Crystal structure of 2-aminoethylammonium (2-oxyacetophenone benzoylhydrazonato)dioxovanadate(V), [H₂N(CH₂)₂NH₃][VO₂(C₁₅H₁₂N₂O₃)]

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Abstract

C₁₇H₂₁N₄O₅V, monoclinic, P12₁/c1 (no. 14), a = 12.088(2) Å, b = 6.900(1) Å, c = 22.655(4) Å, \( \beta \) = 92.964(3)°, \( V = 1887.0 Å^3 \), \( \text{Z} = 4 \), \( R(F) = 0.037, wR(F^2) = 0.105 \), \( T = 294 K \).

Source of material

The ligand 2-hydroxyacetophenone 4-hydroxybenzoic acid hydrazone (L) was prepared according to [1]. Ammonium meta-vanadate (0.12 g, 1 mmol) was added to the solution of H₂L (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 [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 [VO₂(L)]⁻ and the amine cation (H₂NCH₂CH₂NH₃)⁺ 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 is 2.142 Å and similar to that in other analogues. The N₂=C₉ (1.298 Å) and O₄=C₉ 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 (\( \text{d}(N₄—O₄¹) = 2.746 Å, \angle N₄—H₄B—O₄¹ = 154.7°; \text{d}(N₄—O₄²) = 2.755 Å, \angle N₄—H₄C—O₄² = 160.9°; \text{d}(N₃—O₃³) = 2.952 Å, \angle N₃—H₃A—O₃³ = 157.8°; \) \( \text{d}(N₄—O₃³) = 2.852 Å, \angle N₄—H₄B—O₃³ = 155.6°) \) linking the neighboring molecules into layers parallel to the (100) plane (symmetry codes: (i) \( x,—y+1,—z+1 \), (ii) \( x,—y+1/2,—z+1/2 \), (iii) \( —x,—y+2,—z+1 \)). There is also \( \pi—\pi \) packing in the crystal structure with the distance of vicinal \( \pi \) planes of 3.024 Å.

Table 1. Data collection and handling.

| Crystal: | red block, size 0.206 × 0.220 × 0.280 mm |
| Wavelength: | Mo Kα radiation (0.71073 Å) |
| μ: | 5.62 cm⁻¹ |
| Diffractometer, scan mode: | Bruker SMART CCD, φ/ω |
| 2θ max: | 50.04° |
| \( N(\bar{M}D) \) measured, \( N(\bar{h}k\bar{l}) \) unique: | 9194, 3341 |
|Criterion for \( I_{obs} \), \( N(\bar{M}D) \): | \( I_{obs} > 2 \sigma(I_{obs}) \), 2381 |
| \( N(\bar{param}) \) used: | 246 |
Table 2. Atomic coordinates and displacement parameters (in Å²).

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References


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