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A new Schiff base oxovanadium (IV) complex: [*N*,*N*′-bis(4-hydroxysalicylidene)-*o*-phenylenediamine]oxovanadium(IV) bis(dimethyl sulfoxide) dihydrate

Ming-Jin Xie, Shi-Ping Yan,* Dai-Zheng Liao, Zhong-Hui Jian and Peng Chen

Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Correspondence e-mail: yansp@nankai.edu.cn

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The synthesis and characterization of the title V^{IV} complex of a salicylaldimine, $[V(C_{20}H_{14}N_2O_4)O]\cdot 2C_2H_6OS\cdot 2H_2O$, is described. The reaction of 2,4-dihydroxybenzaldehyde and 1,2-phenylenediamine with vanadyl sulfate produces a monomeric V^{IV} complex. Its structure reveals that the vanadium(IV) ion is pentacoordinated and situated in a distorted square-pyramidal environment.

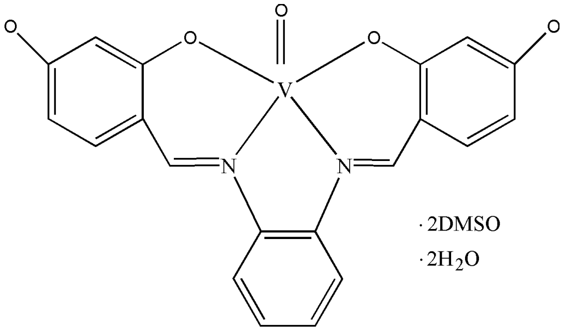
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.061
wR factor = 0.136
Data-to-parameter ratio = 16.0

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

Comment

Interest in vanadium coordination chemistry over the past decade has accelerated because of its biological importance (Amin *et al.*, 2000; Kaliva *et al.*, 2001; Ghosh *et al.*, 2002) and catalytic abilities (Tsuchida *et al.*, 1999; Butler *et al.*, 1994). In particular, the discovery of the insulin-like *in vitro* and *in vivo* activity of oxovanadates(V) and oxovanadium(IV) compounds, such as vanadyl sulfate, has stimulated research into vanadium compounds that may have promising applications in the treatment of non-insulin-dependent type 2 diabetes mellitus (McNeill *et al.*, 1992; Thompson & Orvig, 2001; Sakurai *et al.*, 2002; Takeshita *et al.*, 2001; Song *et al.*, 2002; Woo *et al.*, 1999). Different approaches have been attempted to develop more potent and orally active vanadium-containing insulin-enhancing agents. We report here the title novel pentacoordinated vanadium(IV) complex, (I), with an *N*,*N*′-bis(salicylidene)-*o*-phenylenediamine ligand.



(I)

The asymmetric unit of complex (I) consists of a monomeric vanadium(IV) complex, two dimethyl sulfoxide (DMSO) molecules and two water molecules. The V^{IV} atom is five-coordinate in a distorted square-pyramidal environment. The basal square plane is constituted by the *N*,*N*′-bis(salicylidene)-*o*-phenylenediamine molecule, which acts as a tetradentate ligand through its *o*-phenylenediamine N atoms and its deprotonated phenol O atoms. The V atom is located 0.5997 (2) Å above the mean plane defined by atoms N1/N2/

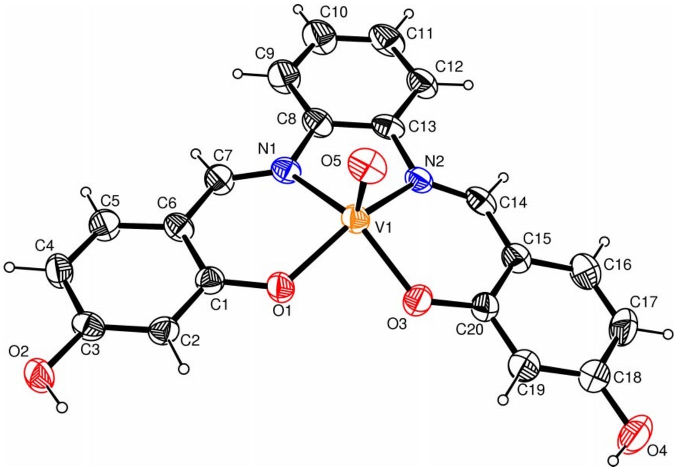


Figure 1
A view of the complex molecule of (I), with the atomic labelling scheme. Displacement ellipsoids are shown at the 30% probability level. The water and DMSO molecules have been omitted.

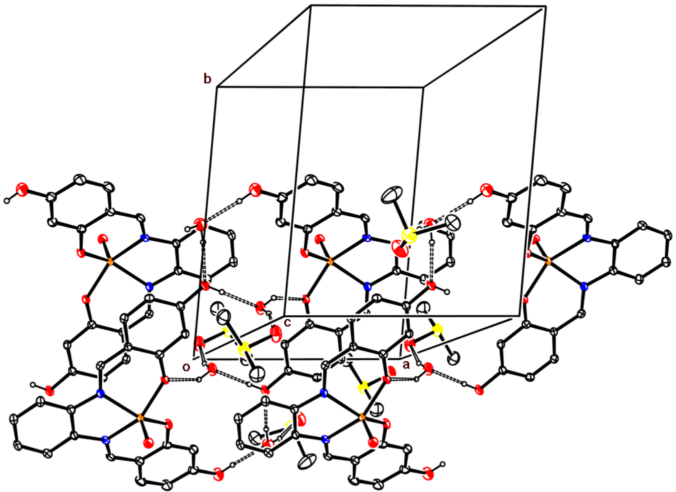


Figure 2
A packing view, showing the O—H···O hydrogen-bond network between the complex molecules, the water molecules and the DMSO molecules. Only the H atoms involved in hydrogen bonding are represented. Hydrogen bonds are shown as dashed lines.

O1/O3. This distance is very similar to those observed for VO(acac)$_2$ (0.55 Å; Dodge *et al.*, 1961) and [VO(acen)] [acen is *N*,*N*-ethylenebis(acetylacetoneiminate); 0.58 Å; Bruins & Weaver, 1970]. The apical position is occupied by the oxo ligand; the V—O$_{\text{oxo}}$ bond distance of 1.592 (3) Å is typical for five-coordinate vanadyl species.

Similar to other VO(salen) [*N*,*N*′-ethylenebis(salicylaldiminato)]oxovanadium(IV)-type compounds (Pasquali *et al.*, 1980; Riley *et al.*, 1986; Wang *et al.*, 1994), the title complex is best described as having purely square-pyramidal geometry, because of its τ value of 0.06. The τ parameter was introduced by Cornman *et al.* (1997) to measure the distortion of a square-pyramidal structure toward trigonal–bipyramidal.

The complex molecules are held together through O—H···O hydrogen bonding involving the hydroxyl groups and the water and DMSO solvent molecules, resulting in an intricate network (Table 2 and Fig. 2).

Experimental

A methanol solution (10 ml) of *o*-phenylenediamine (0.309 g, 3 mmol) was added to a methanol solution (10 ml) of 2,4-dihydroxybenzaldehyde (0.828 g, 6 mmol) and the resulting mixture refluxed for 1 h. The ligands were not isolated from the methanol solution and the solution mixture was added first to an aqueous solution of VOSO$_4$·xH$_2$O (0.783 g, 3 mmol), then to an Et$_3$N (0.602 g, 6 mmol) solution, and refluxed for 2 h. The green precipitate was collected by filtration. Crystals of suitable quality for X-ray analysis were obtained by slow evaporation of a dimethyl sulfoxide solution.

Crystal data

[V(C$_{20}$H$_{14}$N$_2$O$_4$)O]·2C$_2$H$_6$OS·2H$_2$O
M_r = 605.56
Triclinic, $P\overline{1}$
a = 9.325 (3) Å
b = 12.312 (4) Å
c = 12.829 (4) Å
α = 78.464 (5)°
β = 72.067 (6)°
γ = 85.072 (6)°
V = 1372.6 (8) Å^3
Z = 2
D_x = 1.465 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 729 reflections
θ = 2.6–22.8°
μ = 0.57 mm^{-1}
T = 293 (2) K
Block, green
0.20 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min}$ = 0.872, $T_{\max}$ = 0.934
8035 measured reflections
5595 independent reflections
3146 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
$\theta_{\max}$ = 26.5°
$h = -8 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.136
S = 1.00
5595 reflections
349 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.0346P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.56 e Å^{-3}
$\Delta\rho_{\min}$ = −0.35 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

V1—O5	1.592 (3)	V1—N2	2.045 (3)
V1—O3	1.915 (3)	V1—N1	2.049 (3)
V1—O1	1.926 (2)		
O5—V1—O3	110.44 (13)	O1—V1—N2	146.46 (11)
O5—V1—O1	108.63 (12)	O5—V1—N1	106.62 (13)
O3—V1—O1	84.26 (11)	O3—V1—N1	142.71 (12)
O5—V1—N2	104.61 (12)	O1—V1—N1	87.97 (11)
O3—V1—N2	88.37 (12)	N2—V1—N1	78.35 (12)
O5—V1—N1—C7	−93.4 (3)		

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Table 2

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O9—H9B···O6^{i}	0.85	1.87	2.705 (5)	167
O9—H9A···O2^{ii}	0.85	2.01	2.856 (4)	170
O8—H8B···O7^{iii}	0.85	1.93	2.753 (4)	161
O8—H8A···O3^{iv}	0.85	2.29	3.022 (4)	144
O8—H8A···O1^{iv}	0.85	2.21	2.944 (4)	145
O4—H4···O9^{v}	0.82	1.88	2.701 (4)	174
O2—H2···O8^{vi}	0.82	1.78	2.587 (4)	168

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

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C—H = 0.96 Å and $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C), but each group was allowed to rotate freely about its C—C bond. The coordinates of the H atoms attached to the water molecules were treated as riding (O—H = 0.85 Å and H···H = 1.39 Å) and with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(O). All other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å, O—H = 0.82 Å, $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) and $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(O).

Data collection: *SMART* (Bruker, 1994); cell refinement: *SAINT* (Bruker, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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