

Diaqua(2,2'-diamino-4,4'-bi-1,3-thiazole)oxosulfatovanadium(IV) tetrahydrate

Zhi-Yong Wu,^{a*} Yan-Tuan Li^a and Duan-Jun Xu^b^aMarine Drug and Food Institute, Ocean University of China, 266003 Qingdao, People's Republic of China, and ^bDepartment of Chemistry, Zhejiang University, 310027 Hangzhou, Zhejiang, People's Republic of China
Correspondence e-mail: zd_wzy@hotmail.com

Received 2 August 2005

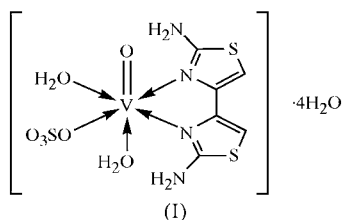
Accepted 13 September 2005

Online 11 October 2005

The title compound, $[\text{VO}(\text{SO}_4)(\text{C}_6\text{H}_6\text{N}_4\text{S}_2)(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$, displays a distorted octahedral coordination geometry. The 2,2'-diamino-4,4'-bithiazole ligand is present in the usual chelating bidentate mode. The sulfate ligand coordinates in a monodentate fashion to the V atom. A large displacement of the V atom from the equatorial plane towards the oxo group correlates with the strong $\text{V}=\text{O}$ double bond. In the crystal structure, a three-dimensional supramolecular network is formed by hydrogen bonds.

Comment

Some transition metal complexes with 2,2'-diamino-4,4'-bithiazole (DABT) or its derivatives have been found to be effective inhibitors of DNA synthesis in tumor cells (Fisher *et al.*, 1985; Waring, 1981). Vanadium plays an important role in various biological processes (Rehder, 1991) and shows potential application in the pharmaceutical field (Sakurai *et al.*, 2002), which has received increased attention in recent years (Butler & Carrano, 1991; Robson *et al.*, 1986; Soedjak & Butler, 1990). As part of an investigation of a series of metal complexes with DABT (Wu *et al.*, 2003), the oxovanadium complex, (I), has recently been prepared and its X-ray structure is presented here.



The molecular structure of (I) is shown in Fig. 1. The title compound contains a vanadium(IV) complex and four solvent water molecules. The octahedral geometry around the vanadium ion is defined by $\{\text{VO}_2(\text{H}_2\text{O})_2\text{N}_2\}$, with the V^{IV} center

coordinated to a terminal oxo group, two water molecules at *cis* positions, two N-atom donors from a chelating DABT ligand and an O-atom donor from a monodentate SO_4^{2-} ligand. The apical positions of the octahedron are occupied by the terminal oxo group (O1) and one coordinated water molecule (O1W); the O1–V1–O1W angle is $172.97(7)^\circ$ (Table 1). The equatorial plane is formed by the rest of the coordinated atoms, with a maximum deviation of $0.0538(8) \text{ \AA}$ (for N2). A large displacement [$0.3287(9) \text{ \AA}$] of the V atom from the equatorial plane towards the oxo group is observed; this displacement correlates with the short $\text{V1}=\text{O1}$ distance of $1.5858(16) \text{ \AA}$, which indicates a strong $\text{V}=\text{O}$ double bond, and an elongated $\text{V1}-\text{O1W}$ bond length of $2.2319(15) \text{ \AA}$.

DABT is present in the usual chelating bidentate mode, forming a five-membered ring, with $\text{V}-\text{N}$ bond lengths of $2.0990(19)$ and $2.1170(18) \text{ \AA}$, and an $\text{N2}-\text{V1}-\text{N4}$ angle of $79.00(7)^\circ$. The dihedral angle between the planes of the two thiazole rings is $2.91(12)^\circ$.

The SO_4^{2-} ligand adopts a monodentate mode, coordinating to the V^{IV} center with a $\text{V1}-\text{O2}$ bond length of $2.0113(15) \text{ \AA}$. The $\text{V1}-\text{O2}-\text{S2}-\text{O3}, \text{O4}, \text{O5}$ torsion angles are $75.40(15)$, $-44.64(17)$ and $-166.03(14)^\circ$, respectively. The $\text{S2}-\text{O2}-\text{V1}$ angle is $136.69(9)^\circ$. The $\text{S2}-\text{O2}$ bond is longer than the bonds to uncoordinated O atoms in the SO_4^{2-} tetrahedron; this situation was also observed in some similar compounds (Doedens *et al.*, 2002; Dong *et al.*, 2000; Khan *et al.*, 1999; Triantafillou *et al.*, 2004). The overall geometry around atom S2 is a distorted tetrahedron.

In the crystal structure, a three-dimensional supramolecular hydrogen-bonding network is observed (Table 2). As illustrated in Fig. 2, the complex molecules are linked to one another and extend along the $[110]$ direction *via* hydrogen bonds between atom O2W, the sulfate group and the amine groups on the bithiazole moiety. These chains are assembled into a two-dimensional layer structure parallel to the (001) crystal plane by solvent water molecules (O4W, O5W and O6W), forming hydrogen bonds to the coordinated water molecules and sulfate groups of the complex molecules. A three-dimensional hydrogen-bonding structure is completed

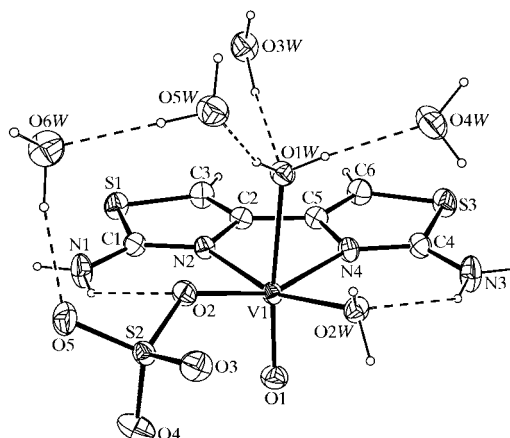


Figure 1

A view of (I). Displacement ellipsoids are drawn at the 30% probability level and dashed lines indicate hydrogen bonds.

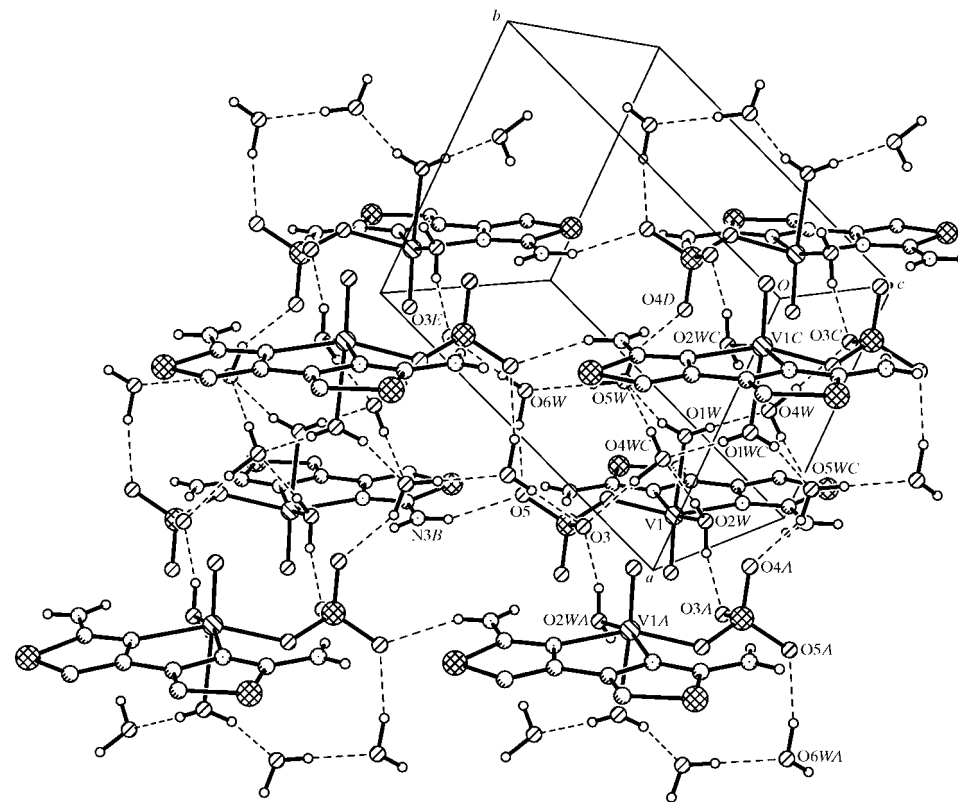


Figure 2
The two-dimensional hydrogen-bonding structure parallel to the (001) plane. The hydrogen-bond linkage among the complex molecules extends along [110]. [Symmetry codes: (A) $-x + 2, -y, -z$; (B) $x + 1, y + 1, z$; (C) $-x + 1, -y, -z$; (D) $x - 1, y, z$; (E) $-x + 2, -y + 1, -z$.]

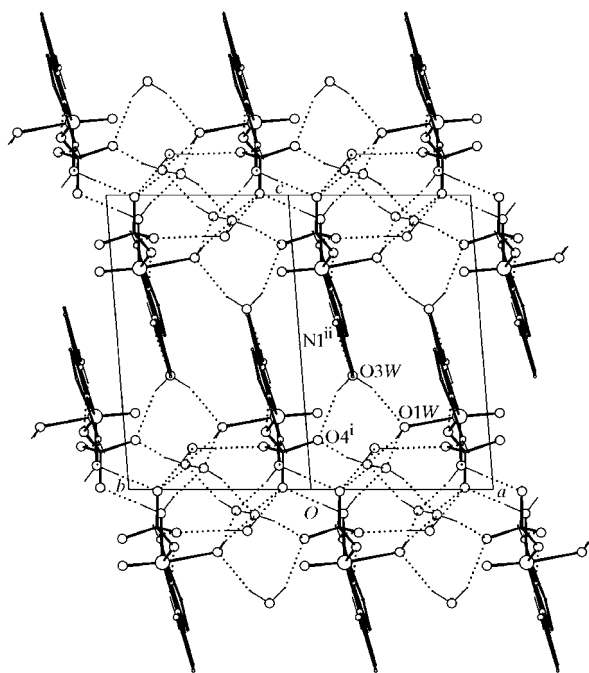


Figure 3
A molecular packing diagram, showing the hydrogen bonds involving O3W and the two distinct regions within the structure. In the region of the DABT ligand, there is π - π stacking between the thiazole rings related by the symmetry code $(2 - x, -y, 1 - z)$. [Symmetry codes: (i) $x - 1, y, z$; (ii) $2 - x, 1 - y, 1 - z$.]

through intralayer hydrogen bonds involving atom O3W (Fig. 3).

The molecular packing is shown in Fig. 3. The crystal has two distinct regions; one contains the DABT ligands and the other contains intimately hydrogen-bonded sulfates and water molecules as described above. In the region of the ligands, neighboring thiazole rings related by the symmetry operation $(2 - x, -y, 1 - z)$ are nearly parallel; separations of between 3.497 (3) (for C3) and 3.598 (2) Å (for S3) suggest π - π stacking between the ligands.

Experimental

DABT (0.10 g, 0.5 mmol) was added to an aqueous solution containing $\text{VO}(\text{SO}_4)$ (0.08 g, 0.5 mmol); the mixture was stirred rapidly until the DABT dissolved. The solution was filtered immediately and the filtrate was kept at room temperature. Crystals (yield 0.16 g, 67.5%) of suitable size were obtained after 2 h.

Crystal data

$[\text{VO}(\text{SO}_4)(\text{C}_6\text{H}_6\text{N}_4\text{S}_2)(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$
 $M_r = 469.36$
 Triclinic, $P\bar{1}$
 $a = 7.9043$ (16) Å
 $b = 10.230$ (2) Å
 $c = 12.597$ (3) Å
 $\alpha = 102.32$ (3)°
 $\beta = 102.61$ (3)°
 $\gamma = 110.50$ (3)°
 $V = 883.0$ (5) Å³

$Z = 2$
 $D_x = 1.765$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3780 reflections
 $\theta = 2.2$ – 27.5 °
 $\mu = 0.98$ mm⁻¹
 $T = 296$ (2) K
 Chunk, blue
 0.28 × 0.22 × 0.20 mm

Data collection

Bruker APEX area-detector diffractometer	4015 independent reflections
φ and ω scans	3573 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$R_{\text{int}} = 0.016$
$T_{\text{min}} = 0.772$, $T_{\text{max}} = 0.829$	$\theta_{\text{max}} = 27.5^\circ$
8440 measured reflections	$h = -10 \rightarrow 10$
	$k = -13 \rightarrow 11$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.4813P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.089$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 0.64 \text{ e } \text{\AA}^{-3}$
4015 reflections	$\Delta\rho_{\text{min}} = -0.40 \text{ e } \text{\AA}^{-3}$
226 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

V1—O1	1.5858 (16)	V1—N4	2.1170 (18)
V1—O2	2.0113 (15)	S2—O2	1.5041 (14)
V1—O1W	2.2319 (15)	S2—O3	1.4716 (17)
V1—O2W	2.0662 (18)	S2—O4	1.4513 (17)
V1—N2	2.0990 (19)	S2—O5	1.4548 (17)
O1—V1—O2	102.46 (8)	O2—V1—O1W	79.66 (6)
O1—V1—O2W	93.86 (8)	O2W—V1—O1W	79.31 (6)
O1—V1—N2	101.30 (8)	N2—V1—O1W	85.31 (7)
O1—V1—N4	99.21 (8)	N4—V1—O1W	79.54 (6)
N2—V1—N4	79.00 (7)	S2—O2—V1	136.69 (9)
O1—V1—O1W	172.97 (7)		
O3—S2—O2—V1	75.40 (15)	O5—S2—O2—V1	-166.03 (14)
O4—S2—O2—V1	-44.64 (17)		

H atoms of water molecules were located in a difference Fourier map and included in structure-factor calculations with fixed positional and displacement parameters (0.08 \AA^2); the range of O—H distances in the water molecules is $0.81\text{--}0.94 \text{ \AA}$. H atoms of aromatic rings and terminal amine groups were placed in calculated positions, with C—H distances of 0.93 \AA and N—H distances of 0.86 \AA , and were included in the final cycles of refinement in a riding model, with $U_{\text{iso}}(\text{H})$ values equal to $1.2U_{\text{eq}}$ of the carrier atoms.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and CAMERON (Watkin *et al.*, 1993); software used to prepare material for publication: WinGX (Farrugia, 1999).

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N1—H1A \cdots O2	0.86	2.24	2.942 (3)	139
N1—H1B \cdots O3W ⁱⁱ	0.86	2.03	2.854 (3)	161
N3—H3A \cdots O2W	0.86	2.27	2.994 (3)	141
N3—H3B \cdots O5 ⁱⁱⁱ	0.86	2.12	2.928 (3)	156
O1W—H1WA \cdots O5W	0.88	1.85	2.714 (2)	165
O1W—H1WB \cdots O4W	0.81	1.97	2.769 (3)	172
O2W—H2WA \cdots O4W ^{iv}	0.88	1.90	2.773 (3)	169
O2W—H2WB \cdots O3 ^v	0.90	1.75	2.640 (2)	167
O3W—H3WA \cdots O4 ⁱ	0.88	2.11	2.940 (3)	157
O3W—H3WB \cdots O1W	0.93	2.02	2.916 (2)	162
O4W—H4WA \cdots O5W ^{iv}	0.86	2.05	2.887 (3)	165
O4W—H4WB \cdots O3 ^v	0.94	2.05	2.870 (3)	144
O5W—H5WA \cdots O6W	0.86	1.87	2.729 (3)	180
O5W—H5WB \cdots O4 ⁱ	0.89	1.93	2.743 (2)	152
O6W—H6WA \cdots O5	0.93	1.90	2.808 (3)	166
O6W—H6WB \cdots O3 ^{vi}	0.90	2.07	2.975 (3)	178

Symmetry codes: (i) $x-1, y, z$; (ii) $2-x, 1-y, 1-z$; (iii) $x-1, y-1, z$; (iv) $1-x, -y, -z$; (v) $2-x, -y, -z$; (vi) $2-x, 1-y, -z$.

This project was supported by the National Natural Science Foundation of China (No. 20471056).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF1012). Services for accessing these data are described at the back of the journal.

References

- Bruker (2002). *SADABS*, *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Butler, A. & Carrano, C. J. (1991). *Coord. Chem. Rev.* **109**, 61–105.
- Doedens, R. J., Yohannes, E. & Khan, M. I. (2002). *Chem. Commun.* pp. 62–63.
- Dong, Y.-H., Narla, R. K., Sudbeck, E. & Uckun, F. M. (2000). *J. Inorg. Biochem.* **78**, 321–330.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Fisher, L. M., Kurod, R. & Sakai, T. (1985). *Biochemistry*, **24**, 3199–3207.
- Khan, M. I., Cevik, S. & Doedens, R. J. (1999). *Inorg. Chim. Acta*, **292**, 112–116.
- Rehder, D. (1991). *Angew. Chem. Int. Ed. Engl.* **30**, 148–167.
- Robson, R. L., Eady, R. R., Richardson, T. H., Miller, R. W., Hawkins, M. & Postgate, J. R. (1986). *Nature (London)*, **322**, 388–390.
- Sakurai, H., Kojima, Y., Yoshikawa, Y., Kawabe, K. & Yasui, H. (2002). *Coord. Chem. Rev.* **226**, 187–198.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Soedjak, H. S. & Butler, A. (1990). *Biochemistry*, **29**, 7974–7981.
- Triantafyllou, G. D., Tolis, E. I., Terzis, A., Deligiannakis, Y., Raptopoulou, C. P., Sigalas, M. P. & Kabanos, T. A. (2004). *Inorg. Chem.* **43**, 79–91.
- Waring, M. J. (1981). *Ann. Rev. Biochem.* **50**, 159–192.
- Watkin, D. M., Pearce, L. & Prout, C. K. (1993). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.
- Wu, Z.-Y., Xu, D.-J., Luo, Y., Wu, J.-Y. & Chiang, M. Y. (2003). *Acta Cryst.* **C59**, m307–m309.