Crystal structure of ammonium oxo(peroxo)(pyridine-2,6-dicarboxylato-*N*,*O*,*O′*)aquavanadate(V), $(NH_4)[VO(O_2)(H_2O)(C_7H_3NO_4)]$

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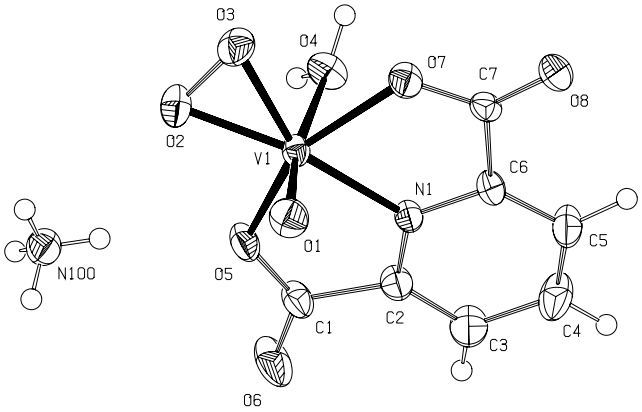

Abstract

$C_7H_9N_2O_8V$, orthorhombic, *Pcca* (No. 54), a = 13.575(4) Å, b = 20.603(6) Å, c = 8.026(3) Å, V = 2244.8 Å^3, Z = 8, $R_{gt}(F)$ = 0.046, $wR_{ref}(F^2)$ = 0.155, T = 293 K.

Source of material

Dark red crystals suitable for X-ray diffraction analysis were obtained by keeping at 253 K a 1:1:1 (molar ratio) mixture of ammonium vanadate, NH_4VO_3, pyridine-2,6-dicarboxylic acid, $C_7H_5NO_4$, and hydrogen peroxide in a water-ethanol mixture.

Discussion

In the frame of research aimed at developing new synthetic procedures of oxide materials, the so-called chelate method, which consists in the thermal decomposition of solid metal precursors obtained from a solution of the complexed metals, was shown to be an appropriate way to get multimetallic oxides [1,2]. During investigations to identify new water-soluble vanadium compounds that could be used as precursors for V-based oxides, the title compound was isolated. The structure of the analogous hydrate derivative, $(NH_4)[VO(O_2)(H_2O)(C_7H_3NO_4)] \cdot xH_2O$ (x ~ 1.3) was reported by Drew et al. from Weissenberg films data [3].

In our analysis, we do not observed any water molecule in the unit cell and the structure of the $[VO(O_2)(H_2O)(C_7H_3NO_4)]^-$ anion is similar to that reported in [3] but with a more precise geometry. The vanadium coordination polyhedron is a pentagonal bipyramid with the peroxo and dipicolinato ligands being bidentate and tridentate, respectively. The coordination of vanadium by the pyridine-2,6-dicarboxylato ligand leads to the formation of two five-membered chelate rings. The axial positions are occupied by a terminal oxo ligand [d(V—O1) = 1.588(3) Å] and one water molecule [d(V—O4) = 2.235(3) Å]. The nitrogen atom from the pyridine ring [d(V—N) = 2.080(3) Å] and the oxygen atoms belonging either to the asymmetrically bound peroxo ligand [d(V—O) = 1.869(2) Å, 1.892(3) Å, d(O—O) = 1.437(4) Å] or to the two deprotonated carboxylato groups [$\bar{d}$(V—O) = 2.044(3) Å] occupy the equatorial positions and form an approximate pentagonal plane. The axial oxygen atom O4 from the water molecule, trans to the vanadyl V=O bond, lies at a significantly longer distance from the vanadium atom (2.235(3) Å) and is thus less tightly bound than the other oxygen atoms in the anion. This phenomenon illustrates the important trans influence of the oxo ligand on the structural parameters. The coordination polyhedron and the bond distances obtained for the title compound are in good agreement with those observed in the hydrated complex, $(NH_4)[VO(O_2)(H_2O)(C_7H_3NO_4)] \cdot xH_2O$ (x ~ 1.3) [3]. Moreover, the O—O distance in the peroxo group is 1.437(4) Å, which does not differ significantly from the values found in the peroxide ion (1.49 Å) and in other peroxo vanadate(V) complexes [4,5]. All the hydrogen atoms of the coordinated water molecule and of the ammonium cation are involved in hydrogen bonds with the oxygen atoms from the ligands, the distances O···O or N···O ranging from 2.66 to 3.07 Å.

Table 1. Data collection and handling.

Crystal:	dark red parallelepiped, size 0.30 × 0.30 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	9.21 cm^{-1}
Diffractometer, scan mode:	MAR345, 70 images, $\Delta\phi$ = 3°
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	23896, 2578
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2298
$N(param)_{refined}$:	192
Programs:	SHELX-97 [6], PLATON [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3)	8*f*	0.752(5)	0.660(3)	–0.008(8)	0.059(7)
H(4)	8*f*	0.803(5)	0.554(3)	–0.006(8)	0.059
H(5)	8*f*	0.694(5)	0.472(3)	0.113(8)	0.059
H(4A)	8*f*	0.521(5)	0.605(3)	0.554(9)	0.059
H(4B)	8*f*	0.548(5)	0.666(3)	0.504(8)	0.059
H(101)	8*f*	0.693(6)	0.313(3)	0.222(9)	0.059
H(102)	8*f*	0.655(5)	0.337(3)	0.36(1)	0.059
H(103)	8*f*	0.607(5)	0.291(4)	0.265(8)	0.059
H(104)	8*f*	0.616(5)	0.359(4)	0.221(9)	0.059

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V(1)	8*f*	0.42410(5)	0.62661(3)	0.25227(9)	0.0161(4)	0.0192(4)	0.0255(4)	0.0008(2)	–0.0002(2)	0.0001(3)
O(1)	8*f*	0.3680(2)	0.6197(2)	0.0796(4)	0.031(2)	0.038(2)	0.033(2)	0.001(1)	–0.006(1)	0.000(1)
O(2)	8*f*	0.3407(2)	0.6848(2)	0.3680(4)	0.029(2)	0.031(2)	0.042(2)	0.008(1)	0.002(1)	–0.004(1)
O(3)	8*f*	0.3226(2)	0.6179(2)	0.4081(4)	0.025(2)	0.034(2)	0.040(2)	–0.002(1)	0.008(1)	0.001(1)
O(4)	8*f*	0.5266(3)	0.6309(2)	0.4699(4)	0.034(2)	0.026(2)	0.031(2)	–0.006(1)	–0.007(1)	0.002(1)
N(1)	8*f*	0.5593(2)	0.5995(2)	0.1521(4)	0.018(2)	0.018(2)	0.027(2)	0.001(1)	0.001(1)	0.002(1)
C(2)	8*f*	0.6186(3)	0.6449(2)	0.0926(6)	0.022(2)	0.023(2)	0.035(2)	–0.000(2)	0.003(2)	0.004(2)
C(3)	8*f*	0.7104(4)	0.6299(2)	0.0305(7)	0.029(2)	0.028(2)	0.053(3)	–0.004(2)	0.011(2)	0.004(2)
C(4)	8*f*	0.7400(4)	0.5652(2)	0.0353(8)	0.025(2)	0.036(2)	0.061(3)	0.002(2)	0.013(2)	–0.006(2)
C(5)	8*f*	0.6770(3)	0.5182(2)	0.0989(6)	0.031(2)	0.024(2)	0.044(3)	0.006(2)	0.005(2)	–0.003(2)
C(6)	8*f*	0.5863(3)	0.5378(2)	0.1567(5)	0.025(2)	0.017(2)	0.028(2)	0.001(2)	–0.003(2)	–0.001(2)
C(1)	8*f*	0.5747(3)	0.7115(2)	0.1099(6)	0.023(2)	0.021(2)	0.043(3)	0.001(2)	0.002(2)	0.008(2)
O(5)	8*f*	0.4919(2)	0.7119(1)	0.1890(4)	0.027(2)	0.018(1)	0.045(2)	0.003(1)	0.004(1)	0.007(1)
O(6)	8*f*	0.6162(3)	0.7588(2)	0.0533(6)	0.035(2)	0.023(2)	0.091(3)	–0.001(1)	0.013(2)	0.021(2)
C(7)	8*f*	0.5085(3)	0.4971(2)	0.2416(5)	0.029(2)	0.016(2)	0.020(2)	–0.002(2)	–0.002(2)	0.000(1)
O(7)	8*f*	0.4361(2)	0.5295(1)	0.2973(4)	0.028(2)	0.020(1)	0.036(2)	–0.004(1)	0.005(1)	0.001(1)
O(8)	8*f*	0.5188(3)	0.4377(2)	0.2525(4)	0.050(2)	0.017(1)	0.041(2)	0.002(1)	0.010(2)	0.004(1)
N(100)	8*f*	0.6414(3)	0.3244(2)	0.2620(6)	0.031(2)	0.025(2)	0.035(2)	0.002(2)	0.005(2)	0.001(2)

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