Crystal structure of ethylenediammonium bis[(2-oxo-1-naphthaldehyde-isonicotinyl hydrazonato-*O,N,O'*)dioxovanadate(V)], $(CH_2NH_3)_2[(C_{16}H_{11}N_3O_2)VO_2]_2$

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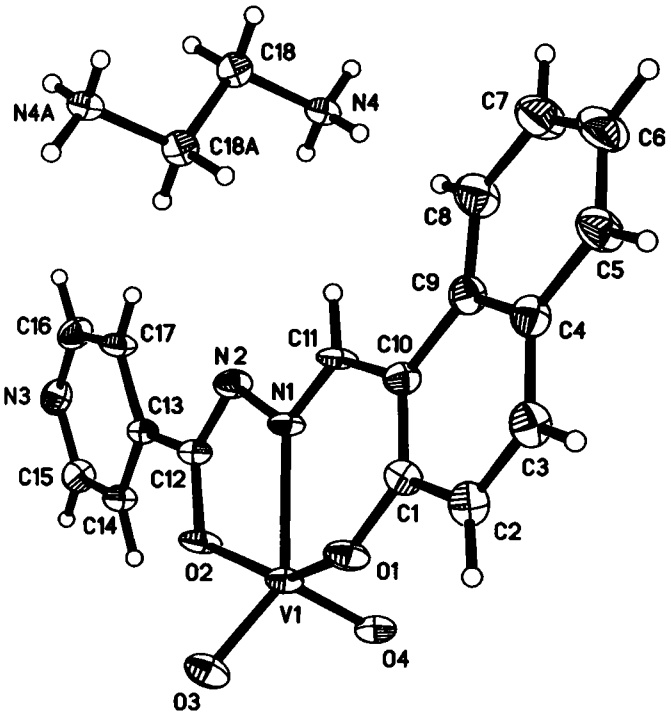

Abstract

$C_{36}H_{32}N_8O_8V_2$, monoclinic, $P12_1/c1$ (no. 14), $a = 16.879(2)$ Å, $b = 6.5076(7)$ Å, $c = 16.893(2)$ Å, $\beta = 111.259(1)°$, $V = 1729.3$ Å^3, $Z = 2$, $R_{gt}(F) = 0.041$, $wR_{ref}(F^2) = 0.115$, $T = 293$ K.

Source of material

The ligand 2-hydroxy-1-naphthaldehyde isonicotinyl hydrazone was prepared according to [1]. 0.13 g $VO(acac)_2$ was dissolved in 10.0 ml CH_3OH, and was added dropwise to an methanol solution of 0.15 g 2-hydroxy-1-naphthaldehyde isonicotinyl hydrazone under continuous stirring. The reaction lasted for 2 hours, and a mixture of 5.5 ml CH_3OH and 5.5 ml ethylenediamine was added. After filtration, the brownish filtrate was layered with Et_2O, allowed to stand at room temperature. Brown plate-like crystals suitable for X-ray diffraction were obtained after 3 days. Vanadium(IV) was oxidized to vanadium(V) by atmospheric oxygen.

Experimental details

The very small N_{gt}/N_{param} ratio is caused by the low quality of the crystals.

Discussion

Vanadium plays an important role in biological systems and some of the vanadium complexes with organic ligands might be candidates for therapy of diabetes. Consequently, design and synthesis of the new complexes have been of great interest recently [2,3].

In the title complex, the coordinating ligand atoms, a monoanionic ONO donor, and the two oxo-oxygen atoms form a trigonal bipyramid around the metal center V1. The imine nitrogen atom N1, the two oxygen atoms O3 and O4 as well as the metal center constitute the equatorial plane, and the axial positions are occupied by the phenolate and enolate oxygen atoms O1 and O2 of the ligand with O1–V1–O2 bond angle of 151.2(1)°. The bond angles O3–V1–O4 (108.0(1)°) and O4–V1–N1 (113.1(1)°) suggest considerable distortion from the ideal coordination polyhedron. The bond lengths between V and the coordinated O atoms of the ligand, d(V1—O1) = 1.899(2) Å and d(V1—O2) = 1.972(2) Å, are in accord with V—O single bonds, while the bond lengths d(V1=O3) = 1.637(2) Å) and d(V1=O4) = 1.622(2) Å are characteristic for double bonds. The V=O (O3 and O4) as well as the V1—N1 and V—O (O1 and O2) bond lengths are within the expected range for *cis*-dioxovanadium complexes. The open angles O3–V1–O1 and O3–V1–O2 amount to 97.4(1)° and 93.0(1)°, respectively, while the bite angles of O2–V1–N1 and O1–V1–N1 are 73.5(1)° and 81.1(2)°, respectively. The anionic nature of the complex and, therefore, the presence of the iminolate form of the ligand is consistent with the observed V1—O2, N2—C12 and O2—C12 bond lengths of 1.972 Å, 1.289(4) Å and 1.311(4) Å [4], respectively. The protonated ethylenediamine cation forms intermolecular hydrogen bonds with the oxo group oxygen O4 (symmetry code: $x,-y+½,z-½$) (N4···O4, 2.760 Å, 159.6°), O3 (symmetry code: $-x+1,y+½,z+½$) (N4···O3, 2.786 Å, 164.2°) and the nitrogen atom N3 of the pyridine (symmetry code: $x,y-1,z$) (N4···N3, 2.863 Å, 168.8°) linking the three neighboring molecules.

Table 1. Data collection and handling.

Crystal:	brown fragment, size 0.24 × 0.18 × 0.16 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.07 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5652, 2039
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1398
$N(param)_{refined}$:	244
Programs:	SHELXS-97 [5], SHELXL-97 [6]

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

Atom	Site	x	y	z	U_{iso}
H(2)	4e	0.2169	−0.5719	0.3669	0.047
H(3)	4e	0.0972	−0.7488	0.2917	0.050
H(5)	4e	−0.0381	−0.7757	0.1695	0.061
H(6)	4e	−0.1340	−0.6443	0.0464	0.078
H(7)	4e	−0.1085	−0.3294	−0.0030	0.079
H(8)	4e	0.0139	−0.1554	0.0635	0.066
H(11)	4e	0.1364	−0.0372	0.1173	0.040
H(14)	4e	0.4232	0.5969	0.2832	0.041
H(15)	4e	0.4548	0.8915	0.2278	0.049
H(16)	4e	0.3019	0.7481	0.0021	0.054
H(17)	4e	0.2616	0.4519	0.0504	0.046
H(4A)	4e	0.3890	0.2715	−0.0004	0.060
H(4B)	4e	0.4182	0.1065	0.0609	0.050
H(4C)	4e	0.4694	0.2706	0.0575	0.050
H(18A)	4e	0.4793	0.1528	−0.0635	0.043
H(18B)	4e	0.4175	−0.0259	−0.0612	0.043

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)	4e	0.32860(4)	0.00578(8)	0.33601(4)	0.0309(4)	0.0239(3)	0.0248(4)	0.0014(3)	0.0004(3)	0.0019(2)
O(1)	4e	0.2761(2)	−0.2557(4)	0.3272(2)	0.037(2)	0.027(1)	0.034(2)	−0.001(1)	−0.003(1)	0.006(1)
O(2)	4e	0.3629(2)	0.2450(4)	0.2843(2)	0.035(1)	0.035(1)	0.026(1)	−0.010(1)	−0.008(1)	0.004(1)
O(3)	4e	0.4269(2)	−0.0700(4)	0.3844(2)	0.036(2)	0.033(1)	0.049(2)	0.003(1)	0.001(2)	0.004(1)
O(4)	4e	0.2980(2)	0.1201(4)	0.4053(2)	0.041(2)	0.036(2)	0.028(1)	0.004(1)	0.002(1)	0.003(1)
N(1)	4e	0.2392(2)	0.0297(4)	0.2105(2)	0.030(2)	0.026(2)	0.021(2)	−0.003(1)	−0.002(1)	0.004(1)
N(2)	4e	0.2484(2)	0.1966(4)	0.1609(2)	0.040(2)	0.031(2)	0.029(2)	−0.007(1)	0.004(2)	0.006(1)
N(3)	4e	0.3815(2)	0.8517(4)	0.1099(2)	0.050(2)	0.033(2)	0.048(2)	−0.007(2)	0.027(2)	0.003(2)
C(1)	4e	0.2015(2)	−0.3373(5)	0.2814(2)	0.033(2)	0.022(2)	0.038(2)	0.001(2)	0.009(2)	−0.003(2)
C(2)	4e	0.1808(3)	−0.5220(5)	0.3147(3)	0.044(2)	0.024(2)	0.052(3)	0.007(2)	0.021(2)	0.010(2)
C(3)	4e	0.1088(3)	−0.6249(5)	0.2706(3)	0.045(2)	0.028(2)	0.054(3)	−0.002(2)	0.021(2)	0.006(2)
C(4)	4e	0.0505(3)	−0.5478(6)	0.1930(3)	0.043(2)	0.033(2)	0.045(3)	−0.007(2)	0.018(2)	−0.004(2)
C(5)	4e	−0.0266(3)	−0.6516(6)	0.1486(3)	0.043(2)	0.045(3)	0.058(3)	−0.016(2)	0.010(2)	0.001(2)
C(6)	4e	−0.0842(3)	−0.5728(8)	0.0758(4)	0.049(3)	0.071(3)	0.064(4)	−0.030(3)	0.006(3)	−0.004(3)
C(7)	4e	−0.0681(3)	−0.3848(8)	0.0457(3)	0.049(3)	0.072(4)	0.062(3)	−0.017(3)	0.004(3)	0.018(3)
C(8)	4e	0.0048(3)	−0.2804(7)	0.0855(3)	0.050(3)	0.050(3)	0.059(3)	−0.014(2)	0.013(3)	0.011(2)
C(9)	4e	0.0671(3)	−0.3581(5)	0.1598(3)	0.041(2)	0.034(2)	0.042(2)	−0.007(2)	0.017(2)	0.002(2)
C(10)	4e	0.1470(2)	−0.2560(5)	0.2058(2)	0.036(2)	0.028(2)	0.031(2)	−0.005(2)	0.009(2)	−0.001(2)
C(11)	4e	0.1713(2)	−0.0789(6)	0.1714(2)	0.031(2)	0.035(2)	0.020(2)	−0.004(2)	−0.008(2)	0.003(2)
C(12)	4e	0.3144(2)	0.2989(5)	0.2072(2)	0.031(2)	0.029(2)	0.024(2)	0.001(2)	0.003(2)	−0.001(2)
C(13)	4e	0.3379(2)	0.4883(5)	0.1729(2)	0.028(2)	0.031(2)	0.024(2)	0.000(2)	0.005(2)	−0.000(1)
C(14)	4e	0.3968(2)	0.6247(5)	0.2256(2)	0.035(2)	0.033(2)	0.028(2)	−0.003(2)	0.004(2)	0.001(2)
C(15)	4e	0.4156(3)	0.8013(6)	0.1914(3)	0.046(2)	0.033(2)	0.044(2)	−0.011(2)	0.017(2)	−0.004(2)
C(16)	4e	0.3259(3)	0.7182(7)	0.0598(3)	0.056(3)	0.046(2)	0.034(2)	−0.005(2)	0.018(2)	0.007(2)
C(17)	4e	0.3017(3)	0.5381(6)	0.0881(3)	0.036(2)	0.043(2)	0.025(2)	−0.010(2)	−0.002(2)	−0.001(2)
N(4)	4e	0.4317(2)	0.1887(5)	0.0297(2)	0.030(2)	0.031(2)	0.029(2)	−0.004(2)	0.003(2)	0.002(1)
C(18)	4e	0.4627(2)	0.0634(5)	−0.0262(2)	0.040(2)	0.030(2)	0.038(2)	0.001(2)	0.014(2)	0.006(2)

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