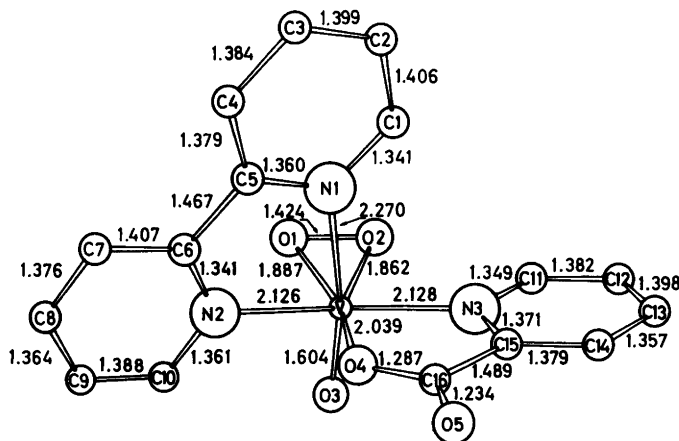


Table 1. Atomic fractional coordinates for [VO(O₂) (C₅H₄NCOO) (C₁₀H₈N₂)] · H₂O. Space group $P2_1/a$. $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cos \alpha_{ij}$.

Atom	x	y	z	$U_{eq}/\text{\AA}^2$ ($U_{iso}/\text{\AA}^2$ for H)
V	0.2609(1)	0.4960(1)	0.3078(1)	0.027(1)
O1	0.3988(3)	0.5169(5)	0.2837(4)	0.036(2)
O2	0.3321(4)	0.6048(5)	0.3672(5)	0.040(3)
O3	0.2263(4)	0.3872(5)	0.4086(4)	0.037(2)
O4	0.1483(4)	0.4585(4)	0.2482(5)	0.034(3)
O5	-0.0093(4)	0.4979(5)	0.2620(4)	0.044(2)
O6	0.2247(4)	0.4880(6)	0.6525(5)	0.062(3)
N1	0.3110(4)	0.6122(5)	0.1348(5)	0.030(3)
N2	0.3335(4)	0.3700(5)	0.1610(5)	0.029(3)
N3	0.1446(4)	0.6281(5)	0.4018(5)	0.031(3)
C1	0.2983(6)	0.7358(7)	0.1279(8)	0.041(4)
C2	0.3318(5)	0.7997(7)	0.0159(8)	0.045(4)
C3	0.3775(6)	0.7315(8)	-0.0923(8)	0.050(4)
C4	0.3904(6)	0.6045(8)	-0.0821(7)	0.045(4)
C5	0.3580(5)	0.5461(7)	0.0300(7)	0.032(3)
C6	0.3723(5)	0.4124(6)	0.0458(6)	0.028(3)
C7	0.4231(5)	0.3311(8)	-0.0524(6)	0.037(4)
C8	0.4300(6)	0.2063(8)	-0.0287(7)	0.044(4)
C9	0.3880(6)	0.1636(7)	0.0885(7)	0.040(4)
C10	0.3400(6)	0.2464(6)	0.1837(7)	0.036(4)
C11	0.1462(6)	0.7167(7)	0.4814(7)	0.040(4)
C12	0.0682(6)	0.8019(8)	0.5342(7)	0.043(4)
C13	-0.0161(6)	0.7953(7)	0.5026(8)	0.045(4)
C14	-0.0203(5)	0.7055(7)	0.4244(7)	0.035(4)
C15	0.0594(5)	0.6222(6)	0.3758(6)	0.028(3)
C16	0.0639(5)	0.5200(6)	0.2892(6)	0.029(3)
H1	0.269(5)	0.783(6)	0.216(6)	0.016
H2	0.322(5)	0.901(6)	0.006(6)	0.018
H3	0.401(5)	0.780(7)	-0.185(6)	0.020
H4	0.426(5)	0.564(6)	-0.140(6)	0.018
H7	0.449(5)	0.365(6)	-0.130(6)	0.015
H8	0.466(5)	0.157(6)	-0.098(6)	0.018
H9	0.394(5)	0.077(6)	0.104(6)	0.016
H10	0.309(5)	0.233(6)	0.270(6)	0.015
H11	0.207(5)	0.717(6)	0.490(6)	0.016
H12	0.074(5)	0.867(6)	0.585(6)	0.018
H13	-0.074(5)	0.846(6)	0.544(6)	0.018
H14	-0.071(5)	0.699(6)	0.393(6)	0.014

STRUCTURE DETERMINATION

The positions of the non-hydrogen atoms were obtained from Fourier-maps based on phases determined by the multi-solution programme MULTAN.⁵ Block-diagonal and, ultimately, full-matrix least-squares refinement of the positional and anisotropic thermal parameters and a scale factor yielded $R=0.058$ ($R=\Sigma ||F_o|-|F_c||/\Sigma |F_o|$). Introduction of hydrogen atoms, except those

belonging to the water molecule, reduced R to 0.043. The B_{eq} value of the corresponding carbon atom was used as B_{iso} for the hydrogen atoms. The weighting scheme used was that of Cruickshank:⁶ $w=(a+|F_o|+c|F_o|^2+d|F_o|^3)^{-1}$ with $a=50.0$, $c=0.005$, and $d=0.0$. The scattering factors were taken from the *International Tables for X-Ray Crystallography*, Vol. IV (1974).

Table 2. Bond angles in $[\text{VO}(\text{O}_2)(\text{C}_5\text{H}_4\text{NCOO})(\text{C}_{10}\text{H}_8\text{N}_2)] \cdot \text{H}_2\text{O}$.

	Angle/ $^\circ$
O1–V–O2	44.7(2)
O2–V–N3	79.2(2)
N3–V–O4	76.0(2)
O4–V–N2	77.3(2)
N2–V–O1	79.2(2)
O3–V–N1	166.4(2)
N1–V–N2	73.9(2)
V–O1–O2	66.8(3)
V–O2–O1	68.6(3)
C5–N1–C1	119.1(6)
N1–C1–C2	122.3(7)
C1–C2–C3	118.9(7)
C2–C3–C4	117.4(8)
C3–C4–C5	121.7(8)
C4–C5–N1	120.6(7)
C4–C5–C6	123.8(7)
N1–C5–C6	115.5(6)
C5–C6–N2	116.1(6)
C5–C6–C7	123.1(7)
N2–C6–C7	120.7(6)
C6–C7–C8	118.9(7)
C7–C8–C9	119.9(7)
C8–C9–C10	119.9(7)
C9–C10–N2	120.5(7)
C10–N2–C6	120.0(6)
C15–N3–C11	117.3(6)
N3–C11–C12	123.2(7)
C11–C12–C13	117.9(7)
C12–C13–C14	120.0(7)
C13–C14–C15	119.4(7)
C14–C15–N3	122.2(6)
C14–C15–C16	124.5(6)
N3–C15–C16	113.3(6)
C15–C16–O4	114.4(6)
C15–C16–O5	121.2(6)
O4–C16–O5	124.4(6)

A difference synthesis calculated after the final cycle of refinement showed a maximum electron density of $0.7 \text{ e } \text{\AA}^{-3}$.

Calculations were carried out on an IBM 3033 computer using the crystallographic programmes described in Ref. 7.

Lists of the structure factors and thermal parameters are available from R.S. upon request.

RESULTS AND DISCUSSION

The positional parameters obtained for $[\text{VO}(\text{O}_2)(\text{pic})(\text{bipy})] \cdot \text{H}_2\text{O}$ in the final refine-

ment cycle, as well as U_{eq} (or U_{iso}), are given in Table 1. The content of the unit cell is shown in Fig. 1. Bond distances are given in Fig. 2 and bond angles in Table 2.

The crystals of $[\text{VO}(\text{O}_2)(\text{pic})(\text{bipy})] \cdot \text{H}_2\text{O}$ consist of (2,2'-bipyridine)oxoperoxo(pyridine-2-carboxylato)vanadium(V) molecules and water of crystallization, held together by van der Waals and weak hydrogen bond forces.

The water molecule is hydrogen bonded to one carboxylate oxygen atom, O5($\bar{x}, 1-y, 1-z$) with the bond distance 2.832(7) \AA .

As shown in Fig. 2, the molecule $[\text{VO}(\text{O}_2)(\text{pic})(\text{bipy})]$ has a pentagonal bipyramidal arrangement of ligands with normal V=O, V–O_{peroxo}, V–N_{equatorial} and V–N_{apical} bond distances (see, e.g., Refs. 8–23 and Table 3). Within the limits of experimental error the atoms defining the equatorial plane all lie in this plane, the maximum deviation being 2.7 σ . The vanadium atom is displaced 0.27 \AA from this plane towards the vanadyl oxygen atom. Such a displacement is usually observed for transition metal peroxo compounds. When the apical atoms are different, or one is missing, this displacement is in the range 0.2–0.5 \AA , the higher value being observed for pentagonal pyramidal complexes like $[\text{VO}(\text{O}_2)_2\text{NH}_3]^-$ and $[\text{CrO}(\text{O}_2)_2\text{py}]$, while 0.3 \AA is commonly encountered in pentagonal bipyramidal compounds (see, e.g., Table 6 in Ref. 10 and Refs. 11, 12 and 20).

The (O–O)_{peroxo} bond length 1.424(7) \AA is rather short but is comparable with 1.411(2) \AA reported for $\text{NH}_4[\text{VO}(\text{O}_2)(\text{H}_2\text{O})\text{dipic}] \cdot x\text{H}_2\text{O}$,¹¹ and 1.419(6) \AA for $[\text{Ti}(\text{O}_2)(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{OPN}_3\text{C}_6\text{H}_{18})]$.¹⁰

Each pyridine ring in the bipyridine ligand is planar within 1.7 σ , and the planes intersect each other at 2.7°. Bond distances and angles within the bipyridine group are in good agreement with data previously reported.²²

In the pyridine-2-carboxylate ligand the pyridine ring and the carboxylate carbon atom are coplanar within 1.5 σ . The dihedral angle between the carboxylate group and the pyridine ring is 4.5°. Bond distances and angles within the pyridine-2-carboxylate ligand show no significant deviations from those previously reported (see Table 4). As is usually observed, one carbon–oxygen bond distance is significantly longer than the other, the corresponding oxygen atom being involved in another bond (to a metal

Table 3. Comparison between distances (Å) found in peroxovanadates (V). L_{equatorial} = equatorial ligands other than O_{peroxo}, L_{apical} = apical ligands other than vanadyl oxygen atom.

Compound	V=O	V—O _{peroxo}	(O—O) _{peroxo}	V—L _{equatorial}	V—L _{apical}	Displacement of V from the pentagonal plane	Ref.
(NH ₄) ₄ [O(VO(O ₂) ₂) ₂]	1.601(3) 1.613(3)	1.896(3) 1.884(3) 1.914(3) 1.875(3) 1.895(3) 1.882(3) 1.912(3) 1.878(3)	1.469(4) 1.465(3) 1.474(4) 1.463(4)	2.013(2) 1.994(2)	2.522(3) 2.480(2)	0.45 0.44	10, 31
NH ₄ [VO(O ₂) ₂ (NH ₃)]	1.599(3)	1.871(3) 1.872(3)	1.463(4)	2.098(4)	—	0.46	20
NH ₄ [VO(O ₂)(H ₂ O)dipic] · xH ₂ O	1.579(2)	1.870(2) 1.872(2)	1.441(3)	2.053(2) 2.064(2) 2.088(2) 2.060(4)	2.211(2)	0.25	11
K ₃ [VO(O ₂) ₂ ox] · H ₂ O	1.622(4)	1.934(4) 1.866(4) 1.856(4) 1.911(4) 1.911(3) 1.883(3) 1.909(3) 1.880(3) 1.887(5) 1.862(5)	1.460(6) 1.451(6)	2.149(4)	2.288(3)	0.28	12
NH ₄ [VO(O ₂) ₂ bipy] · 4H ₂ O	1.619(3)		1.471(4) 1.465(4)			0.32	13
[VO(O ₂)(pic)(bipy)] · H ₂ O	1.604(5)		1.424(7)	2.126(6) 2.128(6) 2.039(5) 2.154(3)	2.270(6)	0.27	This paper
(Hbipy)[H{VO(O ₂) ₂ bipy} ₂] · xH ₂ O ₂ · (6-x)H ₂ O	1.612(2)	1.869(2) 1.892(2) 1.903(2) 1.995(2) ^a	1.471(3) 1.461(3)	2.290(2)		0.31	2
(Hbipy)[VO(O ₂) ₂ bipy] · (3+x)H ₂ O ₂ · (2-x)H ₂ O	1.619(3)	1.942(3) 1.862(3) 1.914(3) 1.938(3)	1.473(4) 1.474(4)	2.137(4)	2.284(4)	0.28	30

^a Attached to a hydrogen atom.

Table 4. Comparison between the carbon-oxygen bond lengths (Å) in the carboxylate group, O(1)-C-O(2), in a number of picolines (C₅H₄NCOO⁻=pic). O(2) is coordinated to a metal atom or a hydrogen atom.

Compound	C-O(1)	C-O(2)	Ref.
Hpic	1.214(3)	1.285(3)	24
Cu(pic) ₂ · KSCN	1.226(9)	1.266(9)	25
Ni(pic) ₂ · 4H ₂ O	1.245(8)	1.273(8)	26
Cu(pic) ₂ · 2H ₂ O	1.234(2)	1.276(2)	27
[Fe(pic) ₂ Cl(H ₂ O)]	1.246(3)	1.286(3)	28
H[MoO(O ₂) ₂ pic] · 2Hpic · H ₂ O	1.226(3)	1.295(3)	17
	1.198(3)	1.292(3)	
	1.227(4)	1.252(3)	
[H ₂ pic] ₄ [Mo(CN) ₈]	1.184(8)	1.290(7)	29
	1.200(8)	1.303(7)	
Ti(O ₂)(pic)HMPT	1.212(4)	1.286(4)	9
[VO(O ₂)(pic)(bipy)] · H ₂ O	1.234(8)	1.287(8)	This paper

atom or hydrogen).

Electron density maps based on single crystal data collected for a second crystal, prepared at higher hydrogen peroxide concentration, showed that some of the water of crystallization can be replaced by hydrogen peroxide. This has also been observed for two other products obtained in the system V₂O₅-H₂O₂-bipy-H₂O, and their structures will be published shortly.^{2,30}

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