Crystal structure of 2-aminoethylammonium (2-oxyacetophenone benzoylhydrazonato)dioxovanadate(V), $[H_2N(CH_2)_2NH_3][VO_2(C_{15}H_{12}N_2O_3)]$

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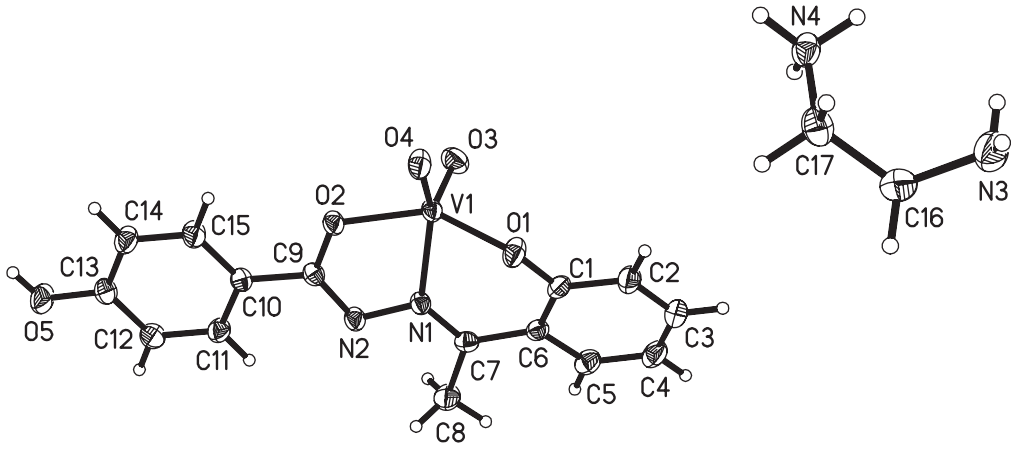

Abstract

$C_{17}H_{21}N_4O_5V$, monoclinic, $P12_1/c1$ (no. 14), a = 12.088(2) Å, b = 6.900(1) Å, c = 22.655(4) Å, β = 92.964(3)°, V = 1887.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.105, T = 294 K.

Source of material

The ligand 2-hydroxyacetophenone 4-hydroxybenzoic acid hydrazone (*L*) was prepared according to [1]. Ammonium metavanadate (0.12 g, 1 mmol) was added to the solution of H_2L (0.27 g, 1 mmol) dissolved in methanol and DMSO with stirring, followed by the addition of little amount of ethylenediamine. The reaction mixture was stirred for 12 h at RT. and the resulting golden solution was filtered off. Red block-shaped crystals were obtained by slow diffusion of diethyl ether vapor into the mother liquor.

Discussion

Vanadium has attained increasing interest in the past few years because of its application in medicine and its presence in living organisms: V(V) and V(IV) have been shown to exert insulin-mimetic behavior, and to be present in haloperoxidases, where the vanadium center promotes the oxidation of halide to hypohalous acid by peroxide [2,3]. Consequently, design and synthesis of new complexes have been of great interest recently [4-7].

X-ray analysis has confirmed that the title complex is a monomeric dioxovanadium(V) species $[VO_2(L)]^-$ and the amine cation $(H_2NCH_2CH_2NH_3)^+$ acts as a counter ion. The *cis*-dioxovanadium(V) moiety adopts pseudo-square pyramidal coordination with the vanadyl oxygen atom O3 at the apical position, the phenolate O1, the enolate O2 oxygen atoms, another vanadyl oxygen O4 atom and the imine nitrogen N1 atom in the basal plane with a mean deviation from the best plane of 0.009 Å. The vanadium atom deviates from this plane by 0.497 Å. The coordination of the central vanadium atom with the hydrazone ligand gives rise to one five- and one six-membered chelate ring. The terminal oxo groups show the short bond distances (1.618 Å and 1.660 Å) being characteristic for V=O double bonds [8]. The bond distances V=O1 of 1.866 Å and V=O2 of 1.948 Å are in the range reported in the literature [9]. The bond length of V—N1 (2.142 Å) is similar to that in other analogues. The N2=C9 (1.298 Å) and C9—O2 (1.319 Å) distances confirm the enolate mode of coordination. The ligand is practically planar with a mean deviation from the plane of 0.186 Å, and its angle with the coordination pseudo-plane is about 9.5°. The protonated ethylenediamine cation forms intermolecular hydrogen bonds with the oxo-group oxygen atoms (d(N4···O4^{i}) = 2.746 Å, ∠N4–H4B···O4^{i} = 154.7°; d(N4···O4^{ii}) = 2.755 Å, ∠N4–H4C···O4^{ii} = 160.9°; d(N3···O3^{iii}) = 2.952 Å, ∠N3–H3A···O3^{iii} = 157.8°; d(N4···O3^{iii}) = 2.852 Å, ∠N4–H4A···O3^{iii} = 155.6°) linking the neighboring molecules into layers parallel to the (100) plane (symmetry codes: (i) $-x,-y+1,-z+1$, (ii) $x,-y+\frac{3}{2},-z+\frac{1}{2}$), (iii) $-x,-y+2,-z+1$). There is also π-π packing in the crystal structure with the distance of vicinal π planes of 3.024 Å.

Table 1. Data collection and handling.

Crystal:	red block, size 0.206 × 0.220 × 0.280 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.62 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9194, 3341
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2381
$N(param)_{refined}$:	246
Programs:	SHELXS-97 [10], SHELXL-97 [11]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(5A)	4*e*	0.2226	–0.0083	–0.0818	0.076
H(2)	4*e*	0.2538	1.3514	0.2969	0.065
H(3)	4*e*	0.3544	1.6321	0.2898	0.068
H(4)	4*e*	0.4653	1.6813	0.2118	0.061
H(5)	4*e*	0.4783	1.4463	0.1413	0.054
H(8A)	4*e*	0.5210	0.9962	0.0904	0.080
H(8B)	4*e*	0.5235	1.2221	0.0976	0.080
H(8C)	4*e*	0.4468	1.1267	0.0478	0.080
H(11)	4*e*	0.3939	0.6167	–0.0026	0.051
H(12)	4*e*	0.3990	0.3638	–0.0688	0.059
H(14)	4*e*	0.1273	0.1379	–0.0026	0.059

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(15)	4*e*	0.1236	0.3891	0.0639	0.056
H(3A)	4*e*	0.0672	0.8205	0.9124	0.082
H(3B)	4*e*	0.1196	0.7242	0.9482	0.082
H(4A)	4*e*	–0.0525	0.6639	0.8331	0.058
H(4B)	4*e*	–0.0617	0.4763	0.8041	0.058
H(4C)	4*e*	0.0040	0.6292	0.7790	0.058
H(16A)	4*e*	0.2315	0.6184	0.8758	0.061
H(16B)	4*e*	0.1645	0.7582	0.8331	0.061
H(17A)	4*e*	0.1223	0.4155	0.8245	0.057
H(17B)	4*e*	0.0587	0.4405	0.8826	0.057

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)	4*e*	0.16639(5)	0.91447(8)	0.17137(2)	0.0357(3)	0.0293(3)	0.0400(4)	–0.0043(3)	0.0134(2)	–0.0054(3)
O(1)	4*e*	0.2429(2)	1.0642(4)	0.2286(1)	0.058(2)	0.050(2)	0.042(1)	–0.023(1)	0.018(1)	–0.014(1)
O(2)	4*e*	0.1765(2)	0.6919(3)	0.11901(9)	0.040(1)	0.035(1)	0.040(1)	–0.006(1)	0.016(1)	–0.009(1)
O(3)	4*e*	0.0854(2)	1.0682(3)	0.1368(1)	0.048(2)	0.043(2)	0.069(2)	0.011(1)	0.008(1)	0.000(1)
O(4)	4*e*	0.0951(2)	0.7858(3)	0.2183(1)	0.060(2)	0.041(1)	0.043(1)	–0.017(1)	0.024(1)	–0.011(1)
O(5)	4*e*	0.2688(2)	0.0835(4)	–0.0839(1)	0.064(2)	0.068(2)	0.059(2)	–0.016(2)	0.019(1)	–0.035(2)
N(1)	4*e*	0.3157(2)	0.9557(4)	0.1260(1)	0.035(2)	0.030(2)	0.032(2)	–0.001(1)	0.007(1)	–0.002(1)
N(2)	4*e*	0.3350(2)	0.8187(4)	0.0824(1)	0.039(2)	0.034(2)	0.036(2)	–0.003(1)	0.011(1)	–0.005(1)
C(1)	4*e*	0.3031(3)	1.2257(5)	0.2217(2)	0.034(2)	0.043(2)	0.041(2)	–0.008(2)	–0.001(2)	–0.007(2)
C(2)	4*e*	0.2982(3)	1.3694(6)	0.2650(2)	0.050(2)	0.058(3)	0.054(2)	–0.014(2)	0.012(2)	–0.023(2)
C(3)	4*e*	0.3587(3)	1.5374(6)	0.2608(2)	0.052(2)	0.054(3)	0.063(3)	–0.006(2)	–0.001(2)	–0.023(2)
C(4)	4*e*	0.4253(3)	1.5669(5)	0.2145(2)	0.049(2)	0.034(2)	0.068(3)	–0.009(2)	–0.011(2)	–0.001(2)
C(5)	4*e*	0.4322(3)	1.4258(5)	0.1723(2)	0.043(2)	0.040(2)	0.051(2)	–0.008(2)	–0.001(2)	0.005(2)
C(6)	4*e*	0.3723(3)	1.2508(5)	0.1741(1)	0.030(2)	0.034(2)	0.038(2)	–0.001(2)	–0.003(1)	0.001(2)
C(7)	4*e*	0.3848(3)	1.1004(5)	0.1296(1)	0.030(2)	0.034(2)	0.037(2)	0.001(2)	0.002(1)	0.006(2)
C(8)	4*e*	0.4775(3)	1.1124(6)	0.0875(2)	0.047(2)	0.057(2)	0.058(2)	–0.015(2)	0.020(2)	–0.008(2)
C(9)	4*e*	0.2571(3)	0.6892(5)	0.0819(1)	0.036(2)	0.032(2)	0.030(2)	0.003(2)	0.006(1)	0.001(2)
C(10)	4*e*	0.2585(3)	0.5296(5)	0.0386(1)	0.038(2)	0.033(2)	0.029(2)	0.001(2)	0.003(1)	0.000(1)
C(11)	4*e*	0.3403(3)	0.5201(5)	–0.0022(2)	0.041(2)	0.043(2)	0.044(2)	–0.010(2)	0.010(2)	–0.008(2)
C(12)	4*e*	0.3430(3)	0.3688(6)	–0.0422(2)	0.045(2)	0.059(2)	0.046(2)	–0.006(2)	0.020(2)	–0.014(2)
C(13)	4*e*	0.2632(3)	0.2247(5)	–0.0430(2)	0.047(2)	0.046(2)	0.036(2)	0.001(2)	0.006(2)	–0.011(2)
C(14)	4*e*	0.1814(3)	0.2338(6)	–0.0027(2)	0.052(2)	0.046(2)	0.052(2)	–0.017(2)	0.017(2)	–0.012(2)
C(15)	4*e*	0.1795(3)	0.3848(5)	0.0372(2)	0.052(2)	0.046(2)	0.045(2)	–0.010(2)	0.022(2)	–0.011(2)
N(3)	4*e*	0.1262(3)	0.7864(5)	0.9171(1)	0.060(2)	0.058(2)	0.046(2)	–0.001(2)	–0.006(2)	–0.008(2)
N(4)	4*e*	–0.0169(2)	0.5760(4)	0.8125(1)	0.047(2)	0.034(2)	0.036(2)	–0.010(1)	0.007(1)	–0.003(1)
C(16)	4*e*	0.1584(3)	0.6717(6)	0.8665(2)	0.040(2)	0.058(2)	0.055(2)	0.002(2)	–0.001(2)	–0.004(2)
C(17)	4*e*	0.0822(3)	0.5074(5)	0.8478(2)	0.056(2)	0.035(2)	0.050(2)	0.008(2)	0.003(2)	–0.003(2)

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