

Triaqua(2,2'-biimidazole)oxovanadium(IV) sulfate dihydrate

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$

R factor = 0.057

wR factor = 0.102

Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The V atom in the oxovanadium(IV) complex $[\text{VO}(\text{H}_2\text{biim})-(\text{H}_2\text{O})_3]\text{SO}_4 \cdot 2\text{H}_2\text{O}$, with a non-deprotonated 2,2'-biimidazole ligand (H_2biim , $\text{C}_6\text{H}_6\text{N}_4$), has a distorted octahedral coordination with the vanadyl O atom in a *trans* position with respect to one of the water molecules. The N–V–N angle within the five-membered chelate ring is the smallest in the coordination octahedron $[78.66(12)^\circ]$; the angles involving the vanadyl bond are somewhat wider than the corresponding angles involving the *trans* V–O(OH_2) coordination bond.

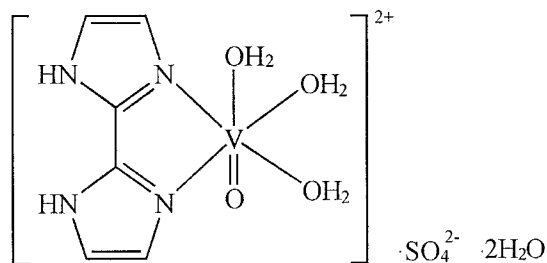
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Comment

The role of vanadium in biological processes has become a topic of study in recent years (Rehder, 1991; Butler & Walker, 1993). The chemistry of vanadium(IV) is dominated by the stable oxovanadium dication (VO^{2+}), which remains intact in various reactions (Cotton & Wilkinson, 1987). A vanadium enzyme has been described which exhibits histidine-nitrogen coordination to vanadium (Messerschmidt & Wever, 1996). This is consistent with the X-ray absorption spectra, which indicate that the vanadium(IV) ion is surrounded by oxygen and/or nitrogen donors (Arber *et al.*, 1989). Vanadium compounds also act as insulin-enhancing agents (Thompson & Orvig, 2000). Therefore, it is important to study the relationship of the syntheses, structures and biological effects of such vanadium complexes.



(I)

2,2'-Biimidazole (H_2biim) is a ligand that can be coordinated to transition metals in non-deprotonated (H_2biim), mono-deprotonated (Hbiim^-) and bis-deprotonated (biim^{2-}) forms. The presence of an imidazole moiety in biological molecules has encouraged studies of H_2biim -containing transition metal complexes. Thus, a variety of geometries and ligating schemes for H_2biim to Cu^{II} , Co^{II} , $\text{Fe}^{\text{II,III}}$, Ni^{II} , Zn^{II} , Ag^{I} , and Cd^{II} have been investigated (Abushamleh & Goodwin, 1979; Liu & Su, 1996; Martinez Lorente *et al.*, 1995; Ye *et al.*, 1999; Hester *et al.*, 1996). In contrast to other first row

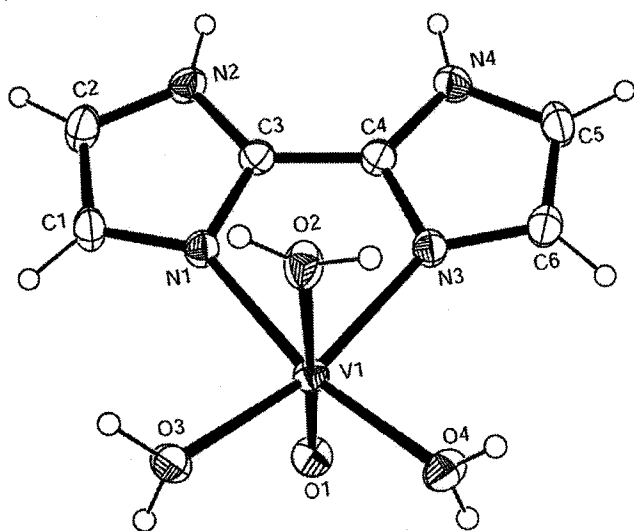


Figure 1

A view of the molecular structure of the title cation, with displacement ellipsoids drawn at the 30% probability level and H atoms shown as small spheres of arbitrary radii.

transition metal ions, only one example of six-coordinated vanadium containing H_2biim , $[VOCl(H_2biim)_2]Cl$, has been reported (Cancela *et al.*, 2001). The synthesis and crystal structure of a complex of oxovanadium(IV) with neutral 2,2'-biimidazole, *viz.* $[VO(H_2biim)(H_2O)_3]SO_4 \cdot 2H_2O$, (I), is reported in this paper.

The crystal of (I) is built of $[VO(H_2biim)(H_2O)_3]^{2+}$ cations, sulfate anions and solvate water molecules. The structure of the cation is shown in Fig. 1. Selected interatomic distances and angles are listed in Table 1.

The V atom has a distorted octahedral coordination formed by vanadyl oxygen, three water ligands and two N atoms of the 2,2'-biimidazole ligand. The water atom O2 is in a *trans* position with respect to the vanadyl atom O1. The $V1=O1$ bond [1.579 (3) Å], is within the range 1.52–1.68 Å observed for vanadyl $V=O$ bonds (Fisher *et al.*, 1989). However, it is somewhat shorter than one found earlier in VO^{2+} groups in octahedral complexes (Kime-Hunt *et al.*, 1989). The $V1-O3$ and $V1-O4$ distances are similar, and in accordance with those in $[HB(Me_2pz)_3]VOCl(DMF)$ (Kime-Hunt *et al.*, 1989) and $VO(O_2)(pyridine-2-carboxylato-N,O) \cdot 2H_2O$ (Mimoun *et al.*, 1983). The $V1-O2(H_2O)$ distance, *trans* to the vanadyl group, is, however, significantly longer.

The mean vanadium–imidazole nitrogen distance [2.099 (3) Å] is quite similar to the $V-N$ distance, derived from EXAFS data, reported for native vanadium(V) and reduced vanadium(IV) forms of vanadium bromoperoxidase, and nearly the same as for six-coordinate vanadium(IV) (Arber *et al.*, 1989).

Angles in the coordination sphere deviate appreciably from the ideal octahedral values, the maximum deviations being, as

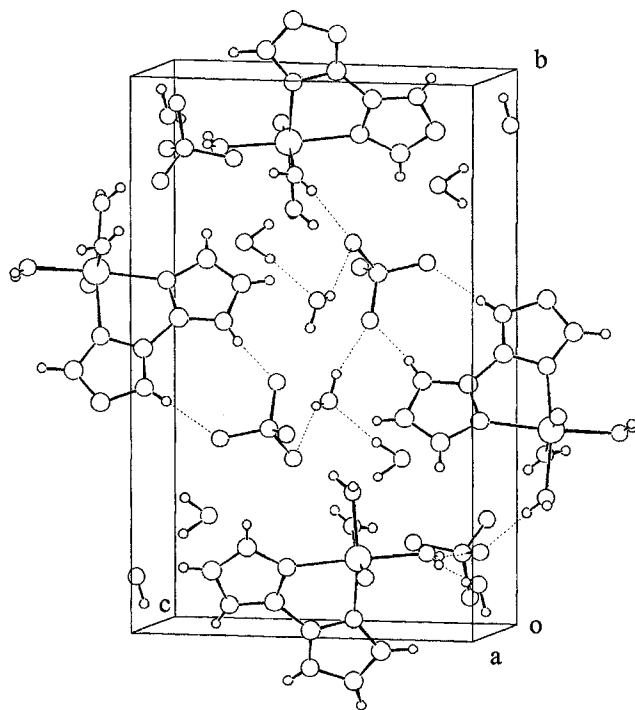


Figure 2

Packing diagram of the title compound. The hydrogen bonds are shown as dotted lines.

expected, due to the chelating 'bite' of the biimidazole. The $N1-V1-N3$ angle, $78.66(12)^\circ$, is, obviously, smaller than the ideal octahedral value, but similar to that found for $[VOCl(H_2biim)_2]Cl$, $77.66(8)^\circ$. The average $O1-V1-N(N1,N3)$ and $O1-V-O(O3,O4)$ angles (100.46 and 94.55° , respectively) are larger than the average $O2-V-N(N1,N3)$ and $O2-V-O(O3,O4)$ angles (82.85 and 81.66° , respectively). Such a difference in bond angles is typical for octahedral VO^{2+} complexes. The $C3-C4$ distance is similar to those found for free biimidazole (Cromer *et al.*, 1987) and for $[Ni(H_2biim)_2(H_2O)_2](NO_3)_2$ (Mighell *et al.*, 1969) of 1.423 and 1.441 Å, respectively. Both imidazole rings are planar, the largest deviation from the ring least-squares plane being $0.009(4)$ Å.

The extensive hydrogen-bonding network links cations, anions and water molecules into an infinite three-dimensional network (Table 2 and Fig. 2).

Experimental

H_2biim was synthesized in accordance with a published procedure (Thummel *et al.*, 1989). $VOSO_4 \cdot 6H_2O$ was commercially available from Acros without further purification. $VOSO_4 \cdot 6H_2O$ (0.217 g, 1 mmol) dissolved in 10 ml of deoxygenated water was added slowly to a suspension of H_2biim (0.067 g, 0.5 mmol) in 15 ml of water in an

inert-atmosphere flask to give a blue-green solution. This solution was left in a refrigerator for a few days. Blue crystals were collected by filtration, washed with water and dried under vacuum. Analysis (%) found: C 18.52, H 4.18, N 14.57; calculated for C₆H₁₆N₄O₁₀S·V: C 18.61, H 4.16, N 14.47. CHN were analysed in a Perkin-Elmer 240 C Elemental Analyzer.

Crystal data

[VO(C₆H₆N₄)(H₂O)₃]SO₄·2H₂O
M_r = 387.23
 Monoclinic, *P*2₁/*n*
a = 8.796 (2) Å
b = 16.337 (5) Å
c = 11.058 (3) Å
 β = 106.994 (3)°
V = 1519.7 (7) Å³
Z = 4
D_x = 1.693 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2919 reflections
 θ = 2.3–27.4°
 μ = 0.85 mm⁻¹
T = 293 (2) K
 Block, blue
 0.30 × 0.20 × 0.20 mm

Data collection

SMART5.0 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.785, *T_{max}* = 0.849
 6656 measured reflections
 2966 independent reflections
 2613 reflections with *I* > 2σ(*I*)
R_{int} = 0.029
 θ_{max} = 26.0°
h = -10 → 10
k = -13 → 20
l = -13 → 13

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.057
wR(*F*²) = 0.102
S = 1.00
 2966 reflections
 239 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0051P)^2 + 5.8095P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.53 e Å⁻³
 Δρ_{min} = -0.50 e Å⁻³

Table 1 Selected geometric parameters (Å, °).

V1–O1	1.579 (3)	N2–C2	1.365 (5)
V1–O2	2.180 (3)	N3–C4	1.328 (5)
V1–O3	2.037 (3)	N3–C6	1.375 (5)
V1–O4	2.042 (3)	N4–C4	1.331 (5)
V1–N1	2.090 (3)	N4–C5	1.366 (5)
V1–N3	2.107 (3)	C1–C2	1.338 (6)
N1–C3	1.329 (5)	C3–C4	1.440 (5)
N1–C1	1.370 (5)	C5–C6	1.346 (6)
N2–C3	1.321 (5)		
O1–V1–O3	95.13 (15)	C1–N1–V1	141.1 (3)
O1–V1–O4	93.96 (14)	C3–N2–C2	107.2 (3)
O3–V1–O4	93.46 (13)	C4–N3–C6	105.5 (3)
O1–V1–N1	98.68 (14)	C4–N3–V1	112.9 (3)
O3–V1–N1	93.03 (13)	C6–N3–V1	141.5 (3)
O4–V1–N1	165.20 (13)	C4–N4–C5	107.8 (3)
O1–V1–N3	102.23 (14)	C2–C1–N1	109.2 (4)
O3–V1–N3	161.67 (14)	N1–C1–H1	125.4
O4–V1–N3	91.21 (13)	C1–C2–N2	107.0 (4)
N1–V1–N3	78.66 (12)	N2–C3–N1	111.3 (3)
O1–V1–O2	174.22 (14)	N2–C3–C4	131.5 (4)
O3–V1–O2	79.97 (13)	N1–C3–C4	117.1 (3)
O4–V1–O2	83.35 (14)	N3–C4–N4	110.9 (3)
N1–V1–O2	84.71 (13)	N3–C4–C3	117.5 (3)
N3–V1–O2	82.98 (13)	N4–C4–C3	131.6 (4)
C3–N1–C1	105.3 (3)	C6–C5–N4	106.4 (4)
C3–N1–V1	113.6 (3)	C5–C6–N3	109.5 (4)

Table 2 Hydrogen-bonding geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
N2–H2...O5 ⁱ	0.86	1.92	2.775 (5)	170
N4–H4...O8 ⁱⁱ	0.86	1.96	2.817 (5)	175
O2–H7...O8 ⁱⁱⁱ	0.84 (5)	1.85 (5)	2.691 (4)	172 (5)
O2–H8...O7 ⁱⁱⁱ	0.78 (5)	1.93 (5)	2.697 (5)	171 (5)
O3–H9...O10 ^{iv}	0.80 (5)	1.81 (5)	2.608 (5)	179 (5)
O3–H10...O6 ⁱⁱⁱ	0.86 (6)	1.88 (6)	2.735 (4)	176 (5)
O4–H11...O6 ⁱⁱ	0.76 (4)	1.91 (4)	2.657 (4)	167 (5)
O4–H12...O9	0.78 (6)	1.88 (6)	2.654 (5)	172 (6)
O9–H13...O7 ^v	0.68 (5)	2.39 (5)	2.971 (6)	145 (6)
O9–H14...O5 ^{vi}	0.78 (6)	2.02 (6)	2.772 (5)	163 (6)
O10–H16...O9 ^{vii}	0.89 (7)	1.94 (7)	2.814 (6)	167 (6)

Symmetry codes: (i) *x*, *y* - 1, *z*; (ii) 1 - *x*, 1 - *y*, 1 - *z*; (iii) $\frac{3}{2} - x$, $y - \frac{1}{2}$, $\frac{3}{2} - z$; (iv) 1 + *x*, *y*, *z*; (v) 2 - *x*, 1 - *y*, 1 - *z*; (vi) *x*, *y* - 1, *z* - 1; (vii) $x - \frac{1}{2}$, $\frac{1}{2} - y$, $\frac{1}{2} + z$.

H atoms attached to C and N atoms were placed in calculated positions (C–H = 0.93 Å and N–H = 0.86 Å), with *U*_{iso}(H) = 1.2*U*_{eq} or 1.5*U*_{eq} of their respective parent atoms. H atoms bonded to O atoms were located in difference Fourier maps and refined isotropically [*U*_{iso}(H) values are in the range 0.01–0.09 Å²; O–H bond lengths span the range 0.68–0.89 Å].

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1994–1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Sheldrick, 1999); software used to prepare material for publication: SHELXTL.

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