

cis-Dichloridobis(ethyl methyl sulfide- κ S)oxidovanadium(IV)

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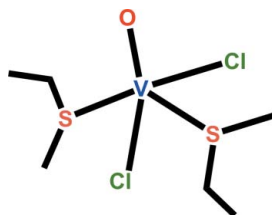
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 Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.031; wR factor = 0.066; data-to-parameter ratio = 23.4.

The mononuclear title complex, $[\text{VCl}_2\text{O}(\text{C}_3\text{H}_8\text{S})_2]$, features a $\text{V}^{\text{IV}}=\text{O}$ double bond [1.5845 (15) Å] in an overall trigonal-bipyramidal coordination environment defined by two Cl^- and the S atoms of two $(\text{CH}_3\text{CH}_2)(\text{CH}_3)\text{S}$ ligands. In the crystal, pairs of molecules form centrosymmetric dimers *via* $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds between the methyl $\text{C}-\text{H}$ group and the oxidovanadium O atom of a neighbouring molecule.

Related literature

For related structures, see: Azuma *et al.* (1994); Bristow *et al.* (1989); Hartung *et al.* (2005); Kakeya, Fujihara, Kasaya *et al.* (2006); Kakeya, Fujihara & Nagasawa (2006); Matsuura *et al.* (2012); Papoutsakis *et al.* (2004); Takano *et al.* (2009). For hydrogen-bonded motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

 $[\text{VCl}_2\text{O}(\text{C}_3\text{H}_8\text{S})_2]$
 $M_r = 290.15$

 Monoclinic, $P2_1/n$
 $a = 10.503$ (3) Å

 $b = 10.386$ (3) Å

 $c = 11.890$ (4) Å

 $\beta = 93.484$ (3)°

 $V = 1294.6$ (7) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 1.46$ mm⁻¹
 $T = 150$ K

 $0.15 \times 0.13 \times 0.11$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Absorption correction: multi-scan

 (*SADABS*; Bruker, 2008)

 $T_{\text{min}} = 0.811$, $T_{\text{max}} = 0.856$

13449 measured reflections

2646 independent reflections

 2125 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.059$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.066$
 $S = 1.24$

2646 reflections

113 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{Cl}-\text{H1}\cdots\text{O1}^i$	0.99	2.57	3.547 (3)	170

 Symmetry code: (i) $-x + 1, -y, -z + 2$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* and *XPREP* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *XCIF* (Bruker, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CQ2002).

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supporting information

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cis-Dichloridobis(ethyl methyl sulfide- κ S)oxidovanadium(IV)

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S1. Comment

The chemistry of the higher oxidation states of vanadium with neutral thioether ligands in discrete complexes remains relatively unexplored due to the instability of such complexes. Our research group has already carried out X-ray crystallographic determinations of lower oxidation state niobium complexes of the general formula $[\text{Nb}_2\text{Cl}_6\text{L}^1_2\text{L}^2]$ ($\text{L}^1 = \text{L}^2 =$ tetrahydrothiophene $\text{C}_4\text{H}_8\text{S}$ (THT) (Kakeya, Fujihara, Kasaya *et al.*, 2006) and dimethyl sulfide $\text{C}_2\text{H}_6\text{S}$ (Kakeya, Fujihara & Nagasawa, 2006)) and ($\text{L}^1 =$ dimethyl selenide $\text{C}_2\text{H}_6\text{Se}$, $\text{L}^2 = \text{C}_2\text{H}_6\text{S}$) (Matsuura *et al.*, 2012). We report here the structure of $[\text{VOCl}_2(\text{C}_3\text{H}_8\text{S})_2]$ (**I**, Scheme I). The molecule has two Cl⁻ and two EtMeS ligands (Fig. 1). Crystal structures have been reported for trigonal bipyramidal complexes formed when the water ligands in $[\text{VOCl}_2(\text{H}_2\text{O})_2]$ are replaced by 8-hydroxyquinolinium chloride (Takano *et al.*, 2009), bis(2-(2-pyridylamino)pyridinium) dichloride (Hartung *et al.*, 2005), diethyl ether (Papoutsakis *et al.*, 2004) and benzo-15-crown-5 (Azuma *et al.*, 1994). The only trigonal bipyramidal complex containing S^{2-} reported to date is $[\text{VOCl}_2(\text{thiourea})_2]$ (**II**, Bristow *et al.*, 1989). In complex **I**, the O atom and two Cl⁻ ligands occupy the equatorial positions and the two EtMeS ligands the axial positions of a distorted trigonal bipyramid. The S2—V1—S1 angle of 166.66 (2)° deviates from the ideal value of 180°. The steric bulkness of the EtMeS ligand may be responsible for controlling the structure. The V—S distances, 2.4803 (9) and 2.4858 (9) Å, in our complex are slightly longer than that of 2.424 (1) Å in **II**. The average V—Cl distance and other geometrical parameters fall within the range of those in **II**. In the crystal, pairs of molecules form centrosymmetric $R_2^2(10)$ dimers (Bernstein *et al.*, 1995) *via* C—H \cdots O hydrogen bonds between the methyl C—H group and the O atom of oxidovanadium in a neighboring molecule (Fig. 2).

S2. Experimental

All the reactions were carried out under a dry argon atmosphere by using standard Schlenk tube techniques. Vanadium trichloride, VCl_3 (1.0 g, 6.4 mmol), was suspended in CH_2Cl_2 (40 mL), and ethylmethyl sulfide ($\text{C}_3\text{H}_8\text{S}$, 1.7 mL, 19 mmol) added to the solution at room temperature. The mixture was stirred at room temperature for 2 d, during which time, a purple precipitate, probably of residual starting material, was generated gradually. This was removed by filtration. The resultant filtrate was concentrated to 5 mL before the addition of *n*-hexane (10 mL). The solution was then set aside in a freezer at 255 K. After several days, blue crystals grew in the solution. The product was too reactive with liquid water to exist at temperatures higher than 273 K even in solvent under an Ar atmosphere.

S3. Refinement

The H atoms were placed in calculated positions, with C—H = 0.98 (methyl) and 0.99 (methylene) Å, and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.5$ (methyl) and 1.2 U_{eq} (methylene).

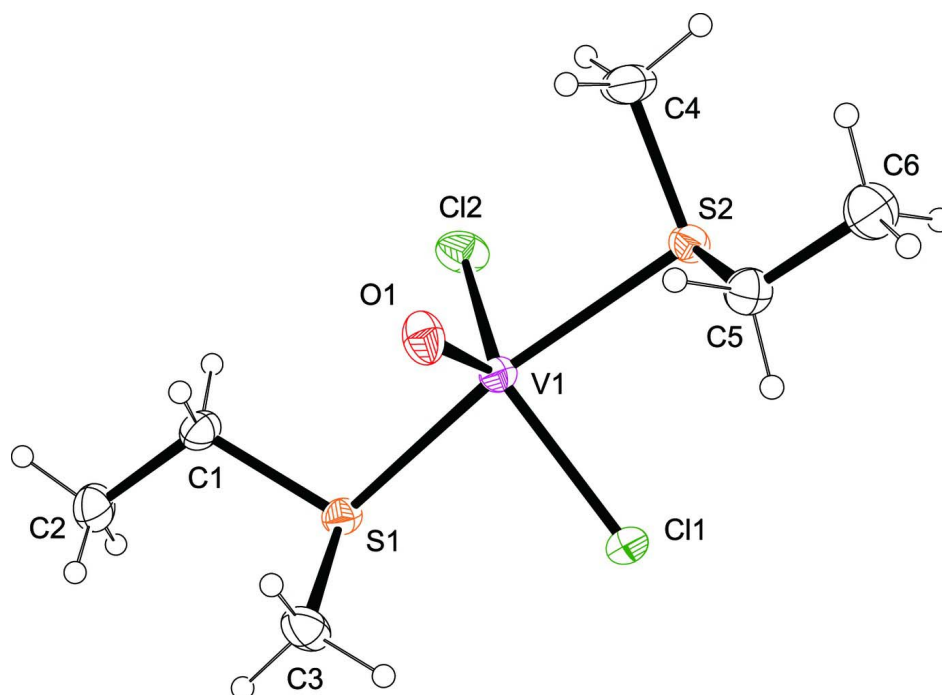
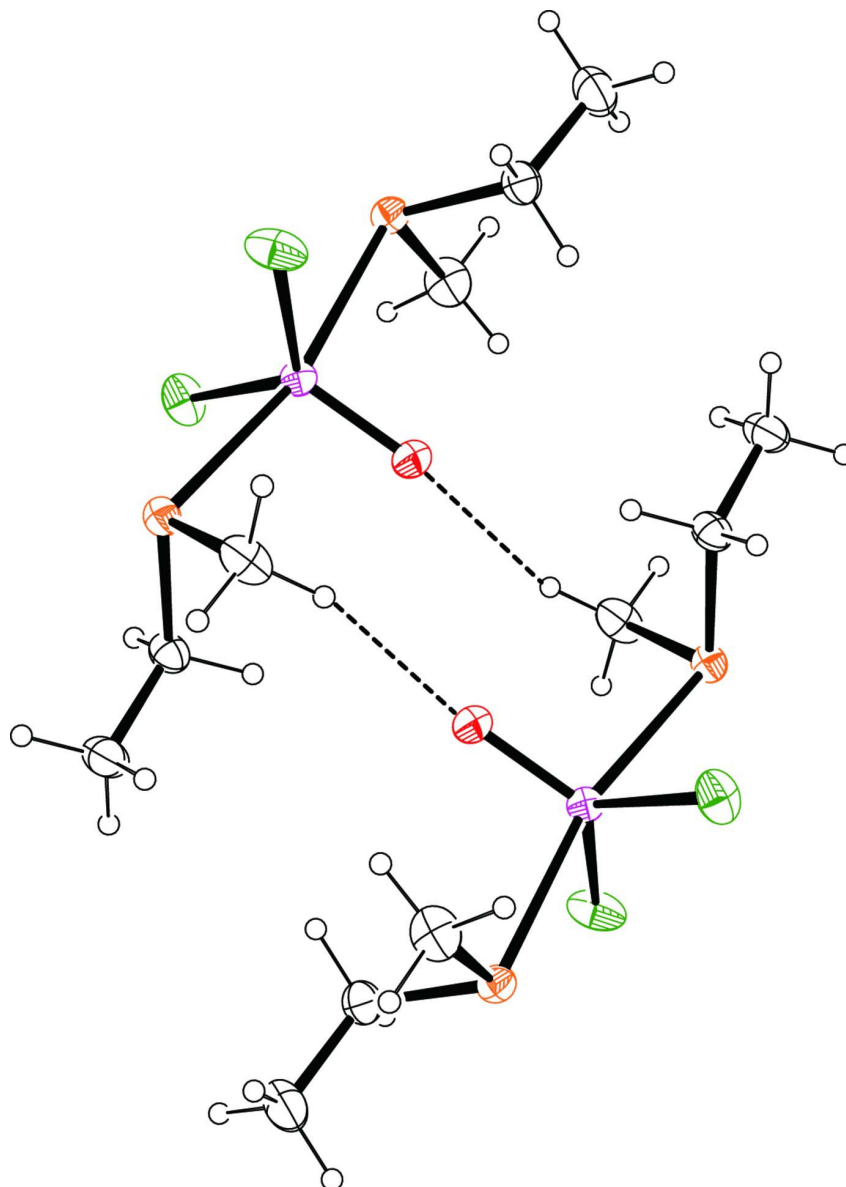


Figure 1

The molecular structure of the complex (I). Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

Centrosymmetric dimer of two molecules of the title compound (I) connected by mutual C—H...O hydrogen bonds (symmetry code = $1 - x, -y, 2 - z$).

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Crystal data

[VCl₂O(C₃H₈S)₂]

$M_r = 290.15$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 10.503\ (3)\ \text{\AA}$

$b = 10.386\ (3)\ \text{\AA}$

$c = 11.890\ (4)\ \text{\AA}$

$\beta = 93.484\ (3)^\circ$

$V = 1294.6\ (7)\ \text{\AA}^3$

$Z = 4$

$F(000) = 596$

$D_x = 1.489\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3238 reflections

$\theta = 2.5\text{--}27.0^\circ$

$\mu = 1.46\ \text{mm}^{-1}$

$T = 150$ K
Block, blue

$0.15 \times 0.13 \times 0.11$ mm

Data collection

Bruker APEXII CCD area-detector
diffractometer
Radiation source: Bruker TXS fine-focus
rotating anode
Bruker Helios multilayer confocal mirror
monochromator
Detector resolution: 8.333 pixels mm^{-1}
 φ and ω scans
Absorption correction: multi-scan
(*SADABS*; Bruker, 2008)

$T_{\min} = 0.811$, $T_{\max} = 0.856$
13449 measured reflections
2646 independent reflections
2125 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.059$
 $\theta_{\max} = 26.4^\circ$, $\theta_{\min} = 2.5^\circ$
 $h = -13 \rightarrow 13$
 $k = -12 \rightarrow 12$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.066$
 $S = 1.24$
2646 reflections
113 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2 , conventional R-factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F , and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
V1	0.29967 (3)	0.19666 (4)	0.98439 (3)	0.02823 (12)
Cl1	0.08892 (5)	0.14880 (7)	0.95318 (5)	0.0513 (2)
Cl2	0.38968 (6)	0.37705 (6)	1.06207 (5)	0.04726 (18)
S1	0.27796 (5)	0.11532 (6)	1.17891 (4)	0.03144 (15)
S2	0.28225 (5)	0.31343 (6)	0.80213 (5)	0.03179 (15)
C1	0.4391 (2)	0.1050 (2)	1.24240 (17)	0.0361 (6)
H1A	0.4932	0.0586	1.1905	0.043*
H1B	0.4740	0.1931	1.2527	0.043*
C2	0.4459 (2)	0.0369 (3)	1.35491 (17)	0.0464 (7)
H2A	0.3901	0.0805	1.4059	0.070*
H2B	0.5339	0.0386	1.3874	0.070*
H2C	0.4182	-0.0526	1.3444	0.070*
C3	0.2416 (2)	-0.0523 (2)	1.15743 (19)	0.0467 (6)

H3A	0.3105	-0.0935	1.1186	0.070*
H3B	0.1613	-0.0607	1.1115	0.070*
H3C	0.2332	-0.0941	1.2305	0.070*
C4	0.4450 (2)	0.3479 (3)	0.7720 (2)	0.0492 (7)
H4A	0.4942	0.2677	0.7732	0.074*
H4B	0.4826	0.4070	0.8291	0.074*
H4C	0.4468	0.3878	0.6974	0.074*
C5	0.2422 (2)	0.1881 (2)	0.70034 (18)	0.0392 (6)
H5A	0.3071	0.1190	0.7085	0.047*
H5B	0.1588	0.1503	0.7169	0.047*
C6	0.2351 (3)	0.2359 (3)	0.5799 (2)	0.0544 (7)
H6A	0.1737	0.3068	0.5718	0.082*
H6B	0.2075	0.1655	0.5292	0.082*
H6C	0.3194	0.2662	0.5606	0.082*
O1	0.39676 (14)	0.09120 (15)	0.94548 (12)	0.0415 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.02533 (19)	0.0281 (2)	0.0312 (2)	-0.00192 (16)	0.00131 (15)	0.00101 (16)
Cl1	0.0309 (3)	0.0701 (5)	0.0518 (4)	-0.0170 (3)	-0.0072 (3)	0.0221 (3)
Cl2	0.0595 (4)	0.0392 (4)	0.0433 (3)	-0.0187 (3)	0.0047 (3)	-0.0057 (3)
S1	0.0290 (3)	0.0353 (4)	0.0302 (3)	-0.0030 (3)	0.0034 (2)	-0.0008 (2)
S2	0.0319 (3)	0.0292 (4)	0.0345 (3)	-0.0001 (3)	0.0044 (2)	0.0039 (2)
C1	0.0298 (11)	0.0464 (16)	0.0317 (12)	-0.0050 (11)	-0.0007 (9)	-0.0011 (11)
C2	0.0441 (14)	0.0599 (19)	0.0344 (13)	0.0017 (13)	-0.0029 (11)	0.0058 (12)
C3	0.0614 (16)	0.0385 (16)	0.0391 (14)	-0.0180 (13)	-0.0068 (12)	0.0046 (12)
C4	0.0378 (14)	0.0590 (19)	0.0517 (15)	-0.0153 (13)	0.0097 (12)	0.0001 (13)
C5	0.0410 (13)	0.0388 (16)	0.0376 (13)	-0.0033 (11)	0.0019 (11)	-0.0036 (11)
C6	0.0561 (16)	0.070 (2)	0.0371 (14)	-0.0027 (15)	0.0041 (12)	-0.0044 (13)
O1	0.0471 (9)	0.0402 (11)	0.0374 (9)	0.0140 (8)	0.0031 (7)	0.0023 (7)

Geometric parameters (Å, °)

V1—O1	1.5845 (15)	C2—H2C	0.9800
V1—Cl2	2.2695 (9)	C3—H3A	0.9800
V1—Cl1	2.2769 (9)	C3—H3B	0.9800
V1—S2	2.4803 (9)	C3—H3C	0.9800
V1—S1	2.4858 (9)	C4—H4A	0.9800
S1—C3	1.797 (3)	C4—H4B	0.9800
S1—C1	1.814 (2)	C4—H4C	0.9800
S2—C4	1.804 (2)	C5—C6	1.513 (3)
S2—C5	1.810 (2)	C5—H5A	0.9900
C1—C2	1.511 (3)	C5—H5B	0.9900
C1—H1A	0.9900	C6—H6A	0.9800
C1—H1B	0.9900	C6—H6B	0.9800
C2—H2A	0.9800	C6—H6C	0.9800
C2—H2B	0.9800		

O1—V1—C12	115.47 (7)	H2A—C2—H2C	109.5
O1—V1—C11	115.97 (7)	H2B—C2—H2C	109.5
C12—V1—C11	128.56 (3)	S1—C3—H3A	109.5
O1—V1—S2	95.60 (6)	S1—C3—H3B	109.5
C12—V1—S2	87.64 (3)	H3A—C3—H3B	109.5
C11—V1—S2	86.85 (2)	S1—C3—H3C	109.5
O1—V1—S1	97.69 (6)	H3A—C3—H3C	109.5
C12—V1—S1	87.79 (3)	H3B—C3—H3C	109.5
C11—V1—S1	86.23 (2)	S2—C4—H4A	109.5
S2—V1—S1	166.66 (2)	S2—C4—H4B	109.5
C3—S1—C1	100.77 (12)	H4A—C4—H4B	109.5
C3—S1—V1	103.16 (8)	S2—C4—H4C	109.5
C1—S1—V1	105.74 (7)	H4A—C4—H4C	109.5
C4—S2—C5	101.24 (11)	H4B—C4—H4C	109.5
C4—S2—V1	104.47 (9)	C6—C5—S2	113.16 (18)
C5—S2—V1	103.56 (8)	C6—C5—H5A	108.9
C2—C1—S1	112.89 (15)	S2—C5—H5A	108.9
C2—C1—H1A	109.0	C6—C5—H5B	108.9
S1—C1—H1A	109.0	S2—C5—H5B	108.9
C2—C1—H1B	109.0	H5A—C5—H5B	107.8
S1—C1—H1B	109.0	C5—C6—H6A	109.5
H1A—C1—H1B	107.8	C5—C6—H6B	109.5
C1—C2—H2A	109.5	H6A—C6—H6B	109.5
C1—C2—H2B	109.5	C5—C6—H6C	109.5
H2A—C2—H2B	109.5	H6A—C6—H6C	109.5
C1—C2—H2C	109.5	H6B—C6—H6C	109.5
O1—V1—S1—C3	-51.05 (11)	C11—V1—S2—C4	-168.84 (9)
C12—V1—S1—C3	-166.45 (9)	S1—V1—S2—C4	132.35 (13)
C11—V1—S1—C3	64.67 (9)	O1—V1—S2—C5	52.59 (10)
S2—V1—S1—C3	123.54 (13)	C12—V1—S2—C5	167.95 (8)
O1—V1—S1—C1	54.33 (10)	C11—V1—S2—C5	-63.22 (8)
C12—V1—S1—C1	-61.07 (9)	S1—V1—S2—C5	-122.02 (13)
C11—V1—S1—C1	170.05 (9)	C3—S1—C1—C2	-63.62 (19)
S2—V1—S1—C1	-131.08 (13)	V1—S1—C1—C2	-170.74 (16)
O1—V1—S2—C4	-53.04 (11)	C4—S2—C5—C6	-68.07 (19)
C12—V1—S2—C4	62.33 (9)	V1—S2—C5—C6	-176.14 (16)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C1—H1···O1 ⁱ	0.99	2.57	3.547 (3)	170

Symmetry code: (i) $-x+1, -y, -z+2$.