

X-ray and DFT-calculated structures of a vanadyl Schiff base complex: (methanol- κO)[2-methoxy-6-({2-[(2-oxido-3-methoxybenzylidene)amino]benzyl}iminomethyl)phenolato- $\kappa^4 O^1, N, N, O^1'$]oxidovanadium(IV) monohydrate

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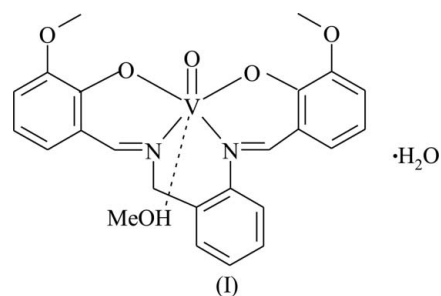
The central V^V atom in the title mononuclear oxovanadium complex, $[VO(C_{23}H_{20}N_2O_4)(CH_3OH)] \cdot H_2O$, has a distorted octahedral coordination. Two N atoms and two O atoms of the Schiff base define the base of the bipyramid and two O atoms are in the apical positions, one from vanadyl and the second from methanol. Density functional theory (DFT) calculations were performed for the title complex and its ligand to compare their geometry in the solid and gas phases. Additional analyses were made of the changes in the geometry of the ligand during complex formation. The HOMA (harmonic oscillator model of aromaticity) descriptor of π -electron delocalization was calculated to estimate the aromaticity of the benzene rings in the title complex and its ligand.

Comment

Schiff bases and their complexes with various metal ions are a very interesting class of compounds, covering coordination chemistry, chemical biology and medical science. Oxovanadium(IV) complexes of Schiff bases are now established as an important class of drugs because of their medical importance due to their insulin-like effect (Thompson *et al.*, 1999). Additionally, these complexes are used in some chemical processes as catalysts (Ben Zid *et al.*, 2010), and also as biological models in understanding the structure of biomolecular and biological processes (Meshkini & Yazdanparast, 2010). Furthermore, vanadium compounds are interesting because of their adverse effect on the hydroprocessing catalysts used in refining crude oil (Bu *et al.*, 1996).

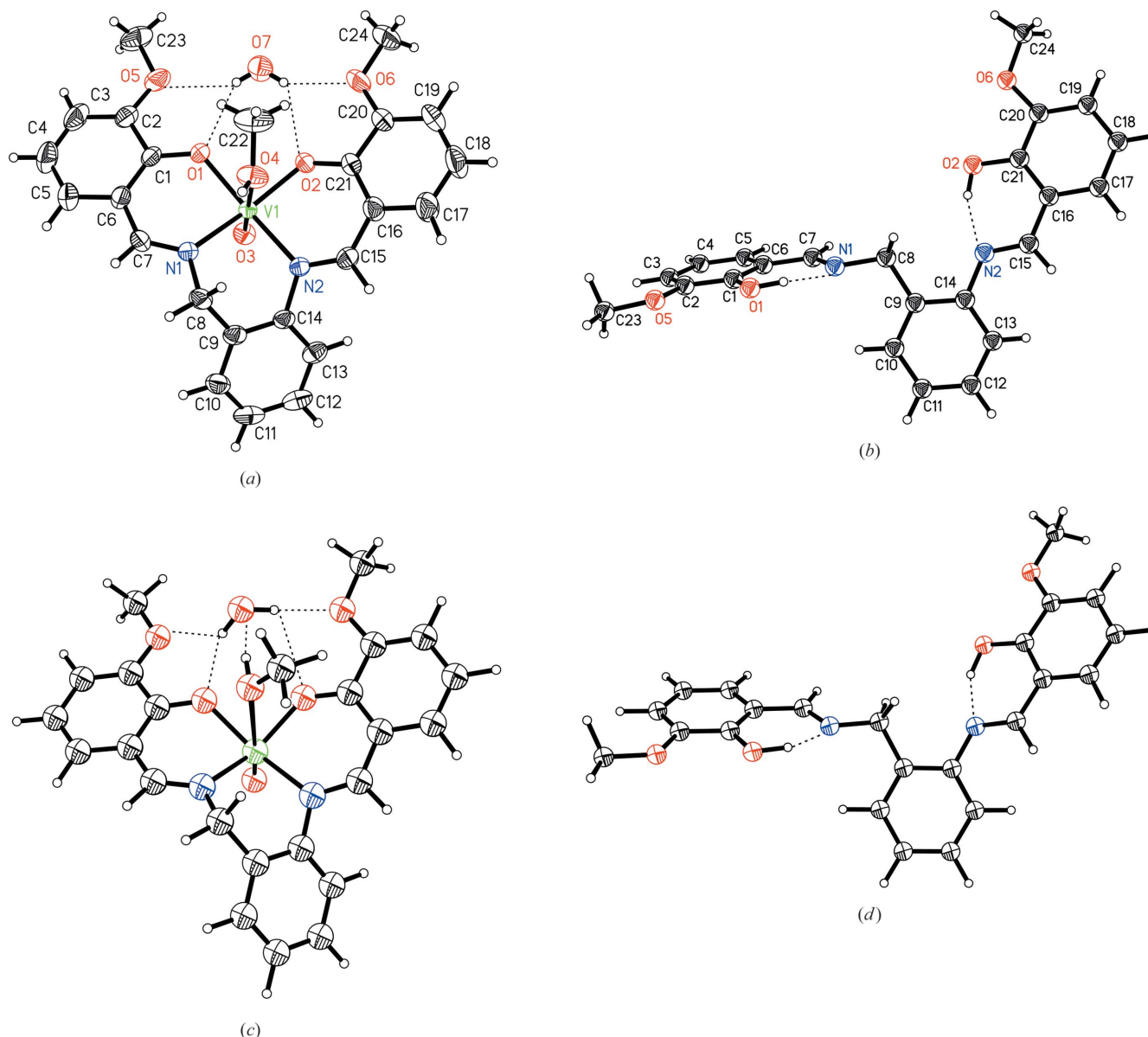
We have recently described the crystal structure of the oxovanadium(IV) complex of a tetradentate Schiff base,

$[VO(\text{acetph})]$, where $H_2\text{acetph}$ is 2,2'-[1,1'-(*o*-phenylenedinitrilo)bis(ethan-1-yl-1-ylidene)]diphenol (Kurzak *et al.*, 2011). Oxovanadium(IV) compounds with this ligand are essentially five-coordinated and form monomeric green crystals containing square-pyramidal coordination structures (Abe *et al.*, 2006; Homden *et al.*, 2008). However, orange polynuclear linear chain structures ($V=O \cdots V=O \cdots$) have also been observed in the solid state for Schiff base oxovanadium(IV) complexes (Nakajima *et al.*, 1996; Tsuchimoto *et al.*, 2000; Fairhurst *et al.*, 1995). Additionally, there is a rare group of oxovanadium(IV) complexes with a weak coordination of solvent molecules. Among these are complexes where the solvent is coordinated in equatorial (Fairhurst *et al.*, 1995; Rayati *et al.*, 2008) or axial positions (Jing *et al.*, 2005; Uemura *et al.*, 2000; Xie *et al.*, 2007). Here, the title oxovanadium(IV) complex, with both a Schiff base and a coordinated methanol molecule (at the 6-position *trans* to the vanadyl O atom), (I), has been structurally characterized.



The molecular structures of (I) in the solid state and of its ligand [2-methoxy-6-({2-[(2-oxido-3-methoxybenzylidene)amino]benzyl}iminomethyl)phenol (H_2L); Dey *et al.*, 2001] are presented in Figs. 1(a) and 1(b), respectively. In order to extend the structural studies, the molecular geometries of (I) and H_2L were optimized using quantum-mechanical density functional theory (DFT) calculations; the DFT-calculated molecular structures of (I) and H_2L are presented in Figs. 1(c) and 1(d), respectively. Selected interatomic distances and bond and torsion angles for the studied compounds, obtained by X-ray diffraction analysis and calculated by DFT, are given in Table 1. Some geometric parameters of H_2L (Dey *et al.*, 2001) are presented for comparison.

In the solid state, (I) contains a distorted octahedral VO^{2+} species, with the terminal oxide (atom O3) and the coordinated methanol molecule (atom O4) occupying the axial positions. The bond angles around the V^V centre formed by the N_2O_2 donor atoms from the Schiff base are almost 90° , so its deviation from strict planarity is quite small. The V^V atom is 0.322 (1) Å above the average plane defined by the N_2O_2 donor atoms and shifted towards vanadyl atom O3. In similar complexes found in the Cambridge Structural Database (CSD; *CONQUEST*, Version 1.13; Allen, 2002), the mean value of this displacement is 0.289 (5) Å (11 hits), and the value in (I) is about half that observed in unambiguously five-coordinate species such as $[VO(\text{acteph})]$ [0.6328 (7) Å; Kurzak *et al.*, 2011].


Figure 1

The molecular structures in the solid state of (a) (I), showing 50% probability displacement ellipsoids (arbitrary spheres for H atoms), and (b) H_2L (Dey *et al.*, 2001), and the DFT-calculated structures of (c) (I) and (d) H_2L . Dashed lines indicate intramolecular hydrogen bonds.

The $V=O$ bond distance and the in-plane $V-O$ distances are comparable with those found in analogous six-coordinated derivatives (Allen, 2002), whereas in the case of the five-coordinated complex $[VO(\text{salen})]$, namely $[N,N'$ -bis(salicylidene)ethane-1,2-diaminato]oxovanadium(IV), the corresponding distances are shorter (Riley *et al.*, 1986).

The axial $V1-O4$ (methanol) distance is similar to the average literature value of 2.3 (2) Å for oxovanadium(IV) complexes with coordinated solvent molecules (Jing *et al.*, 2005; Uemura *et al.*, 2000; Xie *et al.*, 2007).

Comparison of the $V-N$ bond lengths in (I) with the corresponding values reported for six-coordinated complexes, where the solvent molecule occupies the axial position, shows that they are in the same range.

The axis of the $V=O$ bond is tilted by 3.7 (1)° from the normal to the plane defined by the N_2O_2 donor atoms; in

analogous six-coordinated oxovanadium(IV) complexes, this parameter is in the range 2.3–6.7° (Allen, 2002).

The axis of the $V1-O4$ bond is tilted by only 0.2 (1)°. In this case, the average value in similar structures is 1.8 (9)° (Allen, 2002). In the DFT-calculated structure of (I), this angle increases to 4.5°; the value of the $V1-O4$ bond distance is longer than 3 Å and the displacement of the V atom from the N_2O_2 plane increases by more than 0.2 Å. Consequently, the V atom in the DFT-calculated structure of (I) adopts the features of five-coordination.

In the DFT structure of (I) there is an $O4-H_4 \cdots O7$ hydrogen bond between the solvent molecules (MeOH and H_2O). In the solid-state structure of (I), this interaction involves the water molecule accepting a hydrogen-bonding interaction from a neighbouring complex molecule [$O4-H_4 \cdots O7^i$; symmetry code: (i) $x+1, y, z$], in view of the shorter

distance between the atoms constituting this interaction. Otherwise, there are no significant differences between the values of the bond lengths and angles of (I) in the solid-state and calculated structures; the differences do not exceed 0.05 Å for bond distances and 3° for bond angles. However, the formation of the complex results in changes in the geometry of the ligand molecule, and there are three places in the structure where the differences in the torsion angles are particularly marked, *i.e.* rotation around the N1–C8, C8–C9 and C14–N2 bonds (Table 1).

Three planar fragments may be distinguished in (I): plane *A*, formed by atoms C1–C6 (the benzene ring connected to atom O1), plane *B*, formed by atoms C9–C14 (the benzene ring connected to the atom N2), and plane *C*, formed by atoms C16–C21 (the benzene ring connected to atom O2). The values of the *A/B*, *A/C* and *B/C* angles are collected in Table 1. Based on these data, it can be concluded that the ligand molecule adopts a more coplanar conformation in the solid state than in the gas phase, even during complex formation.

The molecular structure of H₂L is partially stabilized by intramolecular O–H···N hydrogen bonds (Table 2), forming five-membered quasi-rings. An extra quasi-ring can be considered as a quasi-aromatic ring, which contains an H atom in the ligand or a metal ion in the 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 substituent interacting through the hydrogen bond is found to influence both the strength of that hydrogen bond and the local aromaticity of the polycyclic aromatic hydrocarbon (PAH) skeleton. Relatively speaking, a greater loss of aromaticity of the *ipso*-ring (benzene ring) can be observed for these kinked structures with an extra quasi-ring because of the greater participation of *ipso*-ring π -electrons in the formation of the quasi-ring (Krygowski *et al.*, 2010; Palusiak *et al.*, 2009).

The harmonic oscillator model of aromaticity (HOMA; Kruszewski & Krygowski, 1973; Krygowski, 1993) is a leading method for the quantitative determination of cyclic π -electron delocalization (aromaticity) in chemical compounds. It is based on the geometric criterion of aromaticity, which stipulates that bond lengths in aromatic systems are between the values typical for single and double bonds. The HOMA values calculated for (I) and H₂L are collected in Table 3. It can be seen that π -electronic effects play an important role in the stabilization of the molecular structures of these chemical species and, additionally, that the hydrogen-bonded quasi-ring can partially adopt the role of a typical aromatic ring. The aromatic characters of benzene rings *A* and *C* in the ligand molecule are almost identical and slightly smaller than in ring *B*. This loss of aromaticity of *ipso*-rings *A* and *C* is a result of the participation of π -electrons from the respective rings in the quasi-rings formed by the intramolecular O–H···N hydrogen bonds. The formation of the complex leads to a subsequent loss of aromaticity for rings *A* and *B* due to more effective π -electron communication with the quasi-rings. Due to the isolation of ring *B* by *sp*³ atom C8, its π -electrons have limited access to the quasi-ring.

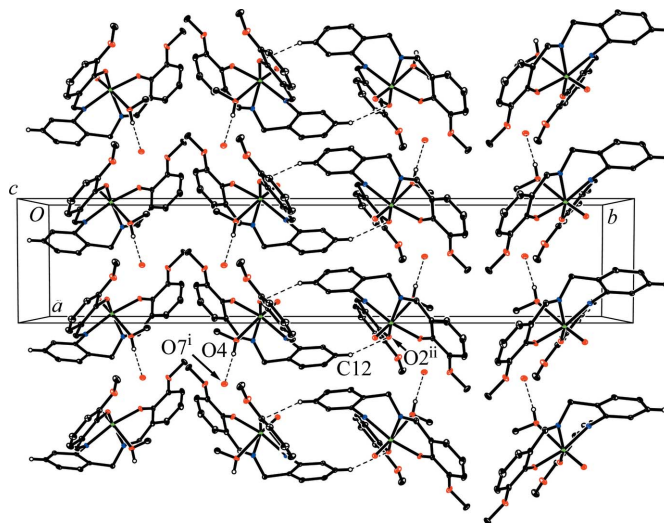


Figure 2

A packing diagram for (I), with the O4–H4···O7ⁱ and C12–H12···O2ⁱⁱ hydrogen bonds shown as dashed lines. [Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 2, -y + 1, -z + 1$.]

A crystal packing diagram for (I) is shown in Fig. 2. Due to the additional O atom of the water molecule, the hydrogen-bond network is enriched in the solid-state structure of (I). The parameters of these interactions are given in Table 4. The two strong intermolecular hydrogen bonds O4–H4A···O7ⁱ and C12–H12···O2ⁱⁱ [symmetry code: (ii) $-x + 2, -y + 1, -z + 1$] form chains along the *a* axis. The V···V distance between neighbouring molecules in the crystal structure is 6.9808 (7) Å.

Experimental

Compound (I) was prepared according to the literature procedure of Boghaei & Mohebi (2002) under ambient conditions. To a hot solution of H₂L (7.7 mmol) with triethylamine (10 drops) in methanol (200 ml), a hot solution of oxovanadium(IV) sulfate (7.7 mmol) in methanol (120 ml) was added. The mixture was heated on a hotplate. The resulting red precipitate was collected by filtration, washed with methanol and dried in a vacuum (yield 64%, m.p. 461–462 K). Analysis found: C 56.68, H 5.44, N 5.47%; C₂₄H₂₆N₂O₇V requires: C 57.03, H 5.18, N 5.54%. IR (KBr, ν , cm⁻¹): 3428 (NH), 1320 (CO), 1613 (C=N), 481 (V–N), 348 (V–O) and 861 (V=O). Crystals of (I) suitable for X-ray crystal structure analysis were grown from methanol.

Crystal data

[V(C ₂₃ H ₂₀ N ₂ O ₄)O(CH ₄ O)]·H ₂ O	$V = 2335.52 (14) \text{ \AA}^3$
$M_r = 505.41$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 6.9808 (2) \text{ \AA}$	$\mu = 0.47 \text{ mm}^{-1}$
$b = 34.6243 (12) \text{ \AA}$	$T = 290 \text{ K}$
$c = 9.6740 (4) \text{ \AA}$	$0.35 \times 0.17 \times 0.15 \text{ mm}$
$\beta = 92.774 (4)^\circ$	

Data collection

Oxford Xcalibur diffractometer	3635 reflections with $I > 2\sigma(I)$
14484 measured reflections	$R_{\text{int}} = 0.033$
4113 independent reflections	

Table 1

Selected geometric parameters (Å, °) for the Schiff base ligand molecule and (I) from both X-ray data and DFT calculations.

Parameter	H ₂ L X-ray	H ₂ L DFT	(I) X-ray	(I) DFT
O1—C1	1.344 (2)	1.339	1.314 (3)	1.306
C1—C6	1.395 (2)	1.411	1.411 (4)	1.419
C6—C7	1.450 (2)	1.456	1.441 (4)	1.434
C7—N1	1.263 (2)	1.281	1.280 (3)	1.294
N1—C8	1.454 (2)	1.452	1.483 (3)	1.473
C8—C9	1.503 (2)	1.519	1.503 (4)	1.509
C9—C14	1.394 (2)	1.411	1.396 (4)	1.404
C14—N2	1.417 (2)	1.410	1.440 (3)	1.426
N2—C15	1.278 (2)	1.289	1.285 (3)	1.303
C15—C16	1.447 (2)	1.450	1.435 (4)	1.428
C16—C21	1.397 (2)	1.413	1.414 (4)	1.422
C21—O2	1.348 (2)	1.339	1.318 (3)	1.296
N1—V1			2.092 (2)	2.095
N2—V1			2.121 (2)	2.137
O1—V1			1.9865 (17)	1.974
O2—V1			1.9640 (16)	1.951
O3—V1			1.5951 (18)	1.578
O4—V1			2.350 (2)	3.487
O1—C1—C6	122.4 (1)	122.4	124.5 (2)	123.2
C1—C6—C7	120.8 (1)	120.6	122.9 (2)	120.4
C6—C7—N1	122.8 (2)	123.0	127.4 (3)	127.0
C7—N1—C8	117.9 (2)	119.1	118.0 (2)	117.7
N1—C8—C9	112.9 (1)	113.4	111.1 (2)	111.8
C8—C9—C14	118.7 (1)	119.1	120.0 (2)	119.8
C9—C14—N2	116.8 (1)	118.4	118.6 (2)	118.6
C14—N2—C15	122.2 (1)	120.9	117.9 (2)	117.5
N2—C15—C16	121.7 (2)	122.9	127.4 (2)	127.5
C15—C16—C21	121.0 (1)	120.8	122.4 (2)	121.5
C16—C21—O2	122.0 (1)	122.4	124.9 (2)	123.9
O1—V1—O2			90.49 (7)	86.47
O1—V1—N1			88.61 (8)	84.66
O2—V1—N2			88.17 (7)	85.63
N1—V1—N2			87.73 (8)	87.20
O3—V1—O4			176.12 (8)	175.56
O1—C1—C6—C7	−1.0 (2)	−0.1	3.2 (4)	4.6
C1—C6—C7—N1	5.0 (2)	1.0	−10.3 (5)	−14.9
C6—C7—N1—C8	179.8 (1)	−178.4	175.9 (3)	171.1
C7—N1—C8—C9	−110.0 (2)	−123.1	123.6 (3)	124.1
N1—C8—C9—C14	−177.9 (1)	−173.3	64.7 (3)	60.8
C8—C9—C14—N2	−1.0 (2)	−1.2	−7.9 (3)	−0.8
C9—C14—N2—C15	159.0 (1)	141.1	140.7 (3)	135.3
C14—N2—C15—C16	176.7 (1)	176.6	169.9 (3)	176.6
N2—C15—C16—C21	3.4 (2)	−0.9	−11.6 (5)	−0.6
C15—C16—C21—O2	−2.2 (2)	0.1	3.1 (4)	−3.2
A/B	78.1	117.7	49.7 (1)	49.3
B/C	22.0	43.2	56.6 (1)	48.7
A/C	64.4	133.2	19.8 (2)	21.7

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.098$
 $S = 1.20$
 4113 reflections
 319 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.32 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e } \text{Å}^{-3}$

Based on the solid-state geometry, the molecular structures of H₂L and (I) were optimized using the B3LYP hybrid function (Becke, 1988, 1993; Lee *et al.*, 1988) at the 6-311+G(d,p) level of theory. All species correspond to 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).

All H atoms were generated in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 (aromatic), 0.97 (methylene) or 0.96 Å (methyl), and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for

Table 2

Intramolecular hydrogen-bond geometry (Å, °) for the Schiff base ligand molecule (Dey *et al.*, 2001; O—H...N) and for (I) (O—H...O) from both X-ray data and DFT calculations.

D—H...A	Method	D—H	H...A	D...A	D—H...A
O1—H1...N1	X-ray	0.91 (2)	1.79 (2)	2.614 (2)	149 (2)
	DFT	0.995	1.732	2.627	147
O2—H2...N2	X-ray	0.89 (2)	1.75 (2)	2.585 (2)	154 (2)
	DFT	0.993	1.736	2.631	148
O7—H7B...O1	X-ray	0.75 (4)	2.31 (4)	2.941 (3)	143 (4)
	DFT	0.97	1.94	2.846	154
O7—H7B...O5	X-ray	0.75 (4)	2.19 (4)	2.838 (4)	146 (4)
	DFT	0.97	2.80	3.619	142
O7—H7A...O2	X-ray	0.78 (5)	2.38 (4)	3.004 (3)	138 (4)
	DFT	0.97	2.50	2.990	111
O7—H7A...O6	X-ray	0.78 (5)	2.08 (5)	2.783 (4)	151 (4)
	DFT	0.97	2.03	3.000	179
O4—H4...O7	DFT	0.98	1.86	2.834	175

Table 3

The values of the HOMA index for H₂L and (I).

Ring	H ₂ L	(I)
A	0.9057	0.8086
B	0.9653	0.9792
C	0.8980	0.7693

Table 4

Complete hydrogen-bond geometry for (I) from X-ray data (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O4—H4A...O7 ⁱ	0.82 (3)	1.86 (4)	2.672 (3)	171 (3)
O7—H7B...O1	0.75 (4)	2.31 (4)	2.941 (3)	143 (4)
O7—H7B...O5	0.75 (4)	2.19 (4)	2.838 (4)	146 (4)
O7—H7A...O2	0.78 (5)	2.38 (4)	3.004 (3)	138 (4)
O7—H7A...O6	0.78 (5)	2.08 (5)	2.783 (4)	151 (4)
C12—H12...O2 ⁱⁱ	0.93	2.56	3.440 (3)	158

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 2, -y + 1, -z + 1$.

methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ otherwise. For O—H groups, H atoms were located in a difference map and subsequently all parameters were refined.

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: SK3437). Services for accessing these data are described at the back of the journal.

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