

A vanadyl Schiff base complex: {2,2'-[1,1'-(*o*-phenylenedinitrilo)- bis(ethan-1-yl-1-ylidene)]- diphenolato}oxovanadium(IV)

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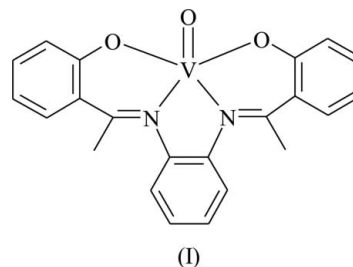
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The green crystals of the title compound, $[V(C_{22}H_{18}N_2O_2)O]$, represent a mononuclear oxovanadium complex. The central V^{IV} centre has a distorted square-pyramidal coordination. Two N atoms and two O atoms of the Schiff base ligand define the base of the pyramid, and the oxide O atom is in the apical position. Density functional theory (DFT) calculations were performed to analyse the changes in the geometry of the ligand during the complex formation. The most significant changes are observed in the values of the torsion angles in the vicinity of the donor N atoms. The HOMA index (Harmonic Oscillator Model of Aromaticity) has been calculated to compare the aromaticity of the benzene rings in the complex and its ligand.

Comment

The most important oxovanadium(IV) compounds are those containing Schiff base units as ligands, and numerous complexes of these combinations have been prepared and studied (*e.g.* Mohebby & Bakhshi, 2008; Kasumov *et al.*, 2010). There is an extensive literature on their application in some important industrial and life processes (Chang *et al.*, 1997; Mohammadi & Yazdanparast, 2009; Boghaei *et al.*, 2006). They are interesting because of their antitumour and antiviral properties (Meshkini & Yazdanparast, 2010; Rehder, 2003); it was also demonstrated that they can show antioxidant activity (Mohammadi & Yazdanparast, 2010) and be applied as catalysts (Ben Zid *et al.*, 2010). The oxide group of oxovanadium complexes has taken part in a number of oxide-transfer reactions (Adão *et al.*, 2009). Some of the important features of these compounds are their preparative accessibility, diversity and structural variability, which make them very attractive. All of these facts have convinced us to look for new oxovanadium(IV) complexes with Schiff bases. We report here the preparation and the crystal and molecular structures of the oxovanadium complex {2,2'-[1,1'-(*o*-phenylenedinitrilo)-

trilo}bis(ethan-1-yl-1-ylidene)diphenolato}oxovanadium(IV), $[V(\text{acetph})O]$, (I), with a $VO(N_2O_2)$ coordination model. A brown form of the $[V(\text{acetph})O]$ complex has been obtained by Boghaei & Mohebi (2002), but the crystal structure has not been determined.



A view of the molecular structure of the complex and its atom-numbering scheme is shown in Fig. 1. The structural analysis of the complex established that both hydroxy groups are deprotonated and coordinated. It means that acetph is a

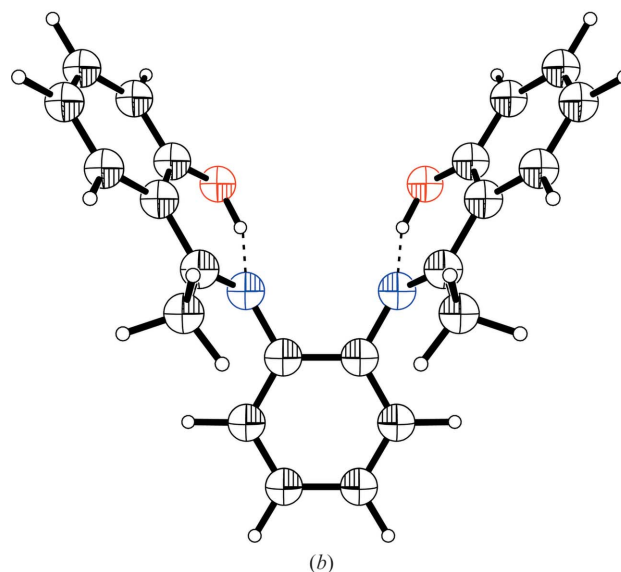
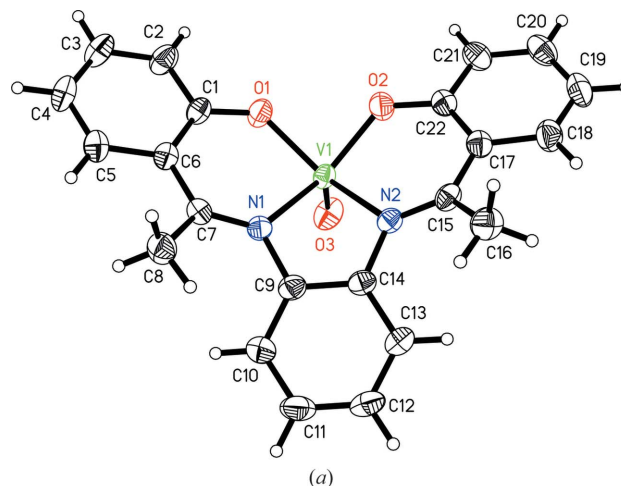


Figure 1
The molecular structure (a) of (I), showing 50% displacement ellipsoids (arbitrary spheres for the H atoms), and (b) of the ligand calculated by DFT. Dashed lines indicate intramolecular hydrogen bonds.

doubly negative tetradentate ligand. To extend structural data analysis, the molecular geometry of (I) was optimized using quantum-mechanical DFT (density functional theory) calculations. The resultant equilibrium structure of (I) in the gas phase is nonplanar with a mirror plane which is perpendicular to the central benzene ring (C9–C14) and passes through V1 and O3 (C_s point-group symmetry). The V^{IV} atom is coordinated in a square-pyramidal geometry by two N atoms and two O atoms from the Schiff base ligand; relevant bond lengths and angles are given in Table 1. The bond lengths to vanadium are in the range accepted for many other vanadium–Schiff base complexes found in the Cambridge Structural Database (CSD; *ConQuest* Version 1.13; Allen, 2002). The $V=O$ bond length of 1.5913 (11) Å is also in good agreement with those observed for other five-coordinate vanadium compounds [average literature values for $V-N$, $V-O$ and $V=O$ bond lengths are 2.06 (2), 1.93 (1) and 1.60 (1) Å, respectively]. The V atom is located 0.6328 (7) Å above the best N_2O_2 least-squares plane of the Schiff base in the X-ray structure and 0.6737 Å above in the calculated structure. This value lies in the range observed for other five-coordinate oxovanadium compounds (0.567–0.692 Å; Allen, 2002). There are no significant differences between the values of the bond lengths and angles of (I) in the solid-state (X-ray) and calculated structures. The differences do not exceed 0.04 Å for bond distances, 3° for bond angles and 10° for torsion angles. The $V=O$ bond axis is tilted 1.10 (6)° from the normal to the plane defined by the N_2O_2 donor atoms, whereas in the analogous five-coordinated oxovanadium(IV) complexes it is in the range 1.35–5.69°.

The extended structure of (I) is presented in Fig. 2. The complex molecules are held together by weak hydrogen bonds. The parameters of these interactions are given in Table 2. The first bond is between an H atom of an outer benzene ring (C3–H3...O3) and the oxide O atom. The second is between a methyl H atom and a phenolate O atom (C16–H16...O2). The last hydrogen bond forms a network of dimers where two axial O atoms of the molecules are directed back to each other. Moreover, the C3–H3...O3 bond links two neighbouring dimers.

Another aim of our studies was to find the differences in the geometry and π -electron delocalization of (I) and its ligand. Unfortunately, the X-ray molecular structure of the ligand is not known. The crystallization of the ligand has been performed many times from different solvents, but in each case the crystals were not suitable for X-ray analysis. This was the reason why the molecular geometry of the ligand was obtained using quantum-mechanical calculations. The DFT study also predicts nonplanar C_s point symmetry as the preferred option for the isolated ligand molecule (Fig. 1*b*). The ligand molecule is stabilized by two intramolecular O–H...N hydrogen bonds which form extra six-membered rings, denoted quasi-rings. An extra quasi-ring can be considered as a quasi-aromatic ring which contains an H atom in a ligand, or a metal ion in a complex. The resulting rings can be investigated as molecular patterns of intramolecular resonance-assisted hydrogen bonds. The position of the extra ring formed

by the substituents interacting through the hydrogen bond is found to influence both the strength of the hydrogen bond and the local aromaticity of the polycyclic aromatic hydrocarbon (PAH) skeleton. Relatively, a greater loss of aromaticity of the *ipso*-ring (benzene ring) can be observed for these kinked-like structures because of the larger participation of π -electrons coming from the *ipso*-ring in the formation of the quasi-ring (Krygowski *et al.*, 2010; Palusiak *et al.*, 2009). From the geometry point of view, the extent of π -electron delocalization can be deduced from the bond lengths of the ring (C–C bond lengths) using the Harmonic Oscillator Model of Aromaticity (HOMA) (Kruszewski & Krygowski, 1973; Krygowski, 1993). The HOMA values of the rings with the quasi-rings in the ligand molecules are 0.904 for C1–C6 and C16–C21, which decrease to 0.874 (C1–C6) and 0.900 (C16–C21) in the X-ray structure of (I) and to 0.778 (C1–C6 and C16–C21) in the calculated geometry of (I), whereas in the ligand and (I) the values of the aromaticity parameters for the C9–C14 ring are significantly higher and equal to 0.959, 0.982 (X-ray) and 0.962 (DFT), respectively. The formation of the complex causes changes in the conformation of the ligand molecule. Firstly, the planarity of the ligand increases as a result of complex formation. The values of the angles between planes defined by the N_2O_2 donor atoms and the planes of the benzene rings decrease in the following order: from 51.11 (ligand) to 21.11 (7) (X-ray) and 22.10° (DFT) in (I) for the C1–C6 ring, from 40.78 (ligand) to 16.98 (8) (X-ray) and 24.00° (DFT) in (I) for C9–C14, and from 51.11 (ligand) to 11.06 (8) (X-ray) and 22.10° (DFT) in (I) for C17–C22. The other consequences of complex formation are changes in the values of torsion angles. The most noticeable changes in (I) (in the X-ray and DFT structures) are found for the following torsion angles: C9–N1–C7–C6, C7–N1–C9–C14, C15–N2–C14–C9 and C14–N2–C15–C17 (Table 1). All of these angles are in the environment of the N1 and N2 atoms but the twist is not at the C=N double bond.

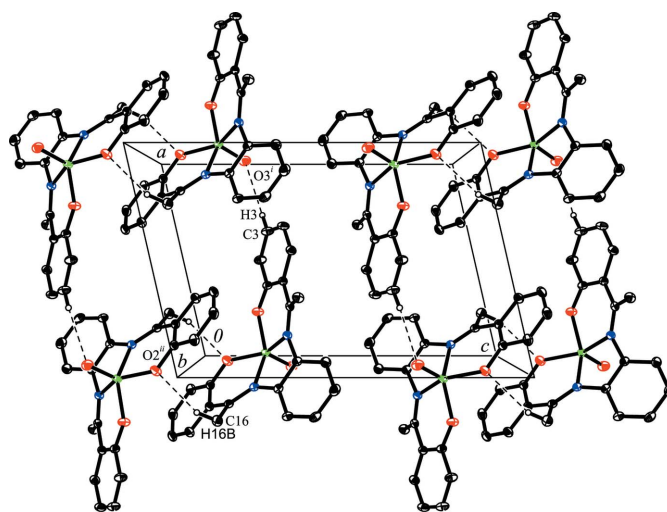


Figure 2

The packing diagram of (I), showing the C–H...O hydrogen bonds between the molecules of the complex (dashed lines).

Experimental

The crude brown powder of (I) (Boghaei & Mohebi, 2002) was prepared according to the procedure published by Farmer & Urbach (1970). Crystals of (I) suitable for X-ray crystal structure analysis were grown from MeOH. The quantum-mechanical calculations were performed using standard DFT and employed the B3LYP hybrid functional (Becke, 1988, 1993; Lee *et al.*, 1988) with the 6-311++G(d,p) level of theory. All species correspond to the minima at the B3LYP/6-311++G(d,p) level with no imaginary frequencies. All calculations were performed using the GAUSSIAN09 program package (Frisch *et al.*, 2010).

Crystal data

[V(C ₂₂ H ₁₈ N ₂ O ₂)O]	$V = 1804.68 (5) \text{ \AA}^3$
$M_r = 409.32$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.3715 (2) \text{ \AA}$	$\mu = 0.58 \text{ mm}^{-1}$
$b = 14.2178 (2) \text{ \AA}$	$T = 293 \text{ K}$
$c = 13.8932 (2) \text{ \AA}$	$0.21 \times 0.18 \times 0.16 \text{ mm}$
$\beta = 102.867 (2)^\circ$	

Data collection

Oxford Diffraction Xcalibur diffractometer	3167 independent reflections
11176 measured reflections	2872 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	307 parameters
$wR(F^2) = 0.073$	Only H-atom coordinates refined
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
3167 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters for (I) (X-ray and DFT) and the Schiff base ligand molecule (DFT) (\AA , $^\circ$).

	(I) X-ray	(I) DFT	Ligand DFT
V1—O1	1.9137 (11)	1.9335	
V1—O2	1.9111 (11)	1.9335	
V1—O3	1.5913 (11)	1.5825	
V1—N1	2.0761 (12)	2.1116	
V1—N2	2.0951 (12)	2.1116	
O1—V1—O2	84.58 (5)	87.00	
O1—V1—O3	110.10 (6)	111.74	
O2—V1—O3	109.97 (6)	111.74	
O1—V1—N1	86.82 (5)	85.12	
O2—V1—N1	143.52 (5)	140.53	
O3—V1—N1	106.28 (6)	107.10	
O1—V1—N2	142.12 (5)	140.53	
O2—V1—N2	86.90 (5)	85.12	
O3—V1—N2	107.51 (5)	107.10	
N1—V1—N2	78.51 (5)	76.99	
O1—C1—C6—C7	0.8 (2)	−5.3	0.5
C1—C6—C7—N1	−14.5 (2)	−10.5	−1.0
C9—N1—C7—C6	−173.3 (1)	−169.0	175.2
C7—N1—C9—C14	−143.1 (1)	−145.1	117.2
N1—C9—C14—N2	−5.5 (2)	0.0	0.0
C15—N2—C14—C9	154.7 (1)	145.1	−117.2
C14—N2—C15—C17	165.7 (1)	169.0	−175.2
N2—C15—C17—C22	21.5 (2)	10.5	1.0
C15—C17—C22—O2	1.3 (2)	5.3	−0.5

Table 2

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 \cdots O3 ⁱ	0.97 (2)	2.51 (2)	3.319 (2)	141.5 (16)
C16—H16B \cdots O2 ⁱⁱⁱ	0.90 (2)	2.61 (2)	3.344 (2)	138.6 (18)

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

All H atoms were generated in idealized positions (aromatic C—H = 0.93 \AA and methyl C—H = 0.96 \AA) and thereafter refined positionally, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms groups and $1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3049). Services for accessing these data are described at the back of the journal.

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